Odor and Corrosion Control in Wastewater Collection Systems Utilizing Sustainable Treatment Gases: Oxygen and Ozone

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Introduction and Review

Sewage collection systems have long been subject to issues with odor and corrosion, which is understandable given the nature of what they convey. Sewage odor, the rotten egg smell almost everyone has experienced, is a localized and political issue and is really the driving force behind implementing controls in sewage collection 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, lift station degradation and other similar forms of equipment and system failure. Failures of this type not only require the repair and replacement of collection system materials and equipment, but also have the potential to expose the environment to unpredictable releases of hazardous waste that are very difficult, if not impossible, to contain or recover. In fact, according to the ASCE’s 2009 Infrastructure Report Card [ASCE, 2009], where a grade of “D-” was given:

"Aging systems discharge billions of gallons of untreated wastewater into U.S. surface waters each year. The Environmental Protection Agency estimates that the nation must invest $390 billion over the next 20 years to update or replace existing systems and build new ones to meet increasing demand."

A major contributor to odor and corrosion in these systems is hydrogen sulfide (H$_2$S) and its associated compounds. All human waste, and subsequently, all wastewater, contains sulfur compounds, which provide the molecular basis for the generation of hydrogen sulfide. Hydrogen sulfide arises from the combination of anaerobic conditions and the presence of sulfites and sulfates in conjunction with the colonies of microorganisms present on the inner walls of all collection system, referred to as the slime layer. Sulfate reducing bacteria (SRB) will utilize these compounds in the absence of free oxygen (O$_2$) for metabolism. These bacteria do not actually utilize the sulfur component, and it is available to react with water, specifically free protons (H$^+$), which results in the generation of hydrogen sulfide. This generation pathway can be represented by the following balanced reactions [Matthews, 2010]:

\[
\begin{align*}
SO_4^{2-} & \rightarrow S^{2-} \quad (1) \\
S^{2-} + H_2O & \rightleftharpoons HS^- + OH^- \quad (2) \\
HS^- + H_2O & \rightleftharpoons H_2S (aq) + OH^- \quad (3) \\
H_2S(aq) & \rightleftharpoons H_2S (g) \quad (4)
\end{align*}
\]

Following its generation, hydrogen sulfide can be released into the atmosphere, as shown in equation (4), and find its way to receptors through manholes or other junctions of the atmosphere and collection system, at which point it is an odor concern. Hydrogen sulfide is a colorless gas that has a characteristic rotten egg odor, is highly toxic and is very corrosive to certain metals. It is heavier than air, meaning it can accumulate in wells, manholes and other similar locations that do not have much ventilation. The effect it can have on humans, at varying concentrations relative to ambient air, is shown in the table below [EPA, 1985].
<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Physiological Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 - 3</td>
<td>Odor Threshold</td>
</tr>
<tr>
<td>3 - 10</td>
<td>Offensive Odor</td>
</tr>
<tr>
<td>10 - 50</td>
<td>Headache</td>
</tr>
<tr>
<td></td>
<td>Nausea</td>
</tr>
<tr>
<td></td>
<td>Throat and Eye Irritation</td>
</tr>
<tr>
<td>50 - 100</td>
<td>Eye Injury</td>
</tr>
<tr>
<td>100 - 300</td>
<td>Conjunctivitis</td>
</tr>
<tr>
<td></td>
<td>Respiratory Tract Irritation</td>
</tr>
<tr>
<td></td>
<td>Olfactory Paralysis</td>
</tr>
<tr>
<td>300 - 500</td>
<td>Pulmonary Edema</td>
</tr>
<tr>
<td></td>
<td>Imminent Threat to Life</td>
</tr>
<tr>
<td>500 - 1,000</td>
<td>Strong Nervous System Stimulation</td>
</tr>
<tr>
<td></td>
<td>Apnea</td>
</tr>
<tr>
<td>1,000 - 2,000</td>
<td>Immediate Collapse with Respiratory Paralysis</td>
</tr>
<tr>
<td></td>
<td>Risk of Death</td>
</tr>
</tbody>
</table>

Table 1 - Hydrogen Sulfide Health Effects at Varying Concentrations

Hydrogen sulfide becomes a corrosion issue when it comes into contact with moist concrete or steel, amongst other metals, in the presence of oxygen, even at very low gaseous concentrations. Conditions such as these are fairly common in the headspace of some pipes as well as at manholes, lift stations and other areas where the collection system is provided with easy access to atmospheric oxygen. Bacteria in these areas are able to convert the H₂S into sulfuric acid (H₂SO₄) which then begins to react with the infrastructure in a destructive manner.

