Wastewater Forcemain Odor Treatment

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1. Introduction

1.1. Causes of Odors in Sewer Systems

The substances responsible for the diffusion of odors into the atmosphere in the vicinity of wastewater treatment plants, lift stations, and manholes are generally gaseous inorganic products or highly volatile organic compounds. The former are mainly the result of biological activity in the sewage, the latter are often caused by the presence in the sewer of industrial wastes. The following compounds are associated with bad odors: mercaptans, skatoles, indoles, inorganic acids, aldehydes, ketones and organic compounds containing nitrogen or sulfur atoms. These compounds can originate from the anaerobic decomposition of compounds with a high molecular weight, especially proteins. These are recognized as being among the causes of bad-smelling odors at the outlet of sewer lines and in treatment plants in general. Fig. 1 shows sewer odors.

Figure1. Wastewater Odor Wheel

Among the inorganic compounds, ammonia (NH_3) and hydrogen sulfide (H_2S) are considered to be the main causes of odor when the sewage comes from mainly domestic sources. The presence of hydrogen sulfide is caused by a reducing environment, i.e. characterized by low values of the oxidation-reduction (ORP) potential. In fact, at estimated potentials ranging between 150-350 mV conditions are favorable to develop sulfur reducing bacteria (SRB).

In gravity sewer systems, in which the speed of the sewage flow allows for continuous re-aeration, there is no significant production of hydrogen sulfide and other odor causing by-products. Under such circumstances, however, it has been determined that odors can still find the favorable conditions to form in the sludge film that covers the submerged surface of the sewer lines. The hydrogen sulfide that is formed in these areas, diffusing into the overlying sewage, lowers the ORP, counter-balancing the opposite effect of the natural re-aeration. It can therefore be understood how septic conditions may arise in low-speed sewage which trigger very intense activities of the sulfate-reducing bacteria. These conditions can become more severe if the collection lines are particularly long and the system is located in a region that experiences high temperatures.

1.2. Measurement of Odors

The following are some parameters to express the concentration of odors:

Perceptibility Threshold (ATC: Absolute Threshold Concentration), defined as the minimum concentration that can be detected by 100% (in some cases by 50%) of the persons involved with an olfactory analysis. In some cases the geometric mean of the measurements of the single members is used.

Odor Number (TON: Threshold Odor Number), or the number of dilutions needed to reduce the concentration of the sample to the ATC.

Maximum Exposure Concentration (PEL: Permissible Exposure Limit). This represents the maximum concentration at which persons can be exposed for a period of 8 hours a day, 5 days a week and 50 weeks a year (weighted average over 8 hours), for a work life of 40 years.

Maximum Allowable Concentration (MAC: Maximum Allowable Concentration): Maximum concentration which should never be exceeded.

Table 1 reports the values of these indices relative to a series of compounds found in the atmosphere of sewage treatment plants and pumping stations.

Table 1. Permissible Exposure Levels for Wastewater Odorous Compounds

Compound	ATC (ppm)	TLV (ppm)	MAC (ppm)	Olfactory Sensation
Hydrogen Sulfide	0.00047	10	50 (USA) 20 (UK)	Rotten Eggs
Ammonia	46.8	25	37.5 (UK)	Pungent
Methyl Mercaptan	0.0021	0.5	10 (US)	Rotting Cabbage
Carbon Disulfide	0.21	1	100 (US)	Sweet/Pungent
Biphenyl Sulfide	0.0047	NA	0.2 (US)	Burned Rubber
Dimethyl Sulfide	0.001	10	NA	Rotting Vegetables
Sulfur Dioxide	0.5	2	5 (US)	Sulfur

1.3. Hydrogen Sulfide

Corrosion of wastewater collection system infrastructure from microbiological reactions and physical and chemical processes within the collection system is a world-wide problem costing billions of dollars in infrastructure rehabilitation costs. The primary cause of this problem is the ability of sulfate reducing bacteria (SRB) to generate hydrogen sulfide in the wastewater under anaerobic conditions, and the ability of sulfate oxidizing bacteria such as *Thiobacilli* that can survive under low pH conditions to oxidize hydrogen sulfide to sulfuric acid. Microbially generated hydrogen sulfide in the solution phase is transferred to the vapor phase by physical and chemical processes operative in the sewer environment, and the gas accumulates on the surfaces of the pipe, or are released to the atmosphere at wet wells and manholes.

There are more than 20,000 wastewater systems in the U.S., and about 40% of them use concrete gravity sewers. There are over 2 million wastewater pumping stations associated with collection systems, and these pumps are designed to accommodate future flow conditions and daily variations in flows. As a result, the pumps operate in an on and off cycle allowing anaerobic conditions to develop in the forcemains. Thus, hydrogen sulfide corrosion affects not only the pipes, but also the forcemains, manholes, wet wells, mechanical and electrical components in the pump stations, and treatment plants. Corrosion problems can begin at a concentration of as low as 0.1 ppm of sulfide (ppm S) in the wastewater. Severe corrosion of concrete materials may occur at a concentration as low as 2 ppm S.

Hydrogen sulfide (H_2S) emissions can create obnoxious odor problems and complaints from residents in the downwind area of a forcemain discharge manhole. It is denser than air and has a half-life of 12 to 37 hours. Gases emitted in the vicinity of manholes can persist and accumulate in that location for several hours under stable atmospheric conditions. Under moderate wind conditions, the gas can be transported to downwind areas resulting in complaints from homeowners or other inhabitants. The odor is barely perceptible at about 0.13 ppm but noticeable at about 4.6 ppm. The odor is unpleasant at a concentration of about 27 ppm. The Occupational Safety and Health Administration (OSHA) has set a permissible limit of 20 ppm and a peak exposure limit of 50 ppm for no more than 10 minutes. Inability to detect the odor due to olfactory paralysis can occur at prolonged exposure to concentrations of about 150 ppm. Inhalation of the gas at 500 - 1000 ppm concentration can cause rapid unconsciousness and death. Sewer gas may also contain organic sulfides such as methyl and dimethyl sulfide that are also toxic. Thus, it is important to prevent the production and accumulation of hydrogen sulfide in wastewaters to minimize the impact on infrastructure, personnel and the community at large.

