

OZONE



IN DRINKING WATER TREATMENT

a brief overview

106 years & still going

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INTRODUCTION

Ozone has been instrumental in protecting earth and its life forms for so long that it is almost incomprehensible. Compared to man, ozone has been around forever. It is not just a beneficial molecule, but is absolutely essential to this planet we call home. **But**, there is much apprehension and misunderstanding regarding ozone use in treating drinking water. Hopefully the following information can help quell some of these concerns.

WHAT IS OZONE ?

Ozone (O_3) or trioxygen is a molecule composed of three (3) oxygen atoms, temporarily existing in a very unstable and reactive state. Ozone is so reactive that a suitable container for storage probably does not exist. Unlike the O_2 molecule described in the next paragraph, this triatomic oxygen defies man's attempts to store or liquefy it. Compared to O_2 , O_3 is an extremely active molecule, probably by a factor of 1,000 times and is sometimes referred to as activated oxygen.

Oxygen (O_2) is normally thought of as the fraction of air which is utilized in breathing. It is very necessary and has many common and obvious uses. This regular oxygen or dioxygen is a relatively stable molecule, composed of two (2) oxygen atoms held together with a fairly firm double bond. This diatomic oxygen is stable enough to compress, liquefy and store, yet it is still quite reactive.

Ozone can be visualized as a regular O_2 molecule with a very nervous, active, reactive, excitable, energetic, corrosive and lively O_1 atom as a side kick. This monatomic O_1 atom does not like to be alone, and near the earth's surface, it refuses to stay with the fairly stable O_2 double bond. It is active and reactive, with energy needing to be channeled in some useful direction. It will combine with virtually anything on contact, or at least will try. This active O_1 will not stabilize until it can break away from the O_2 and form a stable molecule with something else, virtually any other molecule that is available. If no other molecule is available, it will eventually unite with another O_1 atom in the same situation, and restabilize as O_2 .

Ozone is a very strong disinfectant and oxidizer. Any pathogen or contaminant that can be disinfected, altered or removed via an oxidation process will be affected by ozone. It is the strongest of all molecules available for disinfection in water treatment, and is second only to elemental fluorine in oxidizing power. Compared to chlorine, the most common water disinfection chemical, ozone is a more than 50% stronger oxidizer and acts over 3,000 times faster. Both chlorine and fluorine are highly toxic chemicals.

On this planet, ozone is a major work horse. From the highest reaches of the atmosphere to the bottom of the deepest ocean, ozone is a very efficient protector, provider and recycler. It constantly tries to get rid of one oxygen atom, $O_3 \rightarrow O_2 + O_1$, which allows it to react with almost anything it encounters.

When this single oxygen atom (O_1) forms a tight bond with twin hydrogen atoms, we have water (H_2O), without which this planet would be as barren as the moon. Without water, life as we know it can not exist.

WHY USE OZONE ?

There is a logarithmic increase in the human population and a zero increase in the fresh water supply on this planet. Man, by choice, does not necessarily live where the best water is and also tends to abuse the water wherever he does live. Besides contaminating it with various noxins and toxins he produces, man continues to place

more demand, uses and reuses on this existing finite fresh water supply. There is very little doubt that this tendency will continue world wide. Man's pollution will not cease, so it will need to be removed to keep our current and future sources of drinking water safe and palatable.

Ozone treatment is quite efficient and effective in achieving pollution removal, allowing people more flexibility to use water that exists where they are, or where they want to be.

Our ground water, streams, lakes, rivers and oceans are subject to a wide range of human caused assaults. Some of these problems are associated with large molecular structures and unoxidized molecules. Ozone breaks down large and long chain molecules into smaller building blocks. These smaller molecules are then usually more biodegradable and less dangerous. In most cases, the smaller molecules are a lesser pollution problem or impact, as they are more readily recycled or reused in the environment or removable in a filtration process.

Ozone can be used as a disinfectant, decolorizer, deodorizer, detoxifier, precipitant, coagulant and for removing tastes. Consequently, the use of ozone should be considered when there is a need to address any of these problems, and particularly when there is suspicion of water born pathogens.

Ozone coagulates and precipitates many substances by itself, and is also a reasonably effective flocculant. Because of this, it can reduce other chemical loading in treatment facilities.

Ozone production on site, via normal corona discharge, eliminates the problems of transporting, storing and handling of hazardous and dangerous materials.

For efficiency, ozone is outstanding, as it is the most powerful and effective broad spectrum microbiological control or disinfecting agent available. As an example, for the inactivation of Giardia cysts the $C \cdot t$ (*concentration & time*) is about 100 times greater for free chlorine than for ozone. With viruses the $C \cdot t$ is about six times greater for chlorine than for ozone. For Cryptosporidia, ozone is the recommended disinfectant.

Consequently, with ozone, there is less need to add high concentrations of a long lived poison to the water you will soon be drinking. When ozone is utilized, the chlorine need is greatly reduced, as it is then needed only as a way to provide a residual in the distribution system, at 0.2 mgCl₂/L. This minimizes the potential for producing carcinogenic THMs and helps protect your health.

Ozone is of particular value in water treatment systems because of it's ability to disinfect without adding other chemicals which may later need to be removed. As with other treatment methods, the oxidized by-products of ozonation may need to be removed by filtration or settling to provide acceptably clean clear water.

Water, being the universal solvent that it is, seldom remains pure water (H₂O). Even the double distilled water used in laboratories contains dissolved traces of other substances. Ozone will decompose in "pure" water by itself (slower than in air), as well as reacting with almost anything dissolved or carried in the water.

As clean as rain water is assumed to be, it can usually be improved after ozonation and filtration. This statement would be especially true in discussing the acid rains.

The following are some common uses of ozone:

- algicide - very effective, most if not all
- amoebocide - extremely effective, kills all known
- aquaculture aid - many uses
- bactericide - extremely effective, kills all known
- BOD & COD enhancement - quite effective, as this IS real live OXYGEN
- coagulant - quite effective
- contaminant remover - very selective
- decolorizer - usually effective, organic & inorganic, simple & complex, mineral & carbon
- deodorizer - very effective, most are removed
- detoxifier - quite specific; some quick, others slowly, some not at all
- disinfectant - extremely effective, most if not all biota
- dissolved solids - fairly effective, inorganic and organic
- flocculant aid - quite effective, fairly specific
- fungicide - very effective, all known
- hardness - slightly effective with some specific changes
- metals - very effectively on some, manganese and iron
- oxygenator - extremely effective, particularly wells
- particulates - quite effective, inorganic and organic
- pesticide - very effective; kills worms, flukes, fish, snails, eggs, larvae, etc.
- precipitant - quite effective, extremely useful
- precursor reduction - very effective, ie. THMs
- softness - somewhat effective, assists and improves specifically
- taste - very effective, removes or enhances most
- turbidity - quite effective, prepares inorganics & organics for filtration
- viricide - extremely effective, kills all known viruses
- waste & effluent - quite effective, excellent in a wide range of uses

Ozone treated drinking water can be expected to be:

- | | | | |
|----------|-----------|-----------|-------------|
| cleaner | clearer | colorless | nonstaining |
| odorless | palatable | safer | oxygenated |

In 1995, the World Bank estimated that contaminated water causes ten million people (10,000,000) to die annually and is the reason for 80% of all illnesses in developing

countries; and that one billion people (1,000,000,000) have no access to clean drinking water.

Considering all the benefits and lack of drawbacks, ozone is a good choice.

HOW IS OZONE CREATED ?

In nature, the most common and vivid production of Ozone is with lightning discharges. The fresh clean aroma after a lightning storm or a rain shower is ozone.

In the presence of oxygen, nearly any high energy source can and does produce ozone. The two sources we relate to best are electrical and radiation energy. Any energy source powerful enough to break the firm O_2 bond to form O_1 can produce ozone. The ozone created may disassociate quickly, but none the less, it is produced.