Historically, control of odor and/or corrosion has been implemented through either vapor phase techniques, where the headspace of a lift station is treated, or liquid phase techniques, where treatments target the liquid flow. Vapor phase treatments like scrubbers do not provide corrosion control, as opposed to liquid phase techniques, some of which can offer corrosion control. The most common method of inducing liquid phase treatment, or directly treating the wastewater, inside the collection system, has been by drip dosing chemicals into the systems. A constant and continuous dose of chemical is fed from a large reservoir with a small pump into the collection system, typically at a manhole or pump station. These chemicals are meant to react with the odor causing compounds present in the wastewater or cease their formation and/or release from solution.

The main classes of reactions used for control of hydrogen sulfide are briefly described below:

*Oxidation*

Chemical oxidation of hydrogen sulfide is accomplished through use of a compound with a high oxidation potential, called an oxidant, such as hydrogen peroxide or sodium hypochlorite (bleach). This method of treatment involves the direct oxidation of H₂S into more benign forms, such as sulfites, sulfates and elemental sulfur. However, it does not affect the presence of SRB, which will likely continue to grow over time. Upon cessation of treatment, expression of hydrogen sulfide can be even worse than before, due to an increased output of the growing SRB layer. In addition, it is likely that increasing quantities of treatment chemical will be required over time for the same reason.
Sulfide Scavengers (Iron Salts)

Chemicals that interact with hydrogen sulfide and sequester, or scavenge, the sulfur into a relatively insoluble form, such as ferric chloride and ferrous chloride, can be used to remove sulfur from the cycle entirely. This treatment has no effect of the presence or production of the SRB layer, and cessation of use will see a return to the emission of hydrogen sulfide, possibly at an elevated level. For this reason it is likely that increased usage of time will be experienced as well. These chemicals will aggressively remove DO from the wastewater, can form scales on iron surfaces, such as pipes and pumps, and become an ongoing source of sedimentation due to the reaction of iron with sulfur forming FeS precipitate within the collection system. Continued and/or elevated risk of corrosion is a significant challenge with the use of ferrous and ferric chloride, due to the generation of acids as part of the scavenging reaction. An example of a reaction in which hydrochloric acid is generated is shown in equation (5).

\[
3H_2S + 2FeCl_3 \rightarrow S + 2FeS + 6HCl \quad (5)
\]

The bulk scale addition of iron to the collection system also presents the hazard of contamination of downstream solids. In fact, CERCLA considers iron salts a persistent environmental hazard [US Peroxide, 2011]. This aspect can significantly add to plant and biosolids processing costs.

pH Adjustment

Due to the manner in which its ions dissociate in the aqueous phase, the release of hydrogen sulfide from wastewater will not occur if the pH is at 9 or above. Through use of compounds that can induce and maintain significant increases to pH, such as sodium hydroxide or magnesium hydroxide, it is possible to take advantage of this trait and “trap” the sulfide in solution. This can be an expensive process, due to the volume of treatment chemical required to maintain such an elevated pH level and the relatively higher expense per gallon (liter). Also, treatment chemicals can be difficult to keep in solution, as is the case with magnesium hydroxide, especially in colder weather. A good illustration of this is magnesium hydroxide, which has a solubility of only 0.012 g/L in water; bordering on the line of insolubility. There is again no treatment or reduction to SRB, which can cause the problem to grow over time. Also, once pH decreases below 9, as can happen downstream of treatment and/or at the treatment plant, hydrogen sulfide is readily released, possibly at an increased rate due to the increased solution concentration.

