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SENSING AND MEASURING OZONE IN WATER

THE BASICS OF DISSOLVED OZONE

Ozone is generally dissolved in water to disinfect for bacteria, virus and other microorganisms, to oxidize and thus create removable solids of dissolved minerals, and to neutralize undesirable chemicals. It is also used for other purposes such as to allow lower temperature wash water and to minimize residuals in wash processes ranging from laundry to semiconductors. For any application, ozone should be efficiently dissolved into the water, and the dissolved ozone should be measured at various points in the process.

Eco Sensors, Inc. has recently developed a simple, low-cost dissolved ozone meter building upon techniques and insights we have developed in our very popular instruments used to sense and measure ozone in air. During the research and experimentation process in developing this instrument, we sorted through lots of information about dissolved ozone. We thought it would be helpful for everyone to organize and summarize this information. It will be particularly useful for people who are evaluating various potential dissolved ozone instruments for their process. It will also give you a good understanding where our instrument fits among the instrument choices and where it should and should not be used.

Ozone Generation and Transfer Efficiency

Ozone is generated in air and is forced into water by a Venturi effect injector, a high porosity contact block, or is generated directly in the water by electrolysis. The transfer efficiency, or mass transfer, refers to the amount of ozone immediately in the water compared to the amount of ozone injected into the water. The dissolved ozone concentration will vary according to the ozone dosage, transfer efficiency, the contact time of the ozone with the water, and the ozone demand (less demand generally means higher water quality). A major variable affecting transfer efficiency is the water temperature (Colder water will dissolve much higher concentrations of ozone than warmer water). Another variable that should not be overlooked is pH (should be near 7).

Maximizing Ozone Dissolved in Water

The true dissolved ozone content of water will increase when the entrained ozone is forced into solution. This is often done in a vessel called a contact tank. Often there will be a higher concentration of ozone in the tank than in the piping before it. The contact tank, or contact chamber (or a series of chambers), is installed to more completely dissolve the ozone in the water and to facilitate maximum contact with whatever in the water is to be destroyed or inactivated by the ozone such as bacteria or minerals.

Factors Reducing Ozone Concentration

In the flow channel after the contact tank or general contact area, the ozone concentration in the water declines due to consumption by such "ozone demand" factors as microbes, minerals, and organics. It also has a time exponential decline due to its natural "half-life" (time for the concentration to fall in half). Half-life depends on ozone demand, temperature, pH and other factors.

Assuming a neutral pH of about 7 and room temperature, typical ozone half-lives in water are:

1 - Clean, high quality water	Over 10 minutes
2 - Water with some chlorine or minor contaminants	1-10 minutes
3 - Moderately dirty water, water with strong chlorine or organics, etc.	10-60 seconds
4 - Waste water with significant reaction elements	A few seconds

OZONE MEASUREMENTS AND INSTRUMENTATION

Ozone Measurement Points

It is important to be sure what measuring point in the ozonated system someone is referring to, because these often are not specified. The ozone concentrations vary greatly from point to point. Ozone is often measured at one of the following three points in an optimized system:

1 - At the injection point ("ozone dosage") Measurement can be made in the water just after the injection point. It is sometimes preferred to measure the ozone in air just before the injection point. In either case, care must be taken due to high pressures or vacuums, high ozone levels, and high gas or liquid flow rates and volumes. Usually this is not an area for hand-held ozone instruments, and in many cases ozone concentrations here should only be measured by specially designed probes.

2 - At the contact tank In the area called the contact tank or contact chamber, where the ozone is designed to have prolonged contact with the water and its constituents, the dissolved ozone usually has its highest concentration and the flow rates and pressures are often lower than at the ozone injection point. On-line instruments or portable instruments using samples from taps can generally be used here.

3 - At the exit of the system (but before any dissolved ozone destruct unit) This is the point where the "residual" dissolved ozone is measured. This is where samples can be taken from bottled water bottles, swimming pools or spas, vegetable washing areas, cooling towers, etc. This is generally an ideal measurement point for hand-held sampling instruments such as the Eco Sensors EZ-10W, but on-line instruments can also be used here. Ozone concentrations are usually much lower than upstream and so are water pressures.

The residual dissolved ozone is a critical measurement because it indicates that:

1 - Everything upstream is working correctly including of course the ozone generator.

2 - There is a high ozone transfer efficiency.

3 - Any targets such as bacteria to be removed by the ozone would most likely have been removed because ozone was present all through the system.

4 - There is not excessive ozone in the system outflow area where people or animals in the area would be harmed by the ozone.

Common Methods for Measuring Dissolved Ozone

Prior to the introduction of the Eco Sensors dissolved ozone instruments, dissolved ozone has generally been measured by the following methods:

ORP or "Redox" A two-electrode ORP (oxidation-reduction potential) or "redox" meter measures the oxidizing capacity in the water. It is not selective between different oxidizing agents such as chlorine or ozone, but for destroying bacteria and other things that distinction isn't always

important. ORP meters are inexpensive but require local calibration based on local water chemistries and the probes should be maintained frequently. ORP meters don't need temperature compensation.

Electrochemical The ozone migrates through a permeable membrane and then is converted to oxygen. The relative quantity of oxygen is measured by an electrochemical cell. Electrochemical instruments are usually configured for on-line use. The probes are expensive, easily damaged, and require regular maintenance, but these instruments are much more ozone selective than ORP meters, and are widely used in larger systems.

Wet Chemistries and Test Kits Wet chemistries in use mainly are titrations of iodine solutions and indigo trisulfonate (ITS) test kits. With the test kits, the blue indigo is bleached with ozone and the color difference is usually measured by a digital colorimeter. The indigo reagent is purchased in one-time use glass ampules. These test kits are very specific for ozone and are relatively inexpensive if not too many ampules are regularly consumed. They are fairly intricate to use, however, and the reagents lose their calibration if they have been stored for a long time.

Ultraviolet (UV) Absorption The ozone is removed or "stripped" from the water and the ozone is measured in air by a UV absorption analyzer. This method is very specific to ozone, is capable of high accuracy, and many concentration ranges can be accommodated. High concentrations can also be measured by UV absorption directly in the water. The equipment cost tends to be out of range for small systems however.

The Eco Sensors Model EZ-10W and DOM-1 Dissolved Ozone Instruments

The Eco Sensors dissolved ozone instruments are designed to have many of the best features of the instrument types reviewed above. It is a basic new design based on exhaustive research to find a better way. A key concept is to release all of the ozone from the sample water before measuring it by rapid agitation of the sample. This method is the basis of an instrument that is effective, inexpensive and easy to use. Features include:

- Low in cost. No consumables.
- Ozone specific.
- Insensitive to common concentrations of chlorine and salinity. Some interference from strong VOCs.
- Easily understood by non-technical personnel.
- The Sensor and probe do not touch the water.
- The **EZ-10W** is battery operated and is for grab samples. The **DOM-1** is for continuous on-line use and has provisions for process control.

RECOMMENDED REFERENCE:

OZONE for Point-of-use, Point-of-Entry, and Small Water System Water Treatment Applications, Water Quality Association, Lisle, Illinois, USA, www.WQA.org (Hardcover Book, 86 pages)