Article 109

Residual Ozone Monitoring and Control

Introduction

Ozone has been used as a disinfectant for decades and its popularity rises and falls with changing technologies, costs and requirements. Once heralded as the new super disinfectant set to rival chlorine, ozone in water as a disinfectant is a small part of the market and is generally restricted to specialist applications.

What is so great about ozone as a disinfectant?

- It's very efficient ozone is approximately 20 times more efficient than chlorine¹.
- It can tackle chlorine resistant pathogens such as Cryptosporidia Parvum and Giardia Lambia Crypto and Giardia typically spread as oocysts which are resistant to chlorine disinfection².



- It is much better at oxidising organics than chlorine disinfection by-products such as Trihalomethanes (THMs) formed by the reaction of chlorine with organics are believed to be carcinogenic. Ozone can break down the organics such that they cannot form disinfection by-products (DBPs) when chlorine is added later in the process³.
- With ozone disinfection there are no disinfection by-products - ozone oxidation doesn't result in any DBPs⁴.

What are the problems associated with ozone as a disinfectant?

- Very aggressive on materials ozone is not chemically compatible with many common building materials and care must be taken over materials of construction⁵.
- Difficult to get into solution particularly at higher temps - ozone is notoriously difficult to get into solution and sophisticated regimes and mixing systems are required to ensure stability⁶.
- An extreme irritant and possibly toxic ozone

- can be identified by its distinctive smell and exposure to ozone is regulated in most jurisdictions^{7,8}.
- Capital maintenance and power intensive ozone
 is generated at point of use, generally by electrical
 discharge through air or oxygen. The cost of such
 generators far exceeds the costs of a tank and a pump
 (chlorine).
- Difficult to measure residual and control see below.

Applications

As mentioned above, ozone tends not to be the first choice as a disinfectant due to the cost and complexity. There are, however, specific applications when ozone is the most effective overall for the outcomes desired.

The most common specific applications are described below:

- Drinking water treatment pre-treatment (organics) - dissolved ozone is used to destroy the organics from a raw water source in order to reduce the scope for disinfection by-products to form when chorine is added later in the process.
- Water treatment pre-treatment (Fe and Mn removal) ozone can be extremely effective at oxidising both iron and manganese to insoluble forms which allows their removal from drinking water prior to additional treatment⁹.
- Bottled drinking water bottled drinking water is
 often disinfected with ozone because it is extremely
 effective and leaves no residual. In turn this means
 that there is no residual taste. Once treated with
 ozone the bottles are sealed and the water requires no
 residual disinfectant.
- Aquaculture/Aquaria ozone is used in aquaria and aquaculture to disinfect the water and reduce the





residuals required 10 (please see further on in this document for comments on the ozonation of seawater).

- Washing (decay prevention) low levels of ozone can reduce the bacteria on the surface of foodstuffs (particularly fruit), which can greatly prolong the onset of decay, extending its shelflife and therefore increasing its value.
- Some industrial waste waters some industrial waste waters require an extremely powerful oxidiser to make the waste safe for the environment.
- Pools and spas in the 80s and 90s, there was
 a drive to reduce chlorine in pools and spas and
 ozone was introduced. Over time, the cost of
 purchasing and monitoring ozone dosing
 equipment in pools has tended redirect this
 emphasis towards better monitoring and control
 of chlorine dosing.

Measuring and controlling ozone disinfection

Getting ozone to stay in solution long enough to achieve a residual that can be measured consistently, and therefore control the process, is a challenge. Very often the amount of Dissolved Ozone (DO_3) in a solution has less to do with the ozone demand or the amount dosed and more to do with the ambient conditions that can cause ozone to come out of solution. That, and the relatively small residuals required, provide a challenge for the monitoring and control of DO_3 .

Monitoring small residuals requires an extremely sensitive and stable ozone sensor.

Over the years, there have been many varieties of sensor from colorimetric analysers (adding the water reagent so sample changes colour based on the amount of DO₃ present, and then measuring the colour change) to onen electrochemical sensors. Industry has largely settled using membraned amperometric sensors as they give the best balance between speed



response, longevity, capital and maintenance costs, stability, and sensitivity.

These sensors are extremely sensitive (0.001ppm) but can suffer from pressure fluctuations in the sample and bubbles of DO_3 coming out of solution. In addition they

need to utilise ozone resistant materials of construction as ozone is particularly corrosive.

Once a system has been set up such that:

- there is good disinfection of dosed O₃
- the monitoring position is set sufficiently downstream of the dosing point to ensure a steady state but not so far downstream that the DO₃ could have come out of solution

then PID control can be used to control dosing to a residual setpoint.

The ozonation of seawater

Adding ozone to seawater brings an extra level of complexity in that ozone oxidises the bromide ions in seawater to HOBr. This oxidation reaction reduces the DO_3 to OH radicals which in turn also act as an oxidising disinfectant. Effectively, adding O_3 to seawater can mean that disinfection is achieved by both DO_3 and HOBr. There can also be a residual free bromine.

This set of reactions makes it extremely difficult to control dosing using a DO_3 sensor, and many operators simply use a Free Bromine (or Total Bromine) sensor to control their addition rates.

References

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