Alternate Oxygen Source/Sulfate Substitute

In an anaerobic environment, the microbiology in the collection system will utilize oxygen from a nitrate (NO$_3$) molecule more readily than from a sulfate (SO$_4$) and as a result benign nitrogen is released rather than hydrogen sulfide. Chemicals like calcium or sodium nitrate are commercially available and can be utilized for this purpose. These chemicals are expensive and they actually feed and grow the SRB layer, potentially requiring higher volume for treatment over time. Upon cessation of treatment, the expression of hydrogen sulfide can be even worse than before. Excess wet well build-up requiring increased clean-out cycles due to the addition of the waxes used to stabilize the nitrate molecules can be encountered downstream in the collection system. In addition, emerging federal and state regulations are beginning to include nitrate concentrations on discharge limitations. There is seldom much real time, active monitoring of wastewater sulfide levels, so enough chemical to control peak H$_2$S values is typically added on a constant basis. By treating for peak values with chemicals such as these, there is a very high likelihood 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 in order to introduce them into a collection system, a bulk quantity must be stored nearby. In order to ensure that there will always be chemicals available for treatment, there
must be continued deliveries to the bulk storage tank. To make sure that the environment is not adversely affected (directly), various engineered controls, such as secondary containment and leak monitoring, must be designed, implemented and maintained. Essentially, money is being poured down the drain on a recurrent basis with no real solution to the problem ever taking place.

Ideally, successful treatment of wastewater odor and corrosion would cease sulfide production, quickly eliminate sulfides that are present, present no additional hazard to life or the environment, do no harm to the collection system itself and create no additional challenges downstream. In addition it must be cost effective. Such a solution is becoming available through the novel approach of introducing ozone and oxygen into collection systems as a means of odor and corrosion control.

Ozone has long been used in water treatment, dating back to at least the late 19th century, primarily for disinfection and polishing of drinking water [Beltran, 2004]. In Europe, ozone treatment of water is a very common process [Lenntech, 1998]. It is well established that ozone’s superior environmental sustainability and relative safety versus chemical systems has established it as the favored current and future technology. The controlled use of ozone as a treatment does not produce any harmful byproducts that could contaminate or harm the environment or ecology. Typically, the only by products from its reaction is O2 and inert oxides. In recent years, interest in its use in the wastewater industry has led to the development of new and sustainable (green) technology for the treatment of odor and corrosion in wastewater collection systems.

Ozone is a special, naturally occurring form of atmospheric oxygen. Instead of two oxygen atoms it has three, represented by its chemical formula O3. This third oxygen atom makes it a highly reactive molecule with a very high oxidation potential. In fact, it has the highest oxidation potential of any commercially available molecule and fourth highest overall with an oxidation potential of 2.07 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 O2 molecules nearby. This can be represented by the equation:

\[ 3O_2 + \text{Energy} \rightarrow 2O_3 \] (6)

Under the typical treatment conditions, using a relatively pure oxygen stream and a corona discharge chamber, which utilizes a high voltage electrical arc, this reaction can produce up to 9 – 12 wt% ozone [Drago, 2010], although typically output is in 1 – 9 wt% ozone [PTI, 2011]. The remainder of the stream is left as oxygen. The concentration is limited to this range because of the following reaction.

\[ 2O_3 \rightarrow 3O_2 \] (7)

As ozone concentrations rise above this concentration, the destruction reaction (7) becomes more frequent, thus returning greater quantities to O2 and maintaining this equilibrium. This instability is also the reason ozone cannot be stored and must be generated immediately prior to application.

Due to its extreme instability and high oxidation potential, ozone is very powerful and indiscriminate in terms of reactivity with other chemical species. Ozone has been shown as an effective treatment for destruction of volatile organic compounds (VOCs), removal of metals, total suspended solids, organic carbon and many, many more as well as significant reductions to COD. In freshwater the half-life of ozone is typically 10 – 20 minutes, whereas in wastewater, ozone has been documented as being entirely consumed within 8.6 seconds [Terry, 2010]. This is due to the extreme amount of potential reactants that are present in wastewater, foremost of which for the purpose of this paper, is hydrogen sulfide. The simple structure of hydrogen sulfide makes it a very easy target for oxidation by ozone.
In addition to its high oxidation potential, ozone’s unique structure tends to create free radicals, which are chemical species that have unbonded electrons making them highly reactive, especially in water. Not only is the benefit of ozone’s direct reaction with various chemical species realized, but as part of these reactions additional free radicals can form, which can be even more reactive than ozone. Additionally, radicals tend to create additional radicals as they react, in what is termed a free radical chain reaction. These additional reactions are referred to as the indirect effects of ozone [Beltran, 2004].