The energy of a water fall or pounding surf will locally produce trace amounts of ozone, which generates the fresh aroma associated with these areas. In mild concentrations the odor is extremely fresh, somewhat garlicky and quite pleasant. The process of photosynthesis in a leaf, although low energy, produces O_1 , again allowing for pleasant refreshing air in a forest or greenhouse. In an office, the clean smell around a Laser printer is ozone.

Ozone is a naturally occurring molecule. It is Mother Natures' natural cleanser. She produces ozone wherever it is needed for protection, recycling and clean up. The ozone layer of the outer atmosphere shields earth from heavy doses of ultraviolet light emissions from the sun, protecting all forms of life. Destruction of, or even significant reduction of, this stratospheric ozone layer will have dire consequences for most life forms on earth , not just mankind.

In our lower atmosphere the sun continuously produces ozone in small amounts.

Ozone seems to be one of the automatic defense mechanisms of Earth itself, as well as it's best and strongest natural cleanser. The more pollution man dumps into the atmosphere, the more ozone Mother Nature produces to clean it up. In attempting to clean up this smog, the amount of ozone produced photochemically by nature is so precise (as needed-where needed), that scientists use this exact concentration of ozone as the *index* for the total level of pollution. Unfortunately, the scientists forget to footnote that ozone is the "index", so the public is left with the impression that the ozone is actually causing the polluting, rather than being an induced product of the pollution. In heavily polluted areas, the sunlight passing through the air pollutants can produce ozone concentrations so high that it can become a pollutant and hazard also.

HOW DO WE PRODUCE OZONE ?

Since ozone cannot be stored or conveniently purchased by the gram, pound, gallon or ton, it must be produced on site as needed, where needed and when needed.

We have discovered or devised many ways to produce ozone. All of the following processes can be used:

Electrical Discharge - Corona Discharge.

This process seems to be the safest, most effective, economical and dependable means of controlled ozone production. It involves discharging high voltage electricity across a gap through which filtered dry air or pure oxygen is flowing (a glorified spark plug). Corona discharge is somewhat like miniature lightning in a completely controlled and enclosed environment. Many sizes and shapes of these commercial ozone generators are available, from small portable ½ g/hour units to large 50 kg/hour models.

Where ozone is used in the water treatment industry, the corona discharge method of production is used almost exclusively.

Electrolytically - Electrolysis of an Acid.

This is a very easy way to produce ozone with very simple equipment. It could have great appeal in unsophisticated and remote locations, but is a seldom used method of producing ozone for drinking water treatment. At present, this process is probably 2 to 5 times more expensive than Corona Discharge production. It also involves transporting acids to sites of ozone production, and potentially problematic disposal of containers or other materials. The development of new electrodes and membranes should soon reduce the cost and maintenance problems of these systems. Other oxidants can also be produced via these methods.

Photochemically - Ultraviolet radiation (UV light).

Sunlight, with its warming and healing effects can and does produce ozone. Although sunlight produces ozone in the upper atmosphere, which is not where it is needed for drinking water treatment, the photochemical principle can be applied to produce ozone where it is needed. Both black lights and UV bulbs generate wavelengths necessary to produce ozone from oxygen sources. UV can be a very handy, versatile and unique tool for some applications and situations. In effect, they produce ozone at short range in clear water or air, as oxygen is present.

Many UV bulbs are available, with wavelengths within the appropriate range of 180 to 254 nm (nano meters). However, with currently available technology, these bulbs are not an economical or efficient way to generate ozone, producing only up to 0.3-0.4% by weight. Although X-ray machines or microwave ovens have sufficient energy, their frequencies are not right for efficient ozone production.

Radiochemically - High energy irradiation of oxygen will produce ozone. This is not yet used commercially in potable or waste water treatment, because it is quite technical and very political. In the future this may conceivably be a good use of excess fissionable material, but currently there is much more fear of radiation than of bad water. The excess fissionable material is thus considered to be just a hazardous waste instead of a potentially valuable resource.

Other & Misc. - Various other methods, such as reacting yellow phosphorous with oxygen, can produce ozone. As the demand for ozone increases, more sources and techniques for producing it economically will be explored.

WHAT HAPPENS TO OZONE ?

Ozone is quite short lived in water, enduring only about 20 to 30 minutes in distilled water at 20°C and not nearly that long if contaminants are present.

When ozone is destroyed or self destructs, it can revert back to oxygen ($2O_3 \rightarrow 3O_2$). Since it required energy to create ozone, destruction back to O_2 releases energy as an exothermic reaction of 68,800 calories.

Destruction methods for excess ozone (off gasses) are adsorption, catalytic, chemical, dilution, thermal and full utilization. Ozone is usually considered fully utilized or destroyed when the off gas is ≤ 0.12 ppm for outdoor venting to the atmosphere or ≤ 0.10 ppm by volume ($0.002g/m^3$) for indoor venting.

The following are brief descriptions of some ozone destruction mechanisms:

ADSORPTION is normally accomplished with an activated carbon filter. This is not highly recommended, as theoretically it can produce heat, which with carbon dust, in the presence of the oxygen is potentially dangerous.

CATALYTIC conversion is usually accomplished with metals and metal oxides at temperatures from $\sim 85^\circ$ to $\sim 160^\circ F$ ($\sim 30^\circ$ to $\sim 71^\circ C$)

CHEMICAL destruction of off gas is accomplished by scrubbing.

DILUTION by direct venting into the atmosphere on a large scale is not presently considered an option, as it once was. Mechanical dilution via forced venting is sometimes acceptable.

THERMAL destruction takes advantage of ozone's self degradation back to oxygen at various temperatures. The rate of destruction is approximately as follows:

In dry **air**: ~ 20 to 100 hours at room temperature, $70^\circ F$ or $21^\circ C$
 ~ 10 to 115 minutes at $120^\circ F$ or $49^\circ C$,
 ~ 0.05 to 0.5 seconds at $250^\circ F$ or $121^\circ C$.

In moist air these times are significantly reduced.

FULL UTILIZATION, via total consumption is by far the best method of ozone destruction, whether by Reuse, Recycling or Conservation:

REUSE is excess ozone being utilized by pumping it back upstream and reinjecting it, as additional pretreatment or supplementary supply.

RECYCLING ozone is merely off gas being returned as a partial supply source to the ozone generator. Recycling is recommended most when utilizing oxygen systems and least when utilizing air.

CONSERVATION is by far the best means of assuring ozone destruction, via controlling production to only what is needed to complete the oxidation or to initiate reactions required. With proper design and operation, there should be little or no off gas to worry about.

Examples of things to consider for conservation and good operation are as follows;

Demand is the total need of the water and system, or the measured difference between the ozone transferred in and any residual.

Decay is indicated by the competing reactions after the initial demand is satisfied.

Oxidation is calculatable via empirical formula (stoichiometric coefficients) for the ozone dose at a desired level of oxidation. Water samples and testing are a nice starting point, but do not even scratch the surface of the myriad molecules, chemicals or life forms that ozone will react with. Unless a substance is known be present, it's ozone demand cannot be precalculated, so TEST the demand of the water to be treated with ozone.

Disinfection is the ozone dose required to inactivate an organism in a certain time ($C \times t$). Note this should be after the initial demand is satisfied, as this residual must be maintained for a period of time. A disinfectant must physically contact a microbe to kill it, while both are dispersed, and only a few milligrams are used per kilo of water. At present, no pathogen is known to survive 1.5mgO₃/L for 5.0 minutes at reasonable drinking water pH and temperatures. The disinfection phase is normally an ozone off gas source.

For automatic and package plant installations, off gas destruction equipment should be appropriately sized to allow for daily or seasonal fluctuations, without use of expensive automatic monitoring and adjusting systems.

HOW DOES OZONE WORK ?

Ozone will initiate a series of reactions in water that are very complex and quite specific to the water being treated.