Long wastewater residence times in manholes or pipelines, high temperatures, and turbulence (e.g. discharge from forcemain into manhole) are conducive to the production and release of hydrogen sulfide into the vapor phase. The hydrogen sulfide gas (H_2S) along with carbon dioxide collect on the un-wetted portions of the sewer and dissolve in the moisture on the surface. Sulfide oxidizing bacteria such as *Thiobacillus thiooxidans*, *Thiobacillus neapolitanus* and*, Thiobacillus Intermedius* convert hydrogen sulfide to sulfuric acid. Fungi that are operative in pH 2 to 8 range facilitate the colonization of the surface by the *Thiobacilli*. As shown in Figure 2, the alkali in the concrete pipe reacts with the acid produced, forming gypsum and ettringite precipitates that affect the structural integrity of the pipe. Low pH conditions are also conducive to deterioration of other pipe materials including ductile iron.
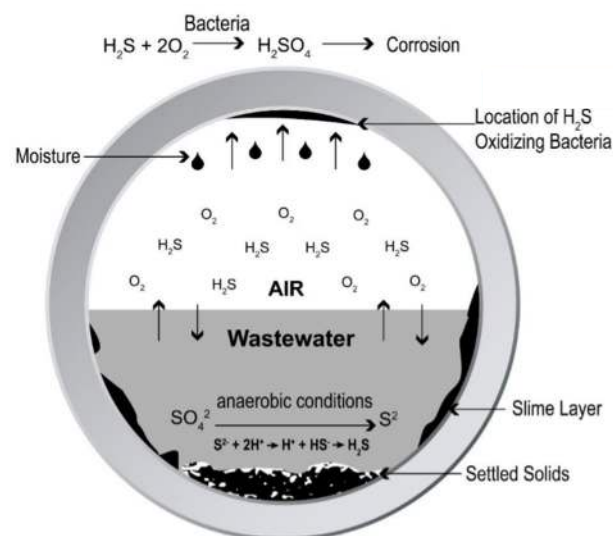

Figure 2. Sulfide Transformation in a Gravity Sewer

Liquid phase control is a method of odor and corrosion prevention by which chemicals are introduced into the wastewater to react with dissolved sulfides or prevent them from being formed, thereby preventing the release of H_2S into the vapor phase. Various chemicals are potentially suitable for liquid phase odor control. Table 2 summarizes generally established methods. Wastewater characteristics and sewer configuration determine which methods are practical for a given situation. Important parameters include wastewater flow rate, temperature, pH, oxidation reduction potential (ORP), biochemical oxygen demand (BOD), process or sewer detention time, location of odor-releasing points (manholes, pump stations), and constraints imposed by downstream treatment processes. The type of odor-causing compound might also prove to be important. Cost and practicalities will determine which method is selected. Factors influencing the cost of liquid phase treatment include chemical dose and regional chemical prices. Practicalities include chemical availability and difficulty of transporting, storing, and applying it. The following sections briefly summarize each liquid phase odor control method.

Table 2. Liquid Phase Odor Control Methods

Method	Description
Oxygenation and aeration	Ambient air or pure oxygen is injected into the waste stream to oxidize sulfides or to maintain an aerobic biofilm.
Chemical oxidation	Chemical oxidizing agents are added to the waste stream to oxidize dissolved sulfide to sulfate, which remains in solution.
Sulfur precipitation	Metal salts are added to the wastewater stream to form a metal sulfide precipitate with the dissolved sulfide, thus removing it from the waste stream.
Nitrate addition	Nitrate salts are added to the wastewater stream, displacing sulfate as the preferred electron acceptor for anaerobic bacteria and preventing sulfide formation.
pH adjustment	The pH of the waste stream is changed to inhibit growth of H_2S-producing bacteria or to drive volatile H_2S to soluble ionic HS^-.
Biological treatment	Process changes or microbial cultures are used to affect the ability of bacteria to produce H_2S.

2. Forcemain Odor Control Methods

2.1. Ozonation, Oxygenation and Aeration

Ozonation, oxygenation and aeration prevent odors by maintaining a layer of aerobic bacteria on the sewer pipe walls and in the wastewater itself. If a sufficient amount of dissolved oxygen is present in the bulk liquid phase, then the outermost layer of the biofilm can support aerobic bacteria capable of biologically oxidizing sulfide as it diffuses outward through the biofilm. Because of biological oxidation, sulfide would not tend to diffuse into the bulk liquid stream. However, when dissolved oxygen concentrations within the bulk phase are close to zero, sulfide generated in the biofilm is able to accumulate in the bulk liquid. In addition to preventing

sulfide from leaving the anaerobic layer, dissolved oxygen in sufficient amounts can oxidize the sulfide in the bulk wastewater stream. At dissolved oxygen concentrations greater than 1.0 mg/L, oxidation can reportedly keep pace with sulfide production and prevent sulfide buildup.

Ozone is a powerful oxidant that can also be used as a biocide against sulfur reducing bacteria (SRB) in forcemains and gravity sewers. The extent of inhibition of SRB activity depends on the wastewater characteristics, the ozone dose and contact time provided. Ozone also reacts with organic and inorganic constituents in the wastewater, and hence the ozone dosage required and its effectiveness in eliminating SRB activity vary broadly. Ozone has a short half-life, and any unreacted ozone decomposes to oxygen. This allows further reduction in H_2S concentration from biological and chemical oxidation of sulfide.

The process developed by Envirozone Corporation (Carthage, Missouri) involves the injection of a gas containing ozone and oxygen into the pump discharge during pump operation. Ozone injection is usually conducted for several days depending upon the forcemain length and wastewater characteristics. Ozonation is discontinued once the gas phase H_2S level is reduced to low levels, and thereafter, pure oxygen is injected. Control of H_2S can be achieved by oxygen alone or by injection of ozone when needed. Methods of adding air, oxygen or ozone include the following:

- Direct air, oxygen or ozone injection into force mains
- Use of Venturi aspirators in side streams to lift stations or force mains
- Use of air lift pumps
- U-tube aeration
- Pressure tank injection into gravity lines
- Use of downflow bubble contactors in side streams to force mains.

