Ozone and oxygen for sustainable odor and corrosion control

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Sustainable oxygen and ozone help improve safety and decrease costly equipment damage, says Paul Turgeon, CEO and Tonya Chandler, VP Sales & Marketing at Anue Water Technologies.

Wastewater systems have long been subject to issues with odor and corrosion, which is understandable given the nature of what they convey. The odor is the driving force behind implementing controls for these systems. Corrosion, however, is the issue with the greatest potential for environmental harm and real systemic and economic damage. This damage can arise in the form of burst pipes and other equipment and system failures.

Failures of this type require the repair and replacement of system materials and equipment, and they have the potential to expose the environment to unpredictable releases of hazardous waste that are difficult, if not impossible, to contain or recover.

Corrosion caused by H_2S

A major contributor to odor and corrosion in industrial systems is hydrogen sulfide (H_2S) and its associated compounds. Some industrial wastewater contains sulfur compounds, which provide the molecular basis for the generation of H_2S. H_2S arises from the combination of anaerobic conditions and the presence of sulfites and sulfates in conjunction with colonies of microorganisms present on the inner walls of all collection systems, referred to as the slime layer. Sulfate reducing bacteria (SRB) will use these compounds in the absence of free oxygen (O_2) for metabolism. These bacteria do not use the sulfur component, and it is available to react with water, specifically free protons (H^+), which results in the generation of H_2S.

Following its generation, H_2S can be released into the atmosphere and find its way to receptors through junctions of the atmosphere and collection system, at which point it is an odor concern. H_2S is a colourless gas that has a characteristic ‘rotten egg’ odor, is highly toxic and is corrosive to certain metals. It is heavier than air, meaning it can accumulate in wells, manholes and other locations that do not have much ventilation.

H_2S becomes a corrosion issue when it contacts moist concrete or steel (among other metals) in the presence of oxygen, even at very low gaseous concentrations. Conditions such as these are common in the headspace of some pipes and other areas where the collection system has easy access to atmospheric oxygen. Bacteria in these areas convert the H_2S into sulfuric acid, which then begins a destructive reaction with the infrastructure.

Historically, control of odor and/or corrosion has been implemented through either vapour phase techniques, where the headspace of a system is treated, or liquid phase techniques, where treatments target the liquid flow. Vapour phase treatments like scrubbers do not provide corrosion control. Some of the liquid phase techniques offer corrosion control.

The most common method of inducing liquid phase treatment, or directly treating the wastewater inside collection systems, has been by dosing chemicals into the systems. These chemicals are meant to react with the odor-causing compounds present in the wastewater, or cease their formation and/or release.

Conventional control options

The conventional classes of reactions used to control H_2S are:

- **Chemical oxidation** – Chemical oxidation of H_2S is accomplished through the use of a compound with a high oxidation potential, such as hydrogen peroxide or sodium hypochlorite (bleach).
- **Sulfide scavengers (iron salts)** – Chemicals that interact with H_2S and scavenge the sulfur into a relatively insoluble form, such as ferric chloride or ferrous chloride, can be used to remove sulfur from the cycle entirely.
- **pH adjustment** – Because of the way that its ions dissociate in the aqueous phase, the release of H_2S from wastewater will not occur if the pH is 9 or above.

In an anaerobic environment, the microbiology in a collection system will use oxygen from a nitrate (NO_3) molecule more readily than from a sulfate (SO_4) molecule and, as a result, benign nitrogen is released rather than H_2S. Chemicals like calcium or sodium nitrate are commercially available and can be used for this purpose. However, they can be expensive, and they feed and grow the SRB layer, potentially requiring a higher volume for treatment over time. Upon cessation of treatment, the amount of H_2S can be even worse than before. Increased clean-out cycles may also be required due to the addition of the waxes used to stabilize the nitrate molecules.

In addition, emerging federal and state regulations are beginning to include nitrate concentrations on discharge limitations. Real-time, active monitoring of wastewater H_2S levels is seldom carried out, so enough chemical to control peak H_2S values is typically added on a constant basis. By treating for peak values with chemicals such as these, the likelihood is very high that excess nitrate will be present and actively added to the wastewater, requiring additional denitrification processes or fines, both of which can be very expensive.

An issue with all chemicals is that, to introduce them to a collection system, a bulk quantity must be stored nearby. To ensure that chemicals are always available for treatment, continued deliveries to the bulk storage tank must be made. To avoid adverse effects to the environment, engineered controls, such as secondary containment and leak monitoring, must be designed, implemented and maintained.

Finding an alternative solution

Ideally, a successful treatment of wastewater odor and corrosion would:

- End sulfide production
- Quickly eliminate sulfides
- Bring about no additional hazard to life or the environment
- Do no harm to the collection system
- Create no additional challenges downstream
- Be cost effective.

One answer is the introduction of ozone and oxygen into wastewater systems to control odor and corrosion.