Unlike the very regular and uniformly shaped O₂ molecule, O₃ is a lopsided dogleg shape. Being of dipolar structure with extreme forms of resonance, it is very versatile while still being quite selective in its direct reactions. Ozone can attack as a dipole, molecule, electrophilicly or as a nucleophilic agent.

Ozone reacts in water, or any aqueous solution, in two ways:

DIRECTLY as molecular ozone via three mechanisms;

(slow and very selective), forming aldehydes, ketones and carboxylic acids,

cyclo addition (+ & -); on unsaturated bonds, as a dipole.

ozonide > carbonyl > hydroxy-hydro peroxide >
carbonyl & hydrogen peroxide

electrophilic (+); on molecular sites with strong electronic density.
aromatics (phenol & aniline)

nucleophilic (-); on molecular sites with an electronic deficit, usually
on carbons carrying electron withdrawing groups.

INDIRECTLY via radicals formed as it decomposes in water;

A few such radicals are as follows;

hydroxyl radical, OH^\cdot , a main reactive ingredient

hydroperoxide radical, HO_2^\cdot

superoxide radical ion, $\text{O}_2^{\cdot-}$

ozonide radical ion, O_3^\cdot

The indirect reactions produced by molecular ozone are limited only by the various radicals it produces, which varies with the initial water quality. The worse the water quality problems are, the more ozone can potentially rise to the occasion. Even with the ozone used up quickly, the radicals it forms will continue reacting.

One indirect example of ozone molecules contacting water ($\text{O}_3 + \text{H}_2\text{O} \rightleftharpoons \text{O}_2 + \text{OH}^\cdot + \text{OH}^\cdot$) results in hydroxide ions, which are ready to assist in cleaning the rest of the water along with other reactions of ozone by itself.

Ozone oxidizes many materials into insoluble oxides that can precipitate or settle out (normally all are filterable), occasionally some are foamy (so can be skimmed). Some combinations of soluble organics and polyvalent cations produce insoluble materials with ozonation.

Ozonation causes surface charges to change from positive to negative. Colloidal particles are usually held in suspension by their surface charges. Thus, ozone can induce some flocculation in turbid waters, depending on the water composition.

By imparting a negative charge to molecules, ozone encourages hydrogen bonding, which also encourages coagulation and flocculation. With hydrogen bonding of oxidized material occurring, conglomerates form which can be precipitated, filtered out or skimmed off.

WHEN CAN OZONE BE USED ?

Quite simply, ozone can be used to oxidize virtually anything that is oxidizable. Ozone can combine or react with all elements except the Inert Gasses. Any molecule that is not in its final state of oxidation is subject to attack by ozone. Even some completely oxidized molecules may react with the radicals and other initiated reactions caused when ozone decomposes in an aqueous solution.

Oxidation is a chemical reaction in which electrons are LOST by atoms, ions or molecules. Reduction is the GAIN of electrons. Regardless of the name similarity, oxidation reactions need not actually involve oxygen atoms or molecules.

Oxidation, for non-chemists and those who have forgotten high school chemistry, is commonly just burning or rusting. If done instantaneously, it is an explosion. If done rapidly, it is burning. If done slowly, it is corrosion. When acting at a molecular level, it is just plain oxidation, or part of the oxidation-reduction process. It can occur in gaseous or solid states as well as in liquids.

Ozone can normally be utilized in water treatment wherever Chlorine (Cl_2), Chlorine dioxide (ClO_2), Potassium permanganate (KMnO_4), Ultraviolet light (UV), Hydrogen peroxide (H_2O_2), Oxygen (O_2) or aeration are used or considered for use. Also, ozone is very compatible with, and can be used in conjunction with other treatments, as in the Advanced Oxidation Processes (AOPs), for special cases or problems.

Ozone is noted for its ability to reduce the molecular weight of molecules, whether from the cell wall of a bacteria or from a carbon source that causes water coloration or poor taste. Ozone is also an initiator of many chain reactions in water, which are solely dependant on the quality of that particular water, plus pH, temperature and etcetera.

If you can wash something, dissolve it in water, burn it, dissolve it with an acid, deteriorate it in the sun light, eat it, or it reproduces, you can probably reduce it, remove it or kill it with ozone

WHAT CAN OZONE TREAT ?

If it can be oxidized at normal temperatures and pressures, ozone can treat it. However, there are cautions. Some impurities that occur in water, such as Bromine, may be very undesirable in an oxidized state. Also, water treated with ozone will almost always need to be filtered or settled, as ozone tends to coagulate and precipitate many impurities in the water.

Essentially, problems in water quality that are usually addressed with acid, peroxide, chlorine or other oxidants are probably prime candidates for ozone treatment. If ozone cannot be used to treat a water quality problem, it is likely that no other available oxidant will to do the job either.

The following contaminants or problems can all be potentially treated with ozone;

- Bacteria - all known, including iron bacteria

- Minerals - inorganics, dyes and others

- Metals - Iron, Manganese and many other

- Organics - color, algae, other carbon compounds

- Protozoans - all known, including Cryptosporidium, Giardia and all Amoebae

Viruses - all known

BOD & COD - reacts quickly, as ozone is a really active form of oxygen

Although ozone is currently known to be the disinfectant most effective for Cryptosporidium, in most cases it should still be combined with or followed by conventional treatment or filtration.

The use of gaseous ozone in combination with UV, ultra sonics and/or hydrogen peroxide produces some interesting results, and these are some of the methods of Advanced Oxidation Processes (AOPs). It is difficult to envision a microbe or molecule that could withstand many of these combined onslaughts.

WHAT SHOULD NOT BE TREATED WITH OZONE ?

Ozone is not a cure all, nor the final single answer to all water treatment problems, even though there is little in water that ozone cannot react with directly or indirectly. The Inert Gasses are not subject to attack by ozone. Some complex pesticides are not broken down completely by ozone. Many other man made molecules cannot be broken by ozone at normal water treatment temperatures and pressures. When working with new problems or chemical compounds, TEST IT FIRST to ensure the cure or effect is not worse than the original problem.

If bromide ions are present, they can be oxidized to bromate and bromoform via reactions with O₃. The MCLs for these contaminants, which can easily be exceeded, are 0.1 and 0.01 mg/L respectively, with MCLGs of zero. These problems can be reduced with bicarbonate, ammonia and other techniques.

When ozone attacks long chain carbon molecules, such as those that cause unwanted color or turbidity, it breaks them down. Just how far they are broken depends on the molecule and other site specific water chemistry. A few pesticides, organics and inorganics may become more noxious, toxic or undesirable in an oxidized state.

Ozonation need not be avoided when these are present, but specific treatment for removal of the by-products will be required. It may be impossible to anticipate every by-product that will be formed, and there may be seasonal variation of these by-products. It is ALWAYS prudent to TEST FIRST.

Ozone cannot be used to reduce calcium and magnesium hardness, as these cannot be oxidized into an insoluble form. Nitrates and sulfates are soluble fully oxidized molecules, so ozone treatment alone is ineffective.

HOW IS OZONE PLACED IN THE WATER ?

One of three basic methods are generally used:

Aspiration - via turbines or high speed agitators

Eduction - via a venturi, with full or side stream flow

- via the inlet of a pump, but carefully here

Pumping - via diffusers or fine air stones

The solubility of ozone in water is quite good, about 10 to 15 times greater than for oxygen under normal drinking water treatment conditions. About 0.1 to 0.6 liters of ozone will dissolve in one liter of water.

The size of the ozone gas bubble is extremely important. A bubble size of 2 to 3 microns is desired, but for good gas to liquid transfer, the smaller the better. Micro bubbles produced via a venturi, or sheared via a turbine are good examples.

Venturi eduction also allows gaseous ozone to be handled under vacuum conditions, which improves working safety and most likely the performance.

Pressure and varying pressures can be useful in accomplishing efficient gas to liquid transfers, as solubility increases directly with pressure. Inversely, the solubility decreases with increasing temperature.

HOW IS OZONE CONCENTRATION MEASURED ?