2.1.1. Injection

Fig. 3 is a schematic concept for injection of air, ozone or oxygen into a force main. Reports of required air injection rates vary greatly depending on wastewater characteristics, temperature, and pressure in the lines. Very simplistic "rules of thumb" for force mains suggest ranges of 1 to 2 scfm per inch diameter of pipe (EPA, 1985), but the true demand can be very site specific, require relatively complete characterization of the wastewater and the conveyance system, and potentially include the need to model the collection system. Recommendations reported by WEF (2004) range from 0.1 to 6.3 scfm per inch of pipe diameter, or on a wastewater flow basis, 0.02 to 0.88 ft^3 of air per gallon of wastewater, with typical reported values between 0.1 and 0.3 ft^3 per gallon. For applications of direct stub into pipe without a diffuser, the value of 25 scfm per inch diameter of pipe is sufficient to drop the dissolved sulfides to 0.1 ppm. This approach assumes 100 % oxygen transfer, which may or may not be achieved in some force

main applications. The typical oxygen injection rate is 10 mg/L-hr (5-15 mg/L-hr depending on the wastewater age).
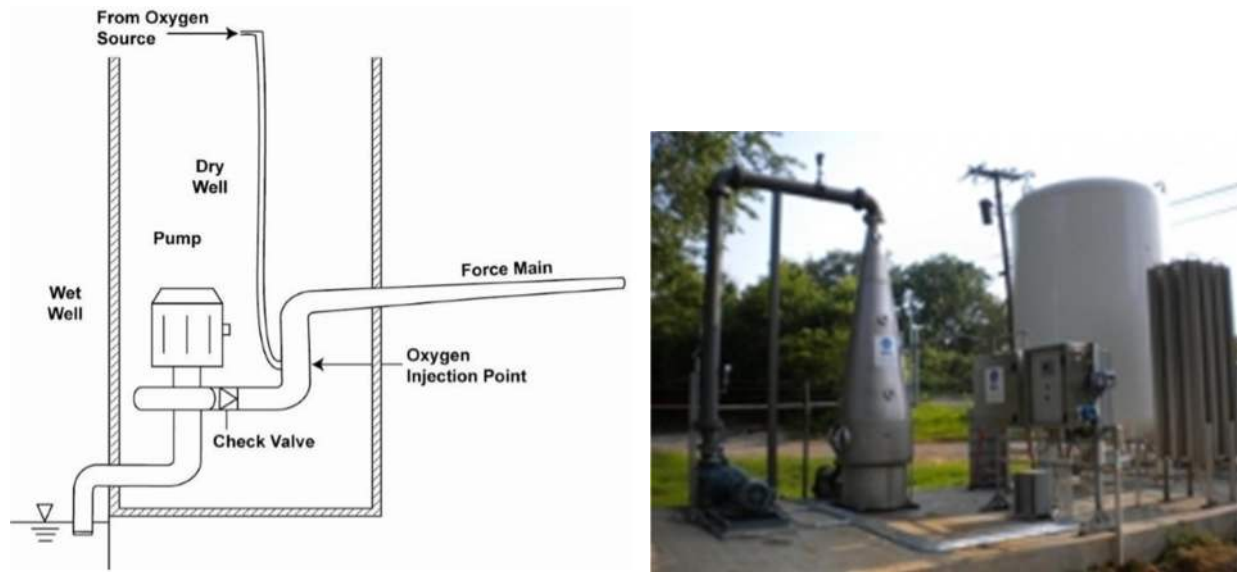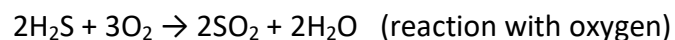

Figure 3. Force Main Air, Oxygen or Ozone Injection

While aeration can be used to strip some of the hydrogen sulfide from the water, this can convert a water problem to an air pollution problem if further treatment is not applied. Hydrogen sulfide is easily oxidized by oxygen and ozone ultimately to form sulfate. The initial oxidation is to form elemental sulfur which is seen as a light colored colloidal suspension. Depending on the pH, further oxidation dissolves the elemental sulfur to sulfite and continued oxidation produces sulfate. As a result, more oxygen and ozone is required to produce sulfate from hydrogen sulfide than is required sulfur. According to the following reactions, both oxygen and ozone oxidize hydrogen sulfide to sulfur dioxide (SO_2) which is a toxic gas:

$$H_2S + O_3 \rightarrow SO_2 + H_2O \quad \text{(reaction with ozone)}$$

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \quad \text{(reaction with oxygen)}$$

Based on the above reactions stoichiometry, 1.4 lbs of either ozone or oxygen are required per each pound of hydrogen sulfide present in wastewater. The most typical and conservative reaction depicted below reacts stoichiometrically at a ratio of 1.9 lb. of oxygen per pound of hydrogen sulfide:

$$H_2S + 2O_2 \rightarrow 2SO_4^{2-} + 2H^+$$
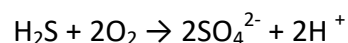
In practice, the ratios as high as 4:1 and 5:1 for ozone and oxygen, respectively, have been reported. This will leave a small ozone and oxygen residual in the water, 0.2-0.3 ppm and 0.5-1 ppm, respectively. These residuals can be used to ensure that the hydrogen sulfide is fully removed. In the case of variable hydrogen sulfide concentration, adjustment in the ozone

dosage rate to maintain complete removal of the ozone is necessarily. Despite a short life of ozone, its OSHA Permissible Exposure Limit (PEL) is 0.1 ppm and as such, the presence of unreacted ozone in the air space at pumping stations, near air relief valves and sewer manholes can be extremely dangerous.

2.1.2. Venturi Aspirators

Venturi-type aspirators and injector aspirators create a high-velocity flow through a nozzle of decreasing diameter, which creates a suction pressure that can be used to aspirate air, oxygen or ozone into a flowing pipeline. The turbulence in the line mixes the injecting gas or liquid and water. Figure 4 is a schematic of this type of system.
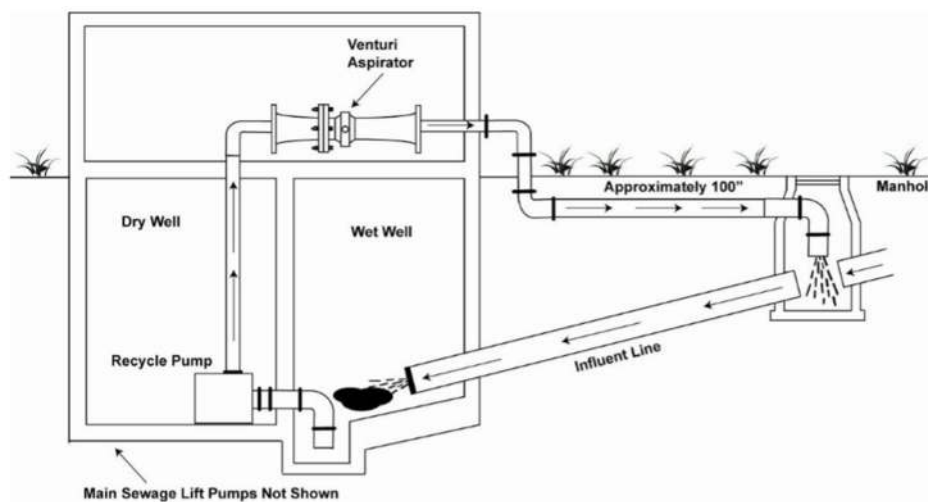

Fig. 4. Venturi Style Aspirator

The optimum (cost-effective) oxygen transfer conditions were found when the systems are operated under the following criteria:

- 14 seconds' contact time in the recycle piping
- 70 psi from the side stream pump
- A oxygen-to-liquid ratio of 0.08 on a volumetric basis
- Velocity of 14 ft per second in the Venturi.