Ozone has long been used in water treatment, dating back at least to the late 19th century (primarily for the disinfection of drinking water),[1] and ozone treatment of water is common in Europe.[2] The controlled use of ozone does not produce harmful by-products – typically, the only by-products are O_2 and inert oxides. In recent years, Its environmental sustainability and relative safety *versus* chemical systems have led to renewed interest in its use to treat wastewater. This has driven the development of new and sustainable (green) technology for odor and corrosion control.

Ozone is a special, naturally occurring form of atmospheric oxygen. Instead of two oxygen atoms it has three, represented by its chemical formula O_3. This third oxygen atom makes it a highly reactive molecule with very high oxidation potential. In fact, it has the highest oxidation potential of any commercially available molecule, and the fourth highest overall with an oxidation potential of 2.07 volts (V). Above it, in terms of oxidation potential, are atomic fluorine (F•, 2.87 V), the hydroxyl radical (•OH, 2.86 V) and atomic oxygen (O•, 2.42 V). Ozone can be generated by exciting a flow of oxygen with sufficient electrical or optical energy. This will cause a certain amount of oxygen atoms to split and recombine with other O_2 molecules nearby.

$$3O_2 + Energy \rightarrow 2O_3$$

Under typical treatment conditions, using a relatively pure oxygen stream and a corona discharge chamber that uses a high-voltage electrical arc, this reaction can produce up to 9 to 12 percentage by weight (wt%) ozone,[3]although typically output is in 1 to 9 wt% ozone.[4] The remainder of the stream is left as oxygen. The concentration is limited to this range because:

$$2O_3 \rightarrow 3O_2$$

As ozone concentrations rise, the latter reaction becomes more frequent, returning greater quantities to O_2 and maintaining an equilibrium. This instability is also the reason why ozone cannot be stored and must be generated immediately before application.

Because of its extreme instability and high oxidation potential, ozone is powerful and indiscriminate in terms of reactivity with other chemical species. Ozone has been shown to be an effective treatment for: the destruction of volatile organic compounds; removal of metals, total suspended solids and organic carbon; and significant reductions to chemical oxygen demand.

In freshwater, the half-life of ozone is typically 10 to 20 minutes, but in wastewater it has been documented as being entirely consumed within 8.6 seconds.[5] This is because of the high levels of potential reactants present in wastewater, including H_2S. The simple structure of H_2S makes it an easy target for oxidation by ozone. In addition to its high oxidation potential, ozone's unique structure tends to create free radicals, chemical species that have unbonded electrons making them highly reactive, especially in water. Not only is the benefit of ozone's direct reaction with different chemical species realised, but also as part of these reactions, additional free radicals, which can be even more reactive than ozone, can form. Additionally, radicals tend to create additional radicals as they react, in what is termed a free radical chain reaction.

With the source of ozone generation being ambient air, it is the ultimate in sustainable and green chemical treatment. The current technology for producing ozone has benefitted from more than 45 years of ongoing development, resulting in cost-effective and robust operation. Using little more than an oxygen separator, a corona discharge chamber and some compressors and other electrical components, onsite generation of ozone is relatively simple and safe. This is in sharp contrast to most other treatments that are currently commercially available.

Because of the way ozone is produced, oxygen is necessarily going to be part of the treatment gas cocktail when using ozone. This is beneficial because oxygen is also an oxidizer. With an oxidation potential of 1.23 V, oxygen reacts more slowly than ozone but is an excellent complementary component. Aside from its ability to assist in oxidation, its primary benefit is increasing the dissolved oxygen (DO) concentration of the wastewater, encouraging the growth of aerobic bacteria, which do not create compounds that are odorous, corrosive or otherwise harmful to collection systems. It also eliminates the ability of SRB to produce sulfides, either by removing the SRB entirely or promoting the growth of aerobic species that will oxidize any sulfides before they are able to enter the wastewater stream.[6]

Combined use of oxygen & ozone for treatment

In terms of a robust and green method for the treatment and prevention of odor and corrosion in collections systems, the combined forces of oxygen and ozone are at the top of the list. Oxygen is widely available, making up roughly 21 percent of the atmosphere, and it is easily converted to ozone. The generation and infusion of these two gases into wastewater collection systems has been shown to be a clean, safe and cost-effective treatment. The first method of action is the powerful destructive effects of ozone on H_2S, quickly converting it to sulfites and sulfates on contact. In addition, ozone's antimicrobial properties can help to reduce the presence of SRB and other microorganism present on pipe walls. As a product of its reaction, oxygen is generated. This in turn adds more power to the oxygen portion of the treatment gas cocktail, which is providing secondary treatment by significantly increasing DO, and allows for more complete utilization of infused treatment gases.

Oxygen will also oxidize H_2S, but at a much slower rate than ozone. Because of these indiscriminate and powerful oxidizing characteristics, the concern is sometimes raised regarding the possibility of ozone attacking the wastewater infrastructure itself. However, this is unlikely to occur in application, especially in wastewater where liquid phase infusion is implemented. This is due to the high ratio of liquid volume compared to pipe surface area per unit pipe length and the high availability of reactants in the liquid portion.

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