Ozone has a very short half life in water. It is highly unstable and reacts by itself, as well as contributing very rapidly to the formation of other oxidants.

In water, ozone is measured electronically, spectromically or via wet chemistry. Measuring electrically, or amperometrically, is accomplished with either bare electrodes or through a membrane, such as conductivity, DO, ORP and pH meters.

As a gas, ozone can be measured in several ways: amperometricly using bare electrodes or with membranes; calorimetrically measuring the heat change; iodometrically as a chemical method; isothermal pressure using volumes; and spectrometrically using wave length, which is usually the preferred method.

The spectrophotometry method takes advantage of UV light absorbing at 254nm or the absorbance range of another known by-product of oxidation.

Of various wet chemical methods available, the 'indigo-blue' is most recommended.

An ORP meter (oxidation-reduction potential) will give a reading of ozone activity in the water, quite economically. Fortunately or unfortunately, the ORP meter also measures the other oxidants present, almost indiscriminately. This will give erroneous readings of the actual ozone concentration present. With the chain reactions ozone initiates, there can be many other ozone-produced oxidants to measure. But, ORP is still a good measure or indicator of activity for comparison. This is particularly true once testing is completed and other reactions are understood.

HOW MUCH OZONE IS NEEDED ?

Two steps are used to determine the amount of ozone required. First is the *CUMULATIVE* need, which is the number of milligrams of ozone necessary to oxidize the number of milligrams of contaminates present. This is the stoichiometry of the reaction representing the consumption of ozone, normally in mgO_3/mg substance.

When several contaminants or substances are present, the totals for each are added together. This includes metals, minerals, organics, pesticides and etcetera. When this need is satisfied, the reaction is done. This is the calculation for oxidization, coagulation, flocculation, precipitation, color removal (ie. 1-3mgO₃/mg Carbon) and etcetera.

Second is the *DISINFECTATION* calculation, measured in mg/L of ozone over a specific period of *contact time*, usually minutes. This is a *concentration & time* (Ct or Ct) needed for inactivating living organisms, from single cell to higher life forms. It is the disinfection calculation for pathogens and pests, such as; algae, amoebae, bacteria, virus and etcetera.

The cumulative demand must be satisfied before a concentration of ozone can be held stable for any period of time in solution.

Both steps require adequate injection, mixing and time for the small amount of ozone to physically contact the target. One mg/L is only 1/1000 of a gram dissolved in one kilogram (1000 grams) of water, or 1:1,000,000. The time required for contact and/or reaction can be from several seconds to many minutes and is the obvious reason for the "t" in the Ct. The ozone must physically contact the target to react with it. It is not just economical and beneficial, but almost essential, to remove substrates or turbidity prior to the disinfecting steps, so that the target organisms are not shielded from the disinfectant. Organisms can be attached to, as well as enclosed within, the turbidity or other particles. This principle applies to other disinfectants as well ozone.

If excess ozone is produced, OFF GAS can be a problem, so don't waste ozone and don't pollute with it. Attention to this will also minimize production costs.

If there is any trick to using ozone, it is to make only as much as is needed and then place it correctly to do what is required. This automatically assumes the following:

1. The raw water quality is known. (= test it).
2. The desired specifications for the finished water quality are decided prior to designing the system. (= the shotgun approach works poorly here).
3. The operation must allow sufficient time at appropriate points in the treatment sequence for the ozone to chemically react with the targets. (=design it)

Ozone will react when injected into water and there will be a reaction of some kind with everything in that water. This means everything, not just the contaminant targeted for treatment. Basically, ozone will try to do it all, even attempting to react with the containers and piping.

IS OZONE TREATMENT EXPENSIVE ?

Ozone is not cheap, but it is very effective. Ozone reacts somewhat differently than other treatments, so in cost comparisons, the apples to oranges problem frequently comes into play. While only barely competitive in some applications, ozone is very economical in others and at times it is the only treatment that will work. If other

methods are not satisfactory, then efficacy becomes the major consideration in rating the cost of treatment.

The designs and costs of equipment used in the production and handling of ozone vary widely at present. However, by making a few assumptions, some estimated costs can be calculated for small systems. Using air as the oxygen source, ozone can be produced at .25-1.8 g/kWhr of electricity. Using pure oxygen, about 15-25 g/kWhr can be expected. Assuming \$.05 per kWhr, the production costs can range from \$28-200/kilogram with air and \$2-3.3/kilogram using oxygen.

Large efficient drinking water facilities are producing ozone for \$1.57-3.30/kg (\$.70-1.50/lb), which includes all capital equipment, depreciation, power, operation, maintenance and the feed gas preparation or oxygen.

With chlorine available at less than \$400/ton in bulk, or less than \$.45/kilogram, it is little wonder that eyes widen at the first mention of ozone. But, the amount of O₃ required, speed of reaction, results, residuals, safety, other accomplishments and efficiencies need to be considered along with the cost per kilo. The smaller amount of ozone needed may result in the same or even less cost to achieve the desired results.

AN EXAMPLE: A single family residence with a contaminated well system could expect to spend ~\$1,000 to \$2,000 for an ozone source, plumbing, electrical outlet and automatic backwashing filter. A typical system may use 5 gO₃/d and could increase the electric bill \$4 to \$8 per month at \$.05 per kWhr.

AN EXAMPLE: A small municipal system serving a population of 5,000 is delivering 500,000gpd from a surface water source and needs to upgrade it's filtration plant facilities to inactivate Cryptosporidium and to address potential contaminate problems, such as pesticides.

Attempting to inactivate the Cryptosporidium by increasing the chlorination disinfection level to a four log reduction would be futile. Although the cost increase for chlorine may only amount to less than 1¢/1000gallons, the water would be unpalatable, no cleaner or clearer and the potential for THMs significantly increased.

To additionally treat their water with 1.5mgO₃/L would require 6.26 pounds per day of ozone generation (~118 gram/hr). To insure adequate public health protection and allow for varying flows, three variable 4lb/day ozone package plants can be installed for about \$55,000. The pumps, plumbing, electrical, misc. and monitors could cost an additional \$20,000. Using a ten year life, this \$75,000 capital equipment expenditure can be amortized for about \$9,500 per year. Assuming \$.05/Kwh, power for producing the 6¼ lb/d of ozone would cost \$8.00/d, plus an estimated \$3.00/d for pumping, monitoring and other. This O&M of \$11.00/d plus \$26.03/d for the capital, provides the additional ozone treatment of the 0.5mgd at \$37.03/d, or about 7.5¢/1000 gallons.

For ozonation of this system, the cost increase per person then amounts to about 0.0074¢ per day, 22.5¢/mo or \$2.70/yr. Some of the O&M expenses will be reduced by longer filter life and less need for coagulant, flocculant and chlorine. Lower chemical

usage will also decrease the requirement for sludge removal and disposal. The reduction in total chlorine need, as well as where and when it is applied, reduces the potential for formation of THMs.

This system will now produce safer, cleaner, clearer, colorless, odorless and more palatable water for its customers. Legal liability should also be diminished, so the system may get a break on insurance or legal fees. It is now better prepared to safely enter the next century. It is also a system that can be altered easily and economically for future contaminate problems. In addition, more efficient use of filters can allow some increase in services without major capital expenditures.

The perception that ozone is a more expensive treatment is one apparent reason for it not being more commonly used in the United States.

Also, widespread availability and distribution of information or publicity on ozone treatment has been very lacking in the United States. Without this ready transfer of knowledge and expertise to designers, planners and regulators, ozone has had little chance of competing with chlorine. There was no high profit major industry, like the huge petro-chemical complex, to foster, research, push, lobby and advertise for the use of ozone.

WHAT ARE THE SAFETY ASPECTS ?

Ozone is a naturally occurring molecule that is with us constantly. Properly utilized and handled, it is safe, natural, and extremely useful. It can become harmful or dangerous only if used improperly or in excess. In 106 years of continuous ozone use in thousands of municipal water treatment facilities worldwide, no case of fatality has yet been attributed to ozone. Unfortunately, the safety record of chlorine is not as good.