With these settings and under these conditions, 80 percent oxygen transfer efficiency was reported. This approach reduced the liquid phase sulfides by 90 percent and the gas phase H_2S by 70 percent.

2.1.3. Air Lift Pumps

Airlift pumps have reportedly been used to raise oxygen levels at lift pump stations (EPA, 1985). However, no recent published literature on this topic was identified.

2.1.4. U-tube Aeration

U-tubes have reportedly been used for both air and oxygen injection into gravity sewer lines. The pressure and contact time in the U-tube promotes oxygen transfer. However, no recent published literature about using U-tube aeration was identified.

2.1.5. Pressure Tank Air Injection

Pressurized tanks increase the solubility of air or oxygen. This approach uses a side stream of flow that is oxygenated under pressure and injected back into the main flow stream. However, no recent published literature about using pressure tank injection was identified.

2.1.6. Hydraulic Fall Injection

Oxygenation can be done using an intentional hydraulic fall or jump when transitioning from a force main into a gravity line. This helps downstream in the gravity line but can release large amounts of H_2S gas at the point of turbulence. However, no recent published literature about using this approach was identified.

2.1.7. Downflow Bubble Contactors

In this case, air or oxygen (but not ozone) is injected into the top of a downflowing cone that widens as the flow goes downward. The tendency for the bubbles to be carried downward with the flow is resisted by the bubbles' natural buoyancy, which tries to keep them moving upward. The long bubble contact time provided in the cone promotes high oxygen transfer. Figure 5 is a schematic diagram of this type of system.
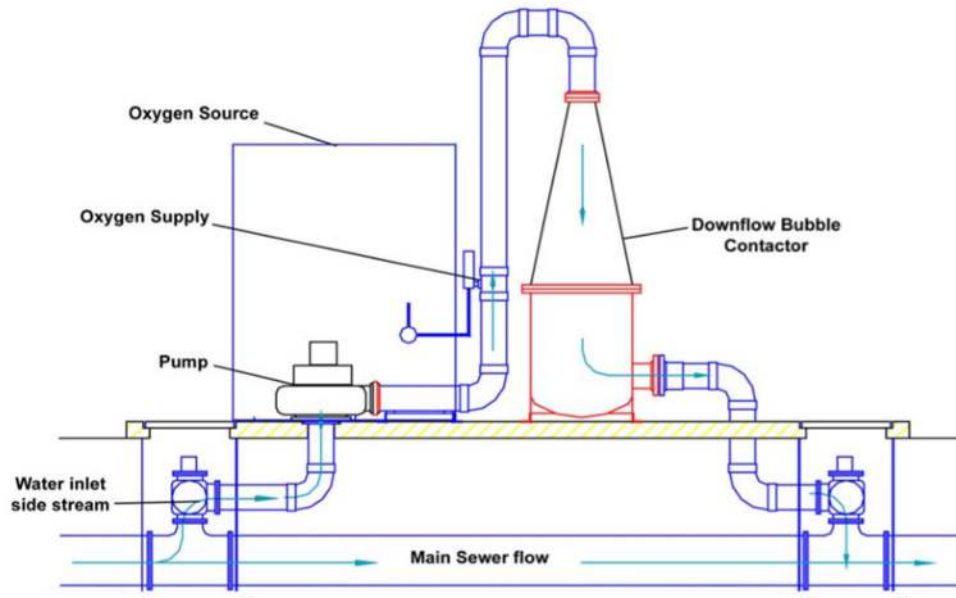
Fig. 5. Downflow Bubble System Schematic

Theoretical oxygen transfer efficiencies as high as 93 percent were reported. Publications on this type of system in collection systems were limited. "Similar" mixing chamber–style versions of these side stream systems are also provided under the brand name Hydroflo. These systems differ in that the contact chamber relies on mixing baffles rather than downflow bubble contact.

2.1.8. Oxygen Injection

For large-scale use, oxygen can be provided by bulk storage systems of liquid oxygen coupled with finned-style heat exchanger vaporizers. Alternatively, for smaller-scale systems, oxygen can be generated onsite using a pressure swing absorption (PSA) system.

Advantages of oxygen injection are the following: (1) A preventative residual can be maintained, (2) oxygen may be injected far upstream of the odor problem, (3) ambient air can be used for some applications with pressure swing systems, (4) chemical costs are reduced, and (5) no harmful byproducts are formed. The same mass of oxygen is provided with one-fifth the volume of gas compared to air.

Disadvantages are the following: (1) effectiveness may be limited by oxygen solubility, (2) oxygen injection may cause gas binding in force mains, (3) it may increase air release valve maintenance costs, and (4) it may not be cost-effective for treating gravity sewers, because

injected gas could volatilize out of solution and be wasted. This would depend on how efficiently oxygen is dissolved and distributed. Although it is consistently reported in the literature that keeping residual oxygen levels above 1 mg/L can control sulfide formation and odors, few data were identified showing the specific effectiveness of this approach for non-H_2S odors identified in Table 1.

