OZONE

{ O_3 } IN DRINKING WATER

TREATMENT

a brief overview
106 years & still going

(CONDENSED VERSION)

DRAFT - JGE - 2/1/99 ??FINAL??
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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. I 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, $O_3 \quad O_2+O_1$, which allows it to react with almost anything it encounters.

Our ground water, steams, 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.

Why Use Ozone?

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 t (*concentration & time)* is about 100 times greater for free chlorine than for ozone. With viruses the C 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 $mgCl_2/L$. 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.
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.

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 ($2O_3$ $3O_2$). Since it required energy to create ozone, destruction back to O_2 releases energy as an exothermic reaction of 68,800 calories.

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.

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 quicky, the radicals it forms will continue reacting.

One indirect example of ozone molecules contacting water ($O_3+H_2O \quad O_2+OH^-+OH^-$) 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.

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.

WHAT SHOULD NOT BE TREATED WITH OZONE ?

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 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.

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

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 1.5mgO_3/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 it's 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.

One very nice characteristic of ozone, when used in water treatment, is that any excess reverts back to normal useable oxygen (O_2) 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

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.

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,

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.

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 O_3 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 (C t) 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.

**Highlights from full article written by Jim Eagleton 2/1/99
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