Although ozone is a naturally occurring molecule, it is abnormal and uncommon for it to exist in high concentrations near ground level. It is quite unstable and has a high activity rate at the temperatures and pressures that occur near the Earth's surface. As natural and necessary as ozone is for Earth and its inhabitants, ground level is not its ideal environment, and this contributes to its reactivity and usefulness in water treatment.

One very nice characteristic of ozone, when used in water treatment, is that any excess reverts back to normal useable oxygen (O₂) when it has finished all other work at hand, making it virtually a nonpollutant. Some energy will have been expended in this process, but no chemical except the oxygen has been added to the water, leaving the water cleaner and safer to drink. This is a very important consideration to keep in mind.

Corona discharge ozone can be used virtually anywhere, even in portable units. Since ozone is made on site, as needed and where needed, there is no need to ship, store, handle or dispose of it, nor any containers, as is the situation with most chemicals utilized in water treatment. With ozone, there are no bags, boxes, barrels, bottles, jugs, tanks or pressure cylinders to ship, store, handle, recycle, return or otherwise dispose

of. No tankers full of gaseous or liquid ozone are traveling our rail roads, highways, streets or shipping lanes -- nor will there ever be.

Cylinders of gaseous or liquid oxygen are very seldom used, if ever, to supply ozone generators, first because of cost and second because of handling. Most systems generate their oxygen on site, others rely on drying systems for their air supply. The advances in development of low pressure (pressure swing absorption) oxygen concentrators brings the price, reliability, operating and maintenance considerations within the reach of almost any system. Good air drying systems are about the same expense, but only half of the ozone is produced in a similar sized ozone generator.

Worker exposure levels are not to exceed 0.002 g/m^3 in the air for an 8 hour work day, or 0.1 ppm by volume. Fortunately, this is well above the threshold a person is able to detect by smell.

The human nose is extremely sensitive to ozone, being able to detect concentrations of about 0.01 to 0.05 ppm or 0.0002 g/m^3 . This sensitivity is superior to some monitors on the market. A big plus for the nose as a monitoring device, is that it is very hard to misplace and needs no batteries. However, it's sensitivity is slightly reduced with prolonged exposure. In high concentrations, ozone will burn (oxidize) the mucus lining in your nose, like no sinus medicine you have ever encountered.

You can notice a whiff of ozone when the concentration is 1/10 the safe legal limit for a whole workday exposure. If you notice a whiff of chlorine gas, run for your life and warn others (if you can).

We cannot live in contact with excessive ozone nor can we live totally without it. Consequently, striking a balance by using ozone properly seems a logical and intelligent path to follow. Even though ozone has a very short half life, less in water than in air, it merits a great deal of respect while it is briefly present. It is a very strong and efficient oxidant and disinfectant. Any life form, including man, can be disinfected by ozone --- permanently.

The knowledge and testing needed for properly designing and operating ozone treatment systems are both here and accessible. Ozone off gas should not be a problem in a properly designed system. Encountering a need to deal with an excessive ozone off-gas problem would be an indication that the system is inefficiently designed or operated improperly, which is wasteful of material, energy and money. Although it is highly unlikely that any excess ozone could ever reach a customer, or cause any problem even if it did, wasting it is still inappropriate.

IS FILTRATION NEEDED ?

Keep in mind that bacteria and viruses can be encased or adsorbed on or in particulates in the water. These particulates, substrates and turbidity should be filtered out prior to any disinfection treatment for a good clean kill of organisms. Without this prior removal,

the ozone concentration and the time necessary to inactivate a protected organism can be much less economical. Both pre- and post-ozonation with filtration is best and is normally recommended. Without filtration, obstructing particulates will still be in the water supply. This holds true for any disinfection process.

Most ozone applications will require filtration, and it is almost always recommended. Settling alone may suffice occasionally, if ozonation is being used primarily to kill organisms in extremely clean water. Even then filtration is recommended, as the thought of a dead sterilized worm in your glass of clear water is not a great deal more appetizing than a live worm.

Flora, fauna and other complex molecules can be broken down sufficiently with ozonation to become a nutrient supply source or substrate for later bacterial growth, if any recontamination occurs. For this reason, this "soup" should be filtered out of your drinking water, particularly in large distribution systems.

Ozonation of any source water with natural organic matter will result in new and smaller units of biodegradable organic matter (BOM). These now smaller BOM units are essentially in more bite-size portions, that other organisms can easily assimilate. In any recontaminated system, this new food will allow easy bacterial regrowth. Such unstable water can most suitably be handled with filters utilizing biological treatment (biofilm) of sand, gravel or GAC with "good" bacterial action.

WHAT ARE THE SIDE EFFECTS AND DOWN SIDES WITH OZONE ?

Good: - short half-life in water, works quickly;
- ozone breaks down Trihalomethane and Total Organic Halide precursors to lower THM and TOX production potentials. This reduces the amount of chlorine required to maintain a residual (a nice double edged sword).
- increases biodegradability in humic and fulvic compounds.
- reduces BOD and COD.
- initially oxygenates ground water.
- can prolong filter media life.
- adds only oxygen to the water.

Bad: - short half-life in water, little residual for distribution systems.
- filtration required in virtually all cases.
- filtration is always recommended with O₃ treatment.
- corrosive as a gas and in solution (that's how it works).
- reputation of being expensive.
- not yet well understood by many designers and regulators.

The contact time (Ct) value is more difficult to determine, as on paper this is a very complex disinfection and treatment technology.

Ozone reacts so rapidly in water, that it is difficult to measure.

Its exceptional oxidizing and corrosive properties need to be fully recognized during design and construction of facilities to avoid unwanted effects.

The small and temporary ozone residual, accompanied with the increased oxygenation of the water, can contribute to the oxidation of interior surface of metal piping systems. Once a finite surface is oxidized, further oxidization is reduced. This is a similar effect to blueing a gun barrel to prevent rusting. In the case of copper plumbing with soldered joints, this oxidized layer may prevent some further leaching of lead and copper into the system, but reliable research to back up this theory has not yet been located.

If manganese is present with excess O_3 , it can be oxidized to permanganate over time, which is normally an undesirable pink.

Ozone gas might be likened to an airborne acid, because it will rust or corrode nearly anything that it contacts. This includes electrical terminals in test instruments.

Information on ozone is only recently becoming readily available and accessible. Formal education about ozone has been virtually nonexistent in American higher education facilities for engineers, designers, regulators and others.

THINGS TO CONSIDER.

Oxygen is used as the oxygen source for small to large applications:

- Yields of 5 to ~16% of ozone by weight can be produced from pure O_2 .
- Pure or enhanced oxygen is highly recommended as the supply source; many options for this are available today.
- Moisture and dust problems are totally avoided.
- Provides oxygenation as an additional treatment with the O_3 .
- Nitrogen and nitrous oxides are not added in the treatment.

Air is used as an oxygen source in all sizes of facilities:

- Yields up to ~5% of ozone by weight from dry air.
- DRYING; is a MUST, as moisture causes corona shorting and allows nitric acid to form, both of these cause severe maintenance and repair problems.
- FILTERING; is a MUST, as dust also may contribute to corona shorting.
- Undried and unfiltered air is never recommended.
- Provides aeration as an additional treatment with the O_3 .
- Nitrogen and nitrous oxides are carried into the water.

Under vacuum conditions, ozone handles very well. Any danger of gas leaks is virtually eliminated with vacuum-type systems, as the gas does not escape with an accident, contributing to improved safety.

O_3 -resistant materials must be used in parts, plumbing and seals. Anything that suffers weather deterioration, rust, corrosion or other natural deterioration will be destroyed by

ozone. Stainless steel, glass, teflon and hypalon are some good choices when handling ozone gas. Ozone is so corrosive that only 316L stainless steel is recommended in specific parts of some systems.