The total oxygen requirement demand includes the concentration of dissolved sulfide, the nonsulfide biochemical oxygen demand (BOD) of the wastewater, such as organics and nitrogen-ammonia; and oxygen demand in the slime layers on the collection system walls and in any sedimentation on the bottom of slow-moving collection systems. Temperature and time in conveyance are important because oxygen is consumed faster at higher temperatures (and oxygen solubility is lower). As such, long-contact-time force mains in relatively high-temperature environments can quickly go anaerobic and begin producing sulfides. Typical oxygen uptake rates reported for domestic wastewater range from 5 to 15 mg/L/hr as noted earlier. The applicability of oxygen injection will depend on the BOD exerted over the detention time of the force main and the solubility of oxygen for conditions inside the force main. If more dissolved oxygen is consumed than can be dissolved during the detention time, then oxygen injection may not work without additional injection points. A variety of equations for calculating oxygen demand and consumption in force mains and collection systems is provided in the literature. Most of these equations, however, significantly overestimate the oxygen injection rates. Laboratory analyses of representative wastewater samples should be done in order to determine the most realistic oxygen or ozone consumption rates. Based on the reaction stoichiometry, the weight of required ozone is by 26% less compared to oxygen. It should be noted albeit that the theoretical half-life of aqueous ozone is 12-15 min at 30^0C. When designing an ozone injection system, the three T's (time, temperature and turbulence) must be carefully modeled against the possible range of both the chemical and biological ozone demand. All possible sources of air containing unreacted aqueous ozone should be filtered using activated carbon or the like media impregnated with manganese oxide or similar catalysts before public exposure.

As in the case of oxygen solubility, ozone half-life should be calculated at the point of injection, the point of lowest pressure inside the force main, and at all air release valves. The amount of ozone/oxygen injected should be planned so that as ozone/oxygen is consumed along the force main and their concentration does not exceed saturation at the air release valves and low-pressure points (high elevation points).

2.2. Chemical Oxidation

Aeration or oxygen injection does in fact promote both chemically and biologically mediated oxidation processes; however, there are stronger oxidizing chemicals that are often used to attack odor- and corrosion-causing compounds and destroy them through oxidation/reduction reactions. Strong oxidants can decrease dissolved sulfide concentrations to below the detectable limit. The practicality of different chemical oxidants, however, depends on several factors, including reaction time, chemical cost and availability, safety issues, and oxidation-reduction potential (ORP). Low ORP (less than -100 mV) tends to indicate that the wastewater is a candidate for chemical oxidation. The discussion of chemical oxidants below includes chlorine-based chemicals, hydrogen peroxide, and potassium permanganate.

2.2.1. Chlorine Gas

Chlorine treatment can come from several sources, including chlorine gas, sodium hypochlorite (bleach), and sodium chlorite. Chlorine gas has been used successfully to oxidize sulfide in sewers, pumping stations, and treatment plants. Although it is used primarily for disinfection, it can also be used to oxidize odorous compounds in the liquid phase. Because of safety concerns regarding workers' and the public's potential exposure to chlorine gas, the use of liquid chlorine and chlorinator systems is typically limited to treatment plants whose facilities are protected and can be monitored and have less potential to impact community safety.

Advantages to using chlorine include the facts that the equipment required is inexpensive and widely available and that chlorine has a long record of effectiveness.

Disadvantages include the following: (1) Reactions may form harmful chlorinated organic byproducts, some of which are regulated; (2) chlorine is consumed by ammonia, which may add to the dose requirement; (3) chlorine may inhibit downstream biological treatment; (4) storage and use of sufficient quantities of chlorine can create reporting requirements under risk management plan programs and represent potential safety challenges; and (5) direct injection of chlorine gas may cause downstream fuming and release potentially dangerous chlorine gas, especially if mixing is not rapid and thorough at the injection point.

Stoichiometrically, 8.57 parts by weight of chlorine are required to oxidize each part of sulfide under acidic pH conditions, whereas 2.14 parts of chlorine per part of sulfide are required for basic conditions.

$$4NaOCl + H_2S \rightarrow 4NaCl + H_2SO_4$$

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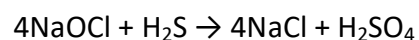
This indicates the sensitivity of the reaction to pH. However, since chlorine indiscriminately oxidizes any reduced compound in wastewater, competing side reactions also influence the required effective dose.

Field studies have shown that, depending upon pH and other wastewater characteristics, 4 to 15 parts by weight of chlorine are often required for each part of sulfide. Unusually high demands (25:1) on a high-strength industrial food waste force main have been reported to sustain effective odor control. This points out the importance of following jar testing with pilot testing to determine the true dosage requirement for a given wastewater and wastewater collection system.

As in the oxygen and ozone cases, regulators and diffusers are also required for chlorine injection. Somewhat similar to ozone, chlorine gas is poisonous and requires special precautions for storage, including containment and scrubbing facilities in case of a leak. Effective mixing is also reported to be very important in full-scale applications (EPA, 1985; WEF, 2004).

2.2.2. Chlorine Dioxide

Chlorine dioxide (ClO2) is applied at or near the source of hydrogen sulfide. Chlorine dioxide, when fed at doses higher than the minimum required to destroy hydrogen sulfide will remove the biofilm layer, which contains the bacteria creating the sulfide. Chlorine dioxide reacts more rapidly and completely than other available oxidizers and does not form colloidal sulfur.

2.2.3. Sodium Hypochlorite

Sodium hypochlorite (NaOCl) is the chemical commonly found in bleach home-cleaning products. In typical odor control applications, industrial strength hypochlorite, approximately triple the strength of home-cleaning products, is used. Hypochlorite is essentially 18 to 20 percent caustic with chlorine injected into it, resulting in a 10 to 15 percent solution of chlorine stabilized in caustic as hypochlorite. The high-pH caustic stabilizes the chlorine and acts as the carrier. Hypochlorite performs comparably to chlorine gas but is preferable for safety reasons related to potential chlorine gas release. Chlorine gas tends to acidify any solution it is added to, whereas hypochlorite tends to make solutions more basic, owing to the presence of the caustic carrier solution. Generally, hypochlorite is much safer to use and is preferred over chlorine gas for collection system applications.

Its advantages are that the equipment required is inexpensive and widely available and that it has a long record of effectiveness. Its disadvantages are that (1) reactions may form toxic and

carcinogenic byproducts, some of which are regulated; (2) it may inhibit downstream biological treatment; and (3) it degrades slowly, thus complicating long-term storage.

Hypochlorite is a strong oxidizing agent. It reacts stoichiometrically with hydrogen sulfide in wastewater at a theoretical ratio of 8.8 lb of sodium hypochlorite per 1 lb of hydrogen sulfide. It is, however, also sensitive to pH, with stoichiometric demand rates similar to those of chlorine gas injection under acidic conditions. Since hypochlorite reacts indiscriminately with other wastewater constituents, the required effective dose is often higher than stoichiometric. In practice, the required dosage is often reported to be in the range of 10 to 15 lb of sodium hypochlorite per 1 lb hydrogen sulfide (EPA, 1985). However, field experience indicates that significantly lower or higher values can also be observed. Jar testing specific wastewaters is therefore recommended to determine true demand.