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 in excess of 45 years of ongoing development, resulting in cost-effective and robust operation. Utilizing 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 today. This is in sharp contrast to the majority of other treatments that are currently commercially available.

Due to the way ozone is produced, oxygen is necessarily going to be part of the treatment gas cocktail when using ozone. This is beneficial as oxygen is also an oxidizer. With an oxidation potential of 1.23 V, oxygen is a slower reactant than ozone, but an excellent complement. Aside from its ability to assist in oxidation, its primary benefit is increasing the 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 over the top that will oxidize any sulfides before they are able to enter the wastewater stream [EPA, 1985].

Combined Use of Oxygen and Ozone for Treatment

In terms of a robust and green methodology 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% of the atmosphere, and has already been seen, is easily converted to ozone. The generation and infusion of these two gases into wastewater collection systems has proven to be a clean, safe and cost effective treatment. The first method of action is the powerful destructive effects of ozone on hydrogen sulfide, quickly converting it to sulfites and sulfates on contact. In addition, ozone’s antimicrobial properties can help to actually 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 hydrogen sulfide, 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. This is very unlikely to occur in application, especially in wastewater where liquid phase infusion is implemented. This is due to the 1) high ratio of liquid volume compared to pipe surface area per unit pipe length and 2) the extreme availability of reactants in the liquid portion. It is highly unlikely that ozone will survive long enough to affect the wastewater infrastructure.

Treatment and Testing Methodology

Anue Water Technologies (AWT) of San Diego, CA designs and manufactures a comprehensive range of systems, referred to as FORSe 5™, that utilize oxygen and ozone for effectively inducing clean, sustainable and cost effective treatment of odor and corrosion in collection systems. The direct treatment of the wastewater is achieved through a proprietary process of treating a factional flow of wastewater and
returning this treated flow into the untreated flow, thus inducing change. This process is termed hydrodynamic infusion.

**Experimental Conditions**

The testing was conducted at a municipal waste water district in southern Arizona that had received numerous complaints from an upscale neighborhood regarding the presence of strong sewage odor. The odor was determined to be originating from the collection system by way of manholes located in their neighborhood. Traditionally, sodium hypochlorite (bleach) had been used for odor control, essentially system wide. This treatment, however, had not proven to be effective in controlling the odor being generated within the collection system. This is evident both by the complaints that were made as well as through the collection of \( \text{H}_2\text{S} \) vapor concentration data.

AWT has a trailer with a self contained treatment system onboard that was used in this test. It is referred to as the Mobile Diagnostic Unit (MDU) and shown in Picture 1. The MDU was placed at the treatment site and attached to a 2” tapping saddle on the force main (Picture 2) on August 18, 2011. The goal was the elimination of odor at the problematic downstream manholes, as well as total and dissolved sulfides, and to increase DO to levels above aerobic, or 1 mg/L. Three downstream manholes were utilized for sample collection, and are referred to as MH1, MH2 and MH3, with 1 being the closest to the point of treatment. MH1 was approximately 2 miles downstream from the treatment site and MH2 and 3 were an additional \( \frac{1}{4} \) to \( \frac{1}{2} \) mile from MH1.