Any residual capability that ozone has in water after all other demands are satisfied is largely a function of alkalinity, pH and temperature.

Ozone seems intent upon reducing the molecular weight of everything, even of itself by self-destructing into O₂.

The actual toxicity level of ozone in larger aquatic animals and vertebrates is not precisely known. Ozone breaks down gill or skin tissue for the immediate cause of death (mechanical). This is toxicology versus toxicity.

The half-life of ozone in water is short; it is measured in seconds and minutes. In very dry air the longevity for ozone is measured in minutes and hours.

Keep ozone cool during generation and when piping it even short distances, as it self-destructs more rapidly at higher temperatures. Above 35°C (95°F), it reverts back to oxygen very quickly. Cooling, which can be a significant problem when compressing air as a source gas, is less of a problem when using a vacuum type system and little or no problem with precompressed air and oxygen systems.

As the ozone concentration is usually less than 15%, considerable aeration is accomplished via the other 85%+ of air or oxygen. Aeration, oxygenation and air stripping are by themselves viable forms of water treatment and the methods most used by Mother Nature. Ozonation merely hypes up some of the oxygen components for increased speed and efficiency.

SOME TREATMENT LEVELS.

Several approximate treatment levels are listed, but are dependent on temperature, pH, facilities and etcetera. Where YES is in a column, the above recommended treatment is normally more than adequate. Where the SPEED is left blank, the author has no experience or reliable data.

Pathogen or Organism	mgO₃/L Min.	Time mg min/L	C × t	Log
ALGAE --(blue-green)-----recommend--	0.30	5.0	1.5	
BACTERIA ---all-----recommend--	0.10	1.0	0.1	4+
Aeromonas & Actinomycetes	yes			
Bacillus, all	yes			
Campylobacters	yes			
Clostridium botulinum & others	yes			
Escherichia coli (E.coli)	0.04	1.0	0.04	4+
“ coliphage MS2	0.20	0.5	0.1	4+
Flavobacterium	yes			

Helicobacter (pylori)	yes				
Heterotrophic Bacteria-HPC	0.20	0.5	0.1	3	
Legionella pneumophila	yes				
Micrococcus, all	yes				
Mycobacterium tuberculosis, leprae	0.01	6.0	0.06	4	
Pseudomonas aeruginosa, fluorescens	0.01	1.0	0.01	~4	
Salmonella, all	0.01	1.0	0.01	~4	
Shigella shigellosis, dysentery	+ yes				
Staphylococcus sp, albus, aureus	+ 0.01	1.0	0.01	4	
Streptococcus, all	0.01	2.0	0.02	~4+	
Vibrio: alginolyticus, anguillarum	yes				
cholerae, comma,	yes				
parahemolyticus	yes				
Yersinia enterocolitica	yes				
FUNGI-MOLDS-YEASTS --recommend--	0.30	5.0	1.5	4+	
Mold Spores	0.03 □ .30				
NEMATODES --all-----recommend--	1.00	5.0	5.0	4+	
hook worm & etc.	0.50				
PROTOZOA --all-----recommend--	1.5	5.0	7.5	~4	
Acanthamoeba & Naegleria	0.2	0.5	0.1	2>4	
Amoebae Trophozoites cysts	0.4	4.0	1.6	>2	
Cryptosporidium	-recommend-1.5	5.0	7.5	~4+	
Cyclospora	yes				
Entamoeba (histolytica)	yes				
Giardia lamblia	-recommend-0.8	5.0	4.0	4+	
Giardia muris	0.50	5.0	2.5	3+	
Microsporidium	yes				
N. gruberi	0.50	5.0	2.5	3+	
TREMATODES --all-----recommend-	1.00	5.0	5.0	4+	
flat worms, flukes & etc.	0.30				
VIRUS --all-----recommend--	0.40	4.0	1.6	4+	
Adenovirus, 7A	0.30	3.0	0.9	4	
Astrovirus	yes				
Calicivirus	yes				
Echovirus 5, 12 & 29	0.40	4.0	1.6	4	
Encephalomyocarditis	yes				
Enterovirus, over 35 types	0.30	4.0	1.2	4	
coxsackie, B3 & B5	0.60	1.0	0.6	4	
poliovirus, 1, 2 & 3	0.30	4.0	1.2	4	
Hepatitis, A, E & HAV	yes		0.2	2	
non-A & non-B	yes				
Myxovirus influenza	yes				
Norwalk	yes				
Picobirnavirus	yes				
Reovirus, 3 types	yes				

Rotavirus, 3 types	yes	-	0.2	4
Substance or Molecule			mgO₃/mg	Speed
Aluminum				rapid
Ammonia to Nitrate, NH ₃ → NO ₂ → NO ₃ , (free > pH 9) (need DO)			4.0	slow
Ammonia □ N + H ₂ O				fair
Aromatic Compounds □ CO ₂ + H ₂ O + O ₂				fair
Aliphatic Compounds □ CO ₂ + H ₂ O + O ₂			fair	
Antimony				
Arsenic				rapid
Barium				slow
Benzene				rapid
Beryllium				
Boron				
Bromine, can go to bromate				fair
Cadmium				slow
Calcium hardness, already fully oxidized and soluble				----
Carbonic Acid □ CO ₂				rapid
Chlorine: chloramine, chlorine dioxide, chlorite, hypochlorite, hypochlorous acid, zinc chloride			fair	fair
Chromium	alone			slow
Cobalt			rapid	
Copper				rapid
Cyanide □ Cyanate □ N + H ₂ O			3.1	rapid
Flocculation, misc.				rapid
Fluoride				slow
Formaldehyde □ H ₂ CO ₃ + CO ₂ + H ₂ O				rapid
Formic Acid □ CO ₂ + H ₂ O				rapid
Ethylene □ CO ₂ + H ₂ O				fair
Iron, Fe siderite FeCO ₃ □ Fe(OH) ₃			0.43	rapid
Ferrous Iron to Ferric Hydroxide				fair
Lead				fair
Magnesium, Mg				slow
“ hardness, already fully oxidized & soluble				----
Manganese, Mn				fair
rhodochrosite, MnCO ₃ □ □ MnO ₃			0.88	fair
Manganese Dioxide to Permanganate, will go pink/excess			2.20	slow
Mercury, with pH & etc.				fair
Methane □ CO ₂ + H ₂ O				fair
Molybdenum				
Nickel			slow	
Nitrate, already fully oxidized				----
Nitrite to Nitrate, NO ₂ → NO ₃			1.04	fast
Organic Acids, □ CO ₂ + H ₂ O + O ₂				rapid
PCBs				slow

Selenium				
Silver				slow
Sodium				
Strontium				
Styrene				fast
Sulfate, already fully oxidized				----
Sulfide to Sulfate, $S \rightarrow SO_3 \rightarrow SO_4$			6.0	fast
Sulphur Compounds, $\rightarrow CO_2 + H_2O + SO_3 + O_2$				rapid
Thallium				
Toluene				fast
Trichloroethylene, $\rightarrow CO_2 + H_2O + HCl$				rapid
Vanadium				
White phosphorous				
Xylene				fast
Zinc				slow
COLOR	TOC	per mg of Carbon	1-3	fair
	DOC	per mg of Carbon	1-3	fast
Natural Organic Matter, per mg TOC / lower MW Carbon			4+	rapid
Synthetic Organic Chemicals, SOCs, some need AOPs				rapid
Coagulation - misc			0.5-1.5	rapid
Precipitation - misc			0.5-2.0	fast

SOME DESIGN PARAMETERS.

Concentration: amount of O_3 in a gas, whether using air or oxygen.

Contact time: $C \times T$, CT , $C \times t$ or $C \times T$; is briefly the Concentration weight in mg multiplied by the Time in minutes per liter solution, $mg \times min/L$ or $mg \times min/L$.

Dose rate: $mg O_3/mg$ substance to be oxidized;
 $mg O_3/L$ for period of time, $C \times t$, for kill.