Equipment required for applying hypochlorite includes a polyethylene or a fiberglass tank, metering pumps, controls, and instrumentation. The equipment is relatively simple to design, operate, and maintain. Personal protection equipment, including gloves, goggles, eyewashes, and safety showers for emergency use, should be included in all chlorine applications, including hypochlorite systems. Under normal conditions, sodium hypochlorite, unlike chlorine gas, is not potentially dangerous to surrounding inhabitants. However, if it were accidentally mixed with an acid, the resulting pH shift could liberate chlorine gas.

2.2.4. Sodium Chlorite

Sodium chlorite ($NaClO_2$) is usually produced as a 25 percent solution and is an alternative source to chlorine sometimes used in sludge applications. It reacts with H2S as follows:

$$2H_2S + NaClO_2 \rightarrow 2S \downarrow + 2H_2O + NaCl$$
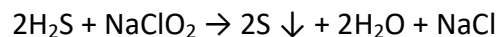
Sodium chlorite is used much less often than hypochlorite because it costs more and there is less knowledge of its application. It reportedly reacts with sulfide selectively, so it may have a longer residual than other forms of chlorine. Elemental sulfur deposits in the collection resulting in more frequent cleaning. Chemical supplier report that 4 to 6 lb of $NaClO_2$ per pound of sulfide removed is sufficient to decrease sulfide concentrations to below detectable levels.
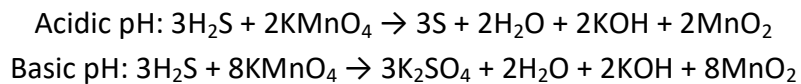
2.2.5. Permanganate

Sodium and potassium permanganate are strong oxidants that can be used to remove sulfide and other odor- and corrosion-causing compounds. Sodium permanganate is more soluble,

whereas potassium permanganate is less expensive, but both are more expensive than other chemicals. Permanganate sometimes is used to treat sludge because it reacts preferentially with sulfide and can be cost effective in this type of application. It is not generally the most cost-effective approach on the full flow of a typical wastewater plant collection system. Permanganate is available in both concentrated liquid and crystal forms. It is most often used as a crystal to make a 3–6 percent solution. The solution is then blended with the waste stream. In crystal form the concentration as permanganate is 97 percent. Also available is a liquid product at approximately 12.5 percent concentration that typically comes in drum-size carboys or drums for small applications.

It has the following advantages: (1) Solids formed from reaction (manganese dioxide) may have a beneficial effect on downstream flocculation in treatment plants; (2) permanganate can be used to treat sludge; and (3) field experience suggests that dewatering equipment will achieve higher dry solids. Permanganate's disadvantages are that it is expensive and that it does not maintain a residual.

Potassium permanganate ($KMnO_4$) is a strong chemical oxidizing agent that reacts with hydrogen sulfide according to the following equations:

$$\text{Acidic pH: } 3H_2S + 2KMnO_4 \rightarrow 3S + 2H_2O + 2KOH + 2MnO_2$$
$$\text{Basic pH: } 3H_2S + 8KMnO_4 \rightarrow 3K_2SO_4 + 2H_2O + 2KOH + 8MnO_2$$

In practice, several reactions ranging between these two may take place to produce elemental sulfur, sulfate, thionates, di-thionates, and manganese sulfide depending upon local wastewater chemistry. Field studies have indicated that between 6 and 7 lbs of $KMnO_4$ are required for each lb of sulfide to mitigate odor and corrosion. Permanganate reportedly reacts preferentially (first) with sulfide. However, permanganate, like chlorine or peroxide, can be considered an indiscriminate oxidant if sufficient contact time and exposure is provided. As such, dosing requirements can depend on how it is applied. Very little experience was identified where permanganate is used in collection systems.

Potassium permanganate is typically available and used in dry form and must be mixed with water to an approximately 3–6 percent solution (with a density of 8.7 lb/gallon) before being used. Mixing with water at temperatures below 40°F may be problematic because of its low solubility; accordingly, heating dilution water may be required. Sodium permanganate is more soluble and is sold in a 12–20 percent solution. The equipment required for a typical potassium permanganate application consists of a dry feeder, mixing tank with mixer, metering pumps, control system, valves, and piping. Potassium permanganate typically is used in smaller applications because its cost makes it prohibitively expensive to treat large flows, such as the

entire plant flow, on a continuous basis. It is most often used on liquid sludge stream applications. When kept dry and cool, potassium permanganate is relatively stable. However, when contaminated with organics or acids, it can become unstable and decompose, causing potentially explosive conditions. Thus, sodium permanganate that is stored and transported in solution may be safer in this respect.

2.2.6. Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a strong oxidizer that reacts with most reduced compounds in wastewater, including sulfide. It is typically available in bulk concentrations of 35 to 50 percent. It has the advantage of having harmless reaction byproducts, and the breakdown of excess H_2O_2 increases dissolved oxygen in wastewater; a disadvantage is that an H_2O_2 residual is very difficult to maintain.

Hydrogen peroxide oxidizes hydrogen sulfide to colloidal elemental sulfur. Under typical wastewater pH ranges, reactions proceed according to the following equation:

$$pH < 8.5 \quad H_2S + H_2O_2 \rightarrow S + 2H_2O$$
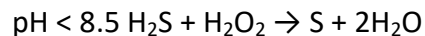
Field studies and bench-scale test reports indicate a required dose of 1 to 4 lbs of H_2O_2 per 1 lb of H_2S depending on target sulfide concentration. Larger doses are needed as the target sulfide concentration approaches zero. Because of the fourfold dose range, bench-scale tests on a wastewater sample from the source to be treated are recommended in order to verify the appropriate dose. A field test reported by USEPA (1985) required a peroxide dose up to 40 mg/L for a 5-mile-long pressure main in order to reduce end-of-pipe dissolved sulfides to near zero. The reaction between hydrogen peroxide and sulfide is relatively slow (30 minutes) when compared to those of other oxidants, which take seconds to minutes. USEPA (1985) reports that 90 percent of the reaction occurs within 10 to 15 minutes and the reaction is essentially complete within 20 to 30 minutes. Therefore, adequate mixing and contact time must be provided and typical designs entail 30 minutes' upstream contact time with good mixing. Catalysts can reduce the reaction time of peroxide and other oxidants to 3 to 5 minutes but are costly.