![Picture 1 - Anue Water Technologies Mobile Diagnostic Unit (MDU)](image1.png)

![Picture 2 - Tapped Force Main with Attached Infuser](image2.png)

AWT began collection of grab samples, prior to treatment, at MH1 and placed an OdaLog sensor on August 17, 2011 at approximately 10:30 am. Grab samples were analyzed for pH, temperature and DO with a Hach HQ40d, \( \text{H}_2\text{S} \) via Drager tubes and total and dissolved sulfides were measured with LaMotte Sulfide test. Additionally, a third party sampling service was hired to collect liquid grab samples and OdaLog data from MH1 and solely OdaLog data from MH2 and 3, starting August 18 at approximately 9:30 am. Third party grab samples were analyzed for pH, temperature, ORP with an Oakton pH11 Series, DO with a Hach SensiION 6, and sulfides were again measured with LaMotte Sulfide test.
Treatment at the force main was initiated midday on August 18 and initially consisted of liquid phase infusion of 40 liters/minute O₂ on a continuous, 24 hour basis and infusion of 120 grams/hr O₃ whenever the force main pumps cycled on. On Friday August 19 the injection amounts were decreased to 20 liters/minute O₂ and 60 grams/hr O₃. The force main was 8” diameter and had a flow of 15,000 GPD, resulting in a significantly long retention time of 25 hours, between the treatment site and MH1. The bleach that had been used for odor control was ceased on August 16 at approximately 9:30 am, giving the system approximately 48 hours to resume untreated conditions.

**Results**

In order to effectively rate the successful treatment of the force main, a background against which to make a comparison must be provided. In this instance, the municipality had used the same third party testing service to quantify H₂S emissions from MH1 and 3. The baseline data, provided from June 30 – July 8, July 12 – 22 at MH 1 and July 15 – 21, 2011 at MH3, does not occur immediately before the MDU test, but is recent enough to provide a good representation of the potential H₂S levels present in these manholes. The OdaLog charts for these dates are included below, figures 1 – 3 are for MH1 and 4 – 6 for MH3.
Figure 1 - Baseline H₂S Concentrations at MH1, 6/30 - 7/4/11

Figure 2 - Baseline H₂S concentrations at MH1, 7/4 - 7/8/11
Figure 3 - Baseline H₂S Concentrations at MH1, 7/12 - 7/22/11

Figure 4 - Baseline H₂S Concentrations at MH3, 6/30 - 7/4/11
Figure 5 - Baseline H$_2$S Concentrations at MH3, 7/4 – 7/8/11

Figure 6 - Baseline H$_2$S Concentrations at MH3, 7/15 – 7/21/11
The first thing that should be noted is that in each chart there is significant “clipping”, as indicated by the plateau’s that occur at the peak values on each chart. This indicates that the H2S concentrations were outside the detection limit of the instrument, meaning that actual values were likely higher. Ignoring this clipping, the highest value provided for background H2S concentrations was 417 ppm and occurred at MH1 multiple times over the date range 7/7 – 7/12, as shown in Figure 3. The highest value recorded at MH3 is 347ppm and occurs on 6/30, as shown in Figure 4.

What is also shown in this data is the general nature of the systems behavior at this point in time. The wide range of concentrations covered within a very short period appears similar to the oscillations typically associated with an uncontrolled system. Variations to system conditions, such as in flow or wastewater chemical composition, yield a clear response, rather than maintaining a quasi “buffered” state with apparent stability within the environment, which would be indicative of overall system health. Due to the clipping it is hard to know exactly how extreme the concentrations are, but they are at least above 200 ppm throughout the entire system and definitely reaching levels above 300 ppm at MH1. These are levels which can present the risk of respiratory irritation as well as more severe threats to human health and they are being achieved on a regular basis while under chemical treatment. In additional to odor and health risks, these concentrations present a significant risk of infrastructure corrosion.

Figure 7 is from an OdaLog placed by AWT in MH1 and shows a small section of H2S concentrations prior to system activation, as well as the effect of the MDU treatment.

![Figure 7 - OdaLog H2S concentrations Prior to and During Treatment at MH1, 8/17 - 8/25](image)

The concentrations recorded between August 17 and 18 present and even more illuminating picture of the H2S generation potential in this portion of the collection system. The maximum and average values were recorded as 3469 ppm and 343 ppm, respectively. There was a heavy rain event that occurred over night between August 18 and 19 that is likely responsible for the extreme spike above 3400 ppm, but the concentrations preceding this spike are realistic and quite elevated; typically in the 500 – 1500 ppm range, and up to 2000 ppm. This also supports the suspicion that the third party OdaLog units were reaching detection limits very quickly and were not indicating the full extent of actual conditions.
The system was turned on around 1:00 PM on August 18. From Figure 7 it is apparent that approximately 24 hours later the H₂S concentration begins an extreme decline that ends at less than 10 ppm, where it stays the remainder of the test period. Detention time for this 2 mile stretch of force main was calculated to be 25 hours, which is in direct agreement with the OdaLog data.

As confirmation of these results, OdaLog data from the third party’s sampling is shown in Figures 8, 9 and 10.

With the exception of the data out of range for this OdaLog, Figure 8 behaves very similarly to Figure 7, providing confirmation that the extreme drop that started in the middle of the day on August 19 is realistic and that the treatment was able to significantly and consistently decrease H₂S concentrations. Again, by the end of the test, H₂S had stabilized at less than 10 ppm. There is some discrepancy between Figures 7 and 8 in the rate at which this decrease happened, and the reason for this is unknown at this time. It may have had to do with variances in saturation and subsequent rate of desaturation of the sensors on the two individual OdaLog units. The following two figures, 9 and 10, undergo a very similar pattern and rate of decline as that shown in Figure 7, which provides some indication that the rate of decline was greater than what is implied by Figure 8 alone.
Figure 9 - H2S Concentrations Prior to and During Treatment at MH2, 8/17 - 8/25

Figure 10 - H2S Concentrations Prior to and During Treatment at MH3, 8/17 - 8/25
Figures 9 and 10, from MH2 and 3, again show very similar reduction trends to Figure 3; a peak followed by a steep, continuous drop to less than 10 ppm, in about a day.

Grab samples were collected concurrently, the results of which are shown below.

![Figure 11 - AWT Grab Sample Results, MH1](image)

AWT collected grab samples while a technician was in the field, through August 20. These results are shown in the Figure 11 above as well as Table 3. Figure 12 and Table 4 contain the grab sample results from the third party.

<table>
<thead>
<tr>
<th>Time</th>
<th>Date</th>
<th>D.O. (mg/l) Hatch Meter</th>
<th>H₂S Vapor (ppm)</th>
<th>Total Sulfides (ppm)</th>
<th>Dissolved Sulfides (ppm)</th>
<th>Output: O₂ (l/m)</th>
<th>Output: O₃ (g/h)</th>
<th>System Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:30 AM</td>
<td>8/17/2011</td>
<td>0.82</td>
<td>12</td>
<td>20</td>
<td>13</td>
<td>N/A</td>
<td>N/A</td>
<td>OFF</td>
</tr>
<tr>
<td>2:30 PM</td>
<td>8/17/2011</td>
<td>0.18</td>
<td>3</td>
<td>20</td>
<td>18</td>
<td>N/A</td>
<td>N/A</td>
<td>OFF</td>
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<tr>
<td>10:30 AM</td>
<td>8/18/2011</td>
<td>0.18</td>
<td>7</td>
<td>17</td>
<td>14</td>
<td>N/A</td>
<td>N/A</td>
<td>OFF</td>
</tr>
<tr>
<td>1:00 PM</td>
<td>8/18/2011</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<td>40</td>
<td>120</td>
<td>ON</td>
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<tr>
<td>10:30 AM</td>
<td>8/19/2011</td>
<td>0.26</td>
<td>1.2</td>
<td>4</td>
<td>2.5</td>
<td>40</td>
<td>120</td>
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<tr>
<td>2:30 PM</td>
<td>8/19/2011</td>
<td>8.71</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>40</td>
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<td>3:00 PM</td>
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<td>60</td>
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<td>0</td>
<td>20</td>
<td>60</td>
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Table 3 - AWT Grab Sample Results at MH1 and System Status
Table 4 - Third Party Grab Sample Results at MH1