Filtration rate: Lpm/m^2 , gpm/ft^2 - surface area, **not** volume.

Flow rate: L or m^3 per minute, hour or day; ie. m^3/h or gpm .

Ionic strength: little at ≤ 1000 TDS mg/L .

Mixing and distribution: system design and operation is as important as the dose rate and or time, as these do not function independently.

Organic matrix: transformed molecules into by-products, some may problematic.

pH: the higher the pH, the lower the stability;
higher pH \rightarrow faster decomposition of O_3 ;

little impact on the bactericidal or virucidal effect of O₃ at 6 to 10 pH, as the pH probably affects the organisms more than the ozone, such as the case with Giardia at pH of 7 to 9; little pH change with ozonation is normal, <0.2 pH.

Pressure: increased pressure increases solubility in water, as well as keeping bubbles smaller for better contact.

Retention time: sufficient time must be allowed for each reaction to initiate and complete. This includes time for dilute molecules to come in contact with the also dilute ozone or radicals. Remember, working with only a milligram (0.001 gram) or so per liter of H₂O (1,000. grams).

Temperature: at higher temperatures O₃ is less stable; a 10°C rise gives a 2 to 3 times reaction rate increase. Increased temperature seems to have little effect on the disinfection rate within the ambient range of water treatment.

Settling time or rate: minutes or hours per liter or gallon.

Turbidity: test all components; TOC (total organic carbon), DOC (dissolved organic carbon), color (carbon or mineral) and other.

AN EXAMPLE OF AN OZONE TREATMENT

COMMUNITY: 200 residents; some farming, light industry and services.

WATER NEED: estimate 40,000 gal/day (28gpm avg); design for 150m³/d with a 200m³ covered holding reservoir.

SOURCE: creek-fed, with some up stream development, farms and forest.

QUALITY:	<i>maximum</i>	<i>minimum</i>	<i>desired</i>	<i>treatment</i>
Temperature 20°C	5		OK	---
pH	8.1	6.9	~7.0	---
Turbidity	21NTU	8	<0.5	floc. & filt.
Color (TOC&Fe)	poor	fair	0	ozone
Taste-Odor(TOC&Fe)	5TON	2	<1	ozone
Color, Pt-Co	36.0mg/L	15.0	1.0	0.10gO ₃ /g
Color, TOC	5.1mg/L	4.0	2.0	1.00gO ₃ /g
Hardness, CaCO ₃	45.0mg/l	37.0	---	magnetically
Iron	1.1mg/L	0.3	0.3	0.43gO ₃ /g
Manganese	0.4mg/L	0.09	0.05	0.88gO ₃ /g
Pathogens:				
E. coli	yes		0	0.01C/t
Cryptosporidia	probable		0	7.5 C/t
G. lamblia	yes		0	4.0 C/t
Viruses	probable & suspected		0	1.6 C/t
Amoebae	yes		0	1.6 C/t

OZONE REQUIREMENTS: (1mg/L=1g/1000L=1g/m³) for 150m³/d.

Cumulative Need; O ₃ for 150m ³ /d of H ₂ O,	g/d	gO₃/g	
Color, Pt-Co	5,250	525.	
Color, TOC	465	465.	
Iron	120	52.	
Manganese	53	<u>47.</u>	= 1,089g/d
Odor & Taste, (/TOC & Fe) - above			
Concentration (C□t); mgO ₃ □min/L, use worst case,			
Cryptosporidium at 1.5mgO ₃ x 5.0min/L,			= <u>225g/d</u>
TOTAL OZONE NEED: (55g/h, 1.31kg/d or 2.90lb/d)			= 1,314g/d

FACILITIES: Design to place the **cumulative** need of 1,089g of O₃ prior to or with the mixing for any flocculation and/or coagulation, which is prior to filtration. The **concentration** need of 225g for the C□t is sustained after filtration. Any off gas is recycled to as near the initial intake area as practical for full reuse. The chlorine for residual requirements in the distribution system will be after the C□t ozonation, but prior to the distribution system.

PHYSICAL PROPERTIES OF OZONE.

Molecular: weight of gas, 47.9982g/mol

bond angle 117.47□

bond length 1.2716A

force constant for bond stretching; 5.74 N/cm or m dyn/A

vibrational frequency: Sym. str. 1103cm⁻¹

Bend 701cm⁻¹

Antisym. str. 1042cm⁻¹

Density: Gas; O₃ 2,141.9mg/L @ 0□C & 1.0atm, (Air=1,293 & O₂=1,429mg/L)

O₃ 1,995mg/L @ 20□C & 1.0atm, (Air=1,204 & O₂=1,331mg/L)

Liquid; 1.614g/L @ -195.4□C, dark blue color

1.090g/L @ 0□C, pale blue color

Solubility in water, @ 1.0atm, 293.13T/K, 1.885x10⁻⁶±10% @ 7.0pH:

Temperature		Solubility mg/L				O ₂
		OZONE, O ₃				
°C	°F	1%	2%	3%	5%	21% (from air)
0	32	8.31	16.62	24.92	41.53	6.95
5	41	7.39	14.79	22.18	39.97	6.12
10	50	6.50	13.00	19.50	32.50	5.37
15	59	5.60	11.19	16.79	27.98	4.73
20	68	4.29	8.57	12.86	21.43	4.34
25	77	3.53	7.05	10.58	26.33	3.91
30	86	2.70	5.39	8.09	13.48	3.59

Oxidation potential, 2.07 volts E□ at 25□C in alkaline solution

Viscosity, 1.56cP @ 90.2□K, 1.56mPas @ -183□C

Surface tension, 38.4dyn-cm @183□C

Melting point, -192.7□C or -420□F

Boiling point, -111.9□C or -169□F

Heat capacity, gas 8.0Cal/DegMole @ 111.9°C
Heat of vaporization, 3410kcal/mol @ -111.9°C or 3650kcal/mol @ -183.0°C
Critical temperature, -12.1°C or 10.2°F
Critical pressure, 54.6atm
Critical volume, 111.0cm³/mol or 6.77in³/mol
Molar volume, 0.08205 L/mol/K, 24.05L/mol @ STP for 20°C
Magnetic susceptibility; gas, 0.002x10⁻⁶cgs; liquid, 6.7x10⁻⁶cgs

HISTORY.

- 1886 Ozone recognized as a disinfectant for water.
- 1891 Pilot Plant proved effective against bacteria in Germany.
- 1893 First ozone drinking water treatment facility in Netherlands
- ~1903 First plant built in the U.S.A., in Niagara Falls, NY.
- by 1915 About 50 major ozone water treatment facilities in Europe.
- WWI Poisonous gas research leads to the development of cheap Chlorine production methods. The war and the chlorine competition slowed down ozone expansion.
- by 1936 France alone had about 100 ozone water treatment facilities, as they found ozone would remove taste and odor, along with iron and manganese, while still disinfecting their water supplies.
- WWII War again puts a crimp in ozone facility development world wide.
- 1940 Oldest currently operating plant in US came on line in Indiana.
- 1970s Concern over chlorination by-products began in US.
- 1990s Cryptosporidium renews interest in ozone treatment.

NEEDLESS TO SAY, THERE IS MORE THAN ENOUGH EXPERIENCE WITH OZONE.

We have been ingesting water sanitized with chlorine since the chemical industry found economical production methods during the development of poisonous gas weapons for WWI. Through the past and present use of chlorine, with ever modernizing water treatment facilities, countless thousands of people in the United States have been spared sickness and/or death from many water borne bacteria, viruses and other organisms. It now appears that Cryptosporidium has become the driver that will focus more attention to ozone for similar purposes. It should be possible to incorporate ozone into current and future treatment installations to dramatically assist the process of sanitizing our drinking water, which has for so long been dependent almost solely on deadly chlorine in the United States.