The type of peroxide storage and feed equipment required depends upon the dosage rate and the concentration of peroxide used. The maintenance and repair of hydrogen peroxide systems requires special training and procedures. Hydrogen peroxide is very reactive with organic materials, including grease and oil. When systems are installed or repaired, all wetted surfaces must be specially cleaned and prepared beforehand through a process called passivation. This

consists of rigorous cleaning with a sequence of detergent, water, nitric acid, and water to avoid possibly dangerous reactions with contaminants. For this reason, hydrogen peroxide feed systems are sometimes contract operated by suppliers. Worker safety issues must be addressed when using hydrogen peroxide. Gloves, goggles, and protective clothing should be worn when handling hydrogen peroxide solutions and contaminated equipment because skin, eyes, and other sensitive body parts can be damaged by exposure. Eyewashes and safety showers must be provided for workers. Adequate water supply should also be provided to dilute any spills.

The use of peroxide in large-diameter sewer systems at 5:1 - 6:1 doses of pounds of peroxide to pounds of sulfide achieve up to 90 percent liquid phase sulfide control but for only 30 to 60 minutes. At dissolved sulfide levels below 1 mg/L the peroxide reaction is reported as very slow, requiring higher dosing rates. Literature indicates a wide range in required dosing from 2.4:1 at a force main discharge for control to 18:1 in a gravity sewer for prevention. This indicates that peroxide dosing to react with existing sulfide may take lower dosing rates than peroxide dosing to control downstream sulfide formation. In one instance, 3.3 kg of peroxide per 1 kg sulfide reduced odors but did not meet the 0.5 mg/L H_2S liquid phase goal.

2.2.7. Sulfur Precipitation

Various metal salts can combine chemically with dissolved sulfide to form relatively insoluble metal sulfide that precipitate from the wastewater, thus preventing the release of H_2S gas. Metal sulfide precipitates exist as soft black or reddish-brown flocs that usually do not settle in the collection system but can be removed at treatment plants. In fact, more-restrictive industrial source control programs have been credited with a tendency for increasing levels of sulfides over the years because of the associated lowering of metals in the wastewater. Effective metals might include iron, zinc, lead, chromium, cadmium, nickel, and copper, but iron is most typically used today. There is a potential concern because heavy metal concentrations could be regulated and make the solids difficult to dispose of.

Sulfur precipitation has several advantages, including the following: (1) long residuals can be maintained to precipitate sulfide as it is generated, which can result in sulfide control over very long collection system reaches; (2) iron salts can be used to treat sludge; (3) reaction byproducts are innocuous; and (4) precipitates are beneficial to downstream treatment processes. The following are its disadvantages: (1) Precipitates can dissociate at pH less than 6.5, allowing sulfide to release back into the wastewater; (2) at typical wastewater pH, dissolved sulfide cannot be decreased to much lower than 0.2 to 0.5 mg/L; (3) some evidence suggests that precipitates form "clinkers" when iron-dosed biosolids are incinerated, and therefore this potential should be considered where sludge cake is incinerated; (4) iron salts

can form a film on pipe walls, instrument sensors, and ultraviolet disinfection equipment; and (5) these precipitates can substantially increase sludge production at the treatment plan.

Ferrous iron salts such as ferric chloride ($FeCl_2$) and ferrous sulfate ($FeSO_4$) are commonly available for sulfur precipitation. Ferrous iron reacts with each sulfide species as shown below:

$$Fe^{2+} + S^{2-} \rightarrow FeS \downarrow$$
$$Fe^{2+} + HS^- \rightarrow FeS + H^+$$
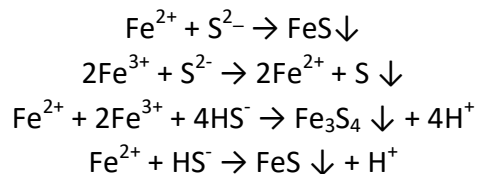$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+$$
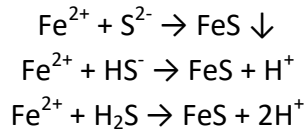
These reactions indicate a stoichiometric dose of 3.8 lb of $FeCl_2$ per 1 lb of sulfide. However, effective doses for reducing the sulfide concentration to below 1.0 mg/L are reported from 4 to 12 lb of $FeCl_2$ per 1 lb of sulfide removed, depending on the target sulfide concentration.

Ferric iron reacts similarly to ferrous iron:

$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S$$
$$2Fe^{3+} + 3HS^- \rightarrow Fe_2S_3 \downarrow + 3H^+$$
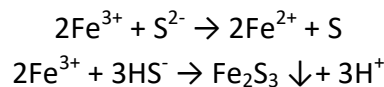
These reactions indicate a "stoichiometric" dose of 3.3 to 4.9 lb $FeCl_3$ per 1 lb of sulfide. However, field and laboratory experiments indicate that the typical required dose to remove sulfide in domestic wastewater is between 3 and 7 lb $FeCl_3$ per 1 lb of sulfide.

Ferrous and ferric iron in combination are often used for sulfide precipitation and odor control, because the combination has a synergistic effect such that the overall dosage is reduced. The following equations show these reactions:

$$Fe^{2+} + S^{2-} \rightarrow FeS \downarrow$$
$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S \downarrow$$
$$Fe^{2+} + 2Fe^{3+} + 4HS^- \rightarrow Fe_3S_4 \downarrow + 4H^+$$
$$Fe^{2+} + HS^- \rightarrow FeS \downarrow + H^+$$

$FeSO_4$ and $FeCl_3$ in combination have been demonstrated to be more effective than either chemical alone. Field experience with reductions down to 0.2 mg/L dissolved H_2S have been reported. Typically, one part of ferrous $FeSO_4$ is used in combination with two parts ferric $FeCl_3$. The limitation of this approach is the requirement for separate chemical feed equipment for each chemical. Some literature suggests that iron salts may not be able to lower the liquid phase sulfide below 0.2 mg/L.

The equipment required for dosing metal salts is similar to that in other liquid chemical–handling systems. However, iron salt solutions are corrosive and hazardous and have a low pH, so special precautions must be taken in handling and storing iron salt solutions. The chemical delivery systems typically require a polyethylene- or fiberglass-reinforced plastic tank, metering pumps, associated valves and piping, adequate spill control, and safety equipment. One of such systems is shown in Fig. 6.