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>H₂S (PPM)</th>
<th>pH</th>
<th>Dissolved Oxygen (PPM)</th>
<th>Temperature (°C)</th>
<th>Total Sulfides (mg/L)</th>
<th>Dissolved Sulfides (mg/L)</th>
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<td>&gt;50</td>
<td>6.92</td>
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<td>34.1</td>
<td>11.0</td>
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<td>2.4</td>
<td>7.12</td>
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<td>33.8</td>
<td>8.0</td>
<td>7.0</td>
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<tr>
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<td>8.9</td>
<td>7.11</td>
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<td>35.2</td>
<td>8.0</td>
<td>7.5</td>
</tr>
<tr>
<td>8/19/2011</td>
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<td>&gt;50</td>
<td>7.25</td>
<td>0.92</td>
<td>27.1</td>
<td>4.0</td>
<td>2.2</td>
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<td>0.0</td>
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<td>0.5</td>
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<td>7.18</td>
<td>11.50</td>
<td>27.9</td>
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Correlation of Vapor to Liquid Grab Samples

Total and dissolved sulfides represent the liquid phase precursor to H₂S gas. By monitoring these values for reductions, we can verify treatment of the source is taking place, rather than simply a reduction in experienced odor. For example, at a pH of 7, H₂S is approximately 50% of the dissolved sulfide value, at pH 6 it is approximately 90%. By ensuring the source is being treated, the effectiveness of the treatment system is better established and it can be better assured that the detrimental effects of sulfide compounds are being actively prevented.

Both sets of the liquid grab samples have a high correlation, in terms of data trends, with the vapor phase data taken from the OdaLog units. In both tables above, there is a definitive decrease in H₂S, total and dissolved sulfides. A desirable inverse relationship of increasing DO levels to decreasing sulfide levels is also evident. The results from all these tests arrive at the same conclusion, indicating that the liquid phase infusion of ozone and oxygen into the force main was able to very effectively induce a significant reduction to H₂S and sulfide levels as well as increasing the DO to well above the point where the environment within the force main would be considered aerobic.

Discussion

Figure 13 below is a “zoomed-in” view of the data that was collected by AWTs OdaLog prior to the infusion process showing an effect in the force main that allows a more representative view of untreated system conditions.

![Figure 13 – AWT OdaLog Data Immediately Prior to System Effect, 8/17 – 8/20](image)

As we have already seen, H₂S levels were very elevated. The average H₂S indicated on Figure 13 is 1070 ppm and even if the extreme spike above 3000 ppm is ignored, the average concentration is still about 700 ppm. After treatment, concentrations as low as 1 ppm were achieved; however, for calculation purposes a more realistic average is 7 ppm H₂S, based on OdaLog values following the steep drop, which were considered treatment induced values. This equates to a 99% reduction in H₂S levels in a matter of days, with real results starting in about a day, as shown in Figure 14.
This is the same chart that was shown as Figure 4, but now includes some interesting time data. The start up of the system is clearly indicated as well as the calculated detention time range, approximately 25 hours. What should be noticed from this chart is how the H$_2$S concentration begins a rapid descent almost exactly at this 25 hour mark (14a). Additionally, the system shut off is included in this chart and about 25 hours later, the H$_2$S levels begin to experience peaks again. When AWT returned to disconnect the system, it was discovered that there was an impingement on the gas feed line and infusion (treatment delivery rate) had significantly decreased. This could be one explanation for the fact that it took slightly less than 25 hours for the increase in concentrations to resume following the system deactivation.

Another very important fact that must be pointed out is that, although the H$_2$S concentration does begin to increase following system deactivation, as would be expected, the peaks are only in the 25 – 80 ppm range. And they stay there for at least four days, which is all the data available. This is very significant as ten days prior the untreated H$_2$S concentrations had been spiking, at times, in excess of 1500 ppm, and suggests that the environment within the force main is directly affected by the infusion of oxygen and ozone in a positive manner.

Aside from H$_2$S vapor levels, the total and dissolved sulfides and DO levels (liquid phase) should be examined. For this discussion only the grab samples collected by the third party will be used. Since both data sets have been shown to be, for the most part, in agreement with each other, this both limits any potential sampling bias as well as simplifies the analysis by only using one data set. This data set, shown in Table 5, is also very complete and has a high level of precision, augmenting the chart in Figure 14.
For the duration of the sampling, pH stayed relatively constant at slightly above 7, averaging 7.11, and the temperature was in the range of 27.1 – 35.2 °C, averaging 32.4. These are relatively normal values for this location and time of the year, indicating that temperature and pH did not play a significant role in the reductions achieved and can be eliminated as alternate explanations for reduced H₂S concentrations. What does change significantly is sulfide and DO concentrations, especially in the range highlighted.