Ozone water treatment is not commonly referenced as 'Best Available Technology' (BAT) in literature or proposals. As well as ozone breaks down or oxidizes many noxious or nuisance compounds, it may never make the BAT list. Most writers, designers and regulators possess limited knowledge and understanding of ozone's usefulness in water treatment, primarily because ozone training in the curriculums of American educational institutions has been virtually absent.

MISCELLANEOUS.

Oxidation-reduction potentials, E° value, + Volts, ORP:

	F ₂	= 2.87	, fluorine
*	OH ⁻	= 2.80	, hydroxyl free radical
*	O ₁	= 2.42	, atomic oxygen
*	O ₃	= 2.08	, ozone, O ₃ +2H ⁺ +2e ⁻ → O ₂ +H ₂ O
*	H ₂ O ₂	= 1.78	, hydrogen peroxide
	MnO ₄ ⁻	= 1.68	, permanganate
	HClO ₂	= 1.57	, chlorous acid
*	HO ₂	= 1.50	, hydrogen dioxide
	HClO	= 1.48	, hypochlorous acid
	Cl ₂	= 1.36	, chlorine gas
	HBrO	= 1.33	, hypobromous acid
	ClO ₂	= 1.28	, chlorine dioxide
*	O ₃	= 1.24	, ozone, O ₃ +H ₂ O+2e ⁻ → O ₂ +2OH ⁻
*	O ₂	= 1.23	, oxygen
	Br ₂	= 1.09	, bromine, aq.
	HIO	= 0.99	, hypoiodous acid
	ClO	= 0.94	, hypochlorite
	ClO ₂ ⁻	= 0.76	, chlorite
	I ₂	= 0.54	, iodine

* Note: these are all expected to be formed and present, if only temporarily, during ozone treatment of drinking water.

If a Log 3 kill is accomplished for Giardia, it should be adequate at the same time for a Log 6 kill of any virus present (ie. MS2).

LOG	1	90.0 %	- kill factor
	2	99.0	
	3	99.9	
	4	99.99	
	5	99.999%	
	6	99.9999%	

Ozone is appropriate for assisting in many drinking water quality issues, such as:

- needs colors removed
- needs disinfecting
- needs inorganics removed, reduced or altered
- needs metals removed
- needs odors removed
- needs organics removed or altered
- needs plankton removed - animal, bacterial, plant or virus
- needs taste improved
- needs toxins removed or altered to a nontoxic state
- needs turbidity reduced

PRIMARY REFERENCES AND RECOMMENDED READING.

ALTERNATIVE DISINFECTION TECHNOLOGIES FOR SMALL DRINKING WATER SYSTEMS.

DeMers, Larry D.; Renner, Robert C.

AWWA Research Foundation and American Water Works Association, 1992

ANALYTICAL ASPECTS OF OZONE TREATMENT OF WATER AND WASTEWATER. EPA/600/4-87/018, PB87-201372

Rice, Rip G.; Bollyky, L. Joseph; Lacy, W. J.

Lewis Publishers, 1987

CRC HANDBOOK OF CHEMISTRY AND PHYSICS, 74th EDITION.

Lide, David R.

CRC Press Inc., 1993

HANDBOOK OF OZONE TECHNOLOGY AND APPLICATIONS: Volume I

Rice, Rip G.; Netzer, Aharon.

Ann Arbor Science, 1982 (NOTE: excellent source and more references)

HANDBOOK OF OZONE TECHNOLOGY AND APPLICATIONS: Volume II

Rice, Rip G.; Netzer, Aharon.

Ann Arbor Science, 1982 (NOTE: excellent source and more references)

IUAC SOLUBILITY DATA SERIES, Vol.7, Oxygen and Ozone.

Battino, R., Editor

Pergamon Press, Oxford, England, 1981

MICROORGANISM REMOVAL FOR SMALL WATER SYSTEMS:

EPA 570/9-83-012, June 1983.

OZONE IN WATER TREATMENT; Application and Engineering,

Cooperative Research Report by American Water Works Association,

Lewis Publishers, Inc., 1991. (NOTE: **a must have**, good text and references)

OZONE TREATMENT OF INDUSTRIAL WASTEWATER:

Rice, R. G.; Browning, M. E.

Noyes Data Corporation, 1981 (NOTE: excellent source and good references)

SWTR Guidance Manual, Appendix "O", EPA.

Also, many miscellaneous sources from a variety of areas and work since 1969; conversations, reports, seminars, study groups, notes, brochures, articles, publications and etcetera.

ABBREVIATION DESCRIPTIONS.

AMW	apparent molecular weight
AOC	assimilable organic carbon
AOPs	advanced oxidation processes
atm	atmosphere, 101 kPa, 14.696psi, 760mm of Hg
Å	angstrom, one ten-billionth of a meter,
BAC	biological activated carbon
BAT	best available technology
BDOC	biodegradable dissolved organic carbon
BOD	biological oxygen demand
BOM	biodegradable organic matter
COD	chemical oxygen demand
CPE	cytopathological effect
$C \times t$	concentration in mg x Minutes / L, or Cxt C is the concentration of dissolved disinfectant , in mg/L t is the nominal contact time, in minutes
CUR	carbon usage rate
DBP	disinfection by-products, MCL of 0.060mg/L proposed
D/DBP	disinfectants/DBP, rule
DO	dissolved oxygen
DOC	dissolved organic carbon
DOM	dissolved organic matter, humic & nonhumic
EBCT	empty bed contact time
GAC	granular activated carbon
gpm	gallons per minute
GOX	gaseous oxygen
gph	grams per hour, g/h, g/hr
HAA	haloacetic acids
HPC	heterotrophic plate count
IC	inorganic carbon
ie	example
kg	kilogram
kPa	pressure, psi x 6.895 or atm x 101.325
LOX	liquid oxygen
Lpm	liters per minute, L/min.
MCL	maximum contaminate level
MCLG	maximum contaminate level goals
MF	mF, microfiltration □0.05-0.1µm or greater pore size
mg	milligrams, 1/1000 of a gram, $1.0 \times 10^{-3}g$
mg/L	milligrams per liter, ppm
mg/SL	milligrams per standard liter
mgd	MGD, million gallons per day
MTC	mass transfer coefficient
MW	molecular weight
N	Newton

NF nF, nano filtration, ~0.0008 to ~0.009µm
 nm nano meters, one billionth of a meter, $1.0 \times 10^{-9} \text{m}$, 10^{-4}
 NOM natural organic matter
 NTU nephelometric turbidity units
 NTP normal temperature and pressure, 0°C or 273K and 1 atm,
 1013mb, 14.696psi or 760 mm Hg
 PAC powdered activated carbon
 PFU plaque forming units
 ppm parts per million, mg/L
 ppm_v parts per million by volume
 ppt parts per thousand
 psig psi, pounds per square inch
 PTA packed tower aeration
 %_v percent by volume
 %_w percent by weight
 Pt-Co color units in U.S., or mgPt-Co/L in Europe
 RO reverse osmosis, 5-15A
 SCFM - scfm or standard cubic feet per minute, American standard is usually
 20°C or 68°F temperature and 1013 mb pressure.
 SDWA safe drinking water act
 SMCL secondary maximum contaminant level
 SOCs synthetic organic chemicals
 STP standard temperature and pressure, 1 atm and 68°C
 SWTR surface water treatment rule
 TC total carbon
 TDS total dissolved solids
 THM trihalometanes, MCL of 0.10mg/L to 0.080mg/L, proposed
 THMFP trihalomethane formation potential
 TMDL total maximum daily load
 TOC total organic carbon
 TON threshold odor number
 TOX total organic halides
 TOXFP total organic halide formation potential
 TU turbidity unit
 UF uF, ultrafiltration, ~15A to ~0.1µm
 UV ultraviolet light
 UV-254 UV absorbance at 254 nm
 µg micro gram, one millionth of a gram, 1/1000 mg, $1.0 \times 10^{-6} \text{g}$
 µm micro meter, micron, one millionth of a meter, 1.0×10^{-6}
 VOC volatile organic compound

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