Fig. 6. Iron Salt Addition System

2.2.8. Nitrate Addition

Nitrate salts can be used to prevent the formation of sulfides by providing an alternative electron acceptor for sulfate-reducing bacteria, which preferentially reduce oxygen, nitrate, and sulfate in that order. Therefore, as long as enough oxygen or nitrate is in solution, sulfate conversion to sulfide will be minimized. Nitrate can also be used as an oxygen source to promote the biological oxidation of sulfide. Nitrate is available in both liquid and dry form as sodium nitrate ($NaNO_3$) or, more commonly, as calcium nitrate ($Ca(NO_3)_2$). Both salts are quite soluble, and liquid solutions of between 40 and 60 percent by weight are usually used.

Nitrate addition has the following advantages: (1) It can maintain a long residual; (2) it is safe and does not require special handling or storage; and (3) reactions do not form hazardous byproducts. Its disadvantages are that nitrate (1) sometimes causes gas binding of long force

mains with inadequate air relief valves and (2) may increase the cost and difficulty of denitrification at the treatment plant.

Nitrate addition can reportedly control dissolved sulfide concentrations exceeding 0.5 mg/L. The required dose ranges from 4 to 15 lb of calcium nitrate per pound of sulfide prevented. Several studies indicate that nitrate dosing upstream needs to be sufficient to keep residual downstream at the discharge point in the range of 0.4 to 0.8 mg/L in order to be effective at keeping headspace H_2S below 10 ppm. This appeared to equate to approximately 12 mg of nitrate per milligram of sulfide reacted or prevented. It is noted that the true dose is dependent on the layout of the collection system, which affects the amount of slime layer that must be impacted, and as a result, dosing requirements based solely on pounds of sulfide prevented or reacted may not be accurate.

Thus, trying to determine accurate nitrate-dosing requirements by means of jar testing would likely prove ineffective because the natural slime layer is not present in a jar test. Some reports indicate ratios as high as 20 or 30 lb of nitrate per 1 lb of sulfide. This may be indicative of the impacts of the slime layer on the collection system walls and in sediment in the bottom of slow-moving collection systems. This may reflect the impact of different levels of slime layer coatings in terms of both surface area and thickness. Nitrate dosing must be continuous. Batch dosing reportedly does not work because the nitrate is consumed, and sulfate-reducing bacteria quickly reestablish themselves. Calcium nitrate dosing requires field testing and cannot be done effectively with a jar test. Some studies indicated that calcium nitrate worked better for the force main application than the gravity lines. Some researchers reported an estimate during batch jar testing of 4.6 g of nitrate required per gram of sulfide. A relatively low dose may be a result of jar testing that does not include all the effects that would be seen in the field. Although a dose rate must be selected in order to design the delivery system, the rate should be varied during operation to avoid waste and excess nitrate loading in the downstream process. One approach, if the necessary monitoring equipment can be installed, is to vary the nitrate dose on the basis of the nitrate concentration entering the treatment plant or at the discharge point of the force main. During startup, the nitrate dose is varied until a minimum nitrate concentration entering the plant headworks or reaching the downstream end of the force main is found that maintains the sulfide concentration below the target.

Nitrate salt solutions are neither corrosive nor hazardous and do not require special equipment. Nitrate feed systems include a storage tank with metering pumps and associated valves and piping. Fig. 7 shows a typical nitrate salt feed system.

Figure 7. Nitrate Storage and Delivery System

2.2.9. pH Adjustment

pH can be an important parameter for most of the liquid phase odor control methods described above, but it can also be used directly to mitigate hydrogen sulfide release. There are two methods of reducing H_2S-related odors using pH adjustment. One is to shift the wastewater pH so that chemical equilibrium favors nonvolatile sulfide species. The other uses a temporary but more drastic pH increase to deactivate the sulfur-reducing bacteria. pH affects the distribution of the three sulfide species, H_2S, HS^-, and S^{2-} in the solution. An increase in pH drives sulfide to ionic forms (HS^- and S^{2-}) that are nonvolatile. For example, at a pH of 7, roughly 50 percent of sulfides are present as H_2S, whereas at a pH of 8.5, only 3 percent are present as H_2S. If wastewater pH drops, the sulfide species ratios shift rapidly toward H_2S, which is volatile. Therefore, increasing wastewater pH can reduce odor problems as long as the higher pH is maintained. Fig .8 shows the relative fraction of each sulfide species as function of pH.
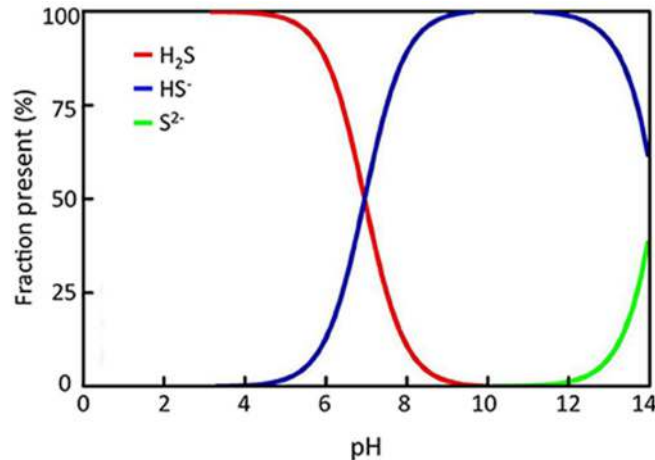
Figure 8. Sulfide speciation as function of pH

Fig. 8 shows that at a pH of 9 or above, almost no dissolved sulfide is in the volatile form and at a neutral pH approximately 50% is present as H_2S. Some literature also suggests that slight shifts in pH can begin to inhibit growths of anaerobic organisms that produce sulfides.

Magnesium hydroxide ($Mg(OH)_2$) and sodium hydroxide (NaOH) are the two chemicals most commonly used to raise pH. Magnesium hydroxide can raise pH to a maximum of 9 and sodium hydroxide to a pH of 14. Even with overdosing, magnesium hydroxide reportedly does not raise the pH over 9 because it is not as soluble and acts as a buffer, whereas caustic is readily soluble and can have a quick effect on pH, driving it up much higher. The chemical dose will depend on the buffering capacity of the wastewater. To estimate the amount of chemical needed to achieve the target pH, a sample of the wastewater should be jar tested with a concentrated solution of the desired control chemical until the target pH is reached. Lime has also reportedly been used. Dosing experiences for each chemical are outlined below. Magnesium hydroxide is most commonly known as an acid-stomach remedy and is essentially industrial-grade milk of magnesia. Typically, magnesium hydroxide comes in a 58- to 60-percent slurry with a paint like consistency. It freezes near 32°F and should be stored in stirred or agitated tanks. It