August 19 is when significant changes occur, for reasons that have already been discussed, and the data above further illustrates the point. The reduction in total and dissolved sulfides between the last sample on August 18 and the first on the 19th is 50% and 70%, respectively. While these are great reductions, even better is the 100% reduction to both these values that occurs by the time the first sample is collected on August 20 and continues throughout the sampling period. The dramatic rise in DO is also very apparent, increasing from 1.1 to 11.5 ppm, an increase of over 1000%. In regard to the suspected feed line impingement mentioned above, it is interesting to note the decrease in DO levels that takes place on August 23, although the levels are still elevated well beyond what is considered aerobic.

**Conclusion**

The current methods of odor control being employed by utilities and municipalities create technical and financial compromises. The technical compromises tend to produce undesirable side effects, ranging from infrastructure corrosion to clogging to actually facilitating the sulfide producing anaerobic slime layer. Additionally, the use of chemicals requires ongoing and escalating year-over-year expense, stressing operations budgets. Often, these technical and financial challenges impact performance and compromise results.

Anue Water Technologies has introduced a new technology that concurrently advances the effectiveness of treatment and decreases ongoing cost. Using the sustainable approach of onsite oxygen and ozone...
The FORSe 5 system has demonstrated its ability to quickly and completely control H2S production and increase DO levels under extreme conditions.

The theory of operation is supported by pilot tests cited herein. Furthermore, this treatment is accompanied by minimal to zero negative side effects. In these terms it is a much more effective means of treating wastewater collection systems for odor and corrosion than traditional methods.

To illustrate the cost effectiveness of FORSe 5, consider the situation where a municipality is using, on average, 210 gallons of iron salts per day in one of their force mains. For nitrates, the approximate stoichiometric equivalent is about 33% less usage than iron, or about 139 GPD. The costs associated with these treatment methodologies can then be compared to that of an appropriately sized FORSe 5 system, which would actually be expected to provide a higher level of overall performance, over a number of years, so that an accurate comparison can be made between them, as shown in Figure 15.

![Figure 15 - 5-Year Annual Costs for Iron, Nitrate and FORSe 5 Hydrogen Sulfide Treatments](image)

The assumptions used to create this chart were:

- Iron – 210 GPD average usage at $0.75/gallon;
- Nitrate – 139 GPD average usage at $2.25/gallon;
- FORSe 5 - Capital equipment cost and operating costs of 16 kW @ $0.08/kWh, 24 hrs, 365 days, miscellaneous consumables;
- All costs are assumed to increase at a rate of 2% annually, which is believed to be very conservative.

It is clear that after the first year, costs associated with FORSe 5 quickly fall below those associated with chemical usage. To further illustrate this, the total 5-year costs associated with each treatment methodology are shown in Figure 16.
Figure 16 clearly indicates that a FORSe 5 system will be less expensive to operate over 5 years than either of the two other treatment chemicals discussed here, which are basically the two ends of the chemical pricing spectrum. The actual years to break even and total 5 year cost savings are included in Table 6.

<table>
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<th>FORSe 5</th>
<th>Years to Break Even</th>
<th>5-Year cost savings</th>
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<td>Iron</td>
<td>3.83</td>
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<tr>
<td>Nitrate</td>
<td>1.94</td>
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Table 6 - FORSe 5 Years to Break Even and 5-Year Cost Savings

Additionally, what are not included in the chemical costs are the unseen costs; the potential for damage to infrastructure or increased usage issues that were discussed previously. This is in sharp contrast to the fact that FORSe 5 systems will tend to improve the collection system environment over time, as has also been previously discussed.

Overall, the application of oxygen and ozone into the wastewater environment brings with it not only a much more technologically and cost effective means of treatment than traditionally available, but is also much more effective from a sustainability standpoint, an issue that is gaining in both technological and social importance.
Contact

The authors of this paper are available and welcome any questions or comments. They can be reached at (760) 476-9090 or at info@anuewater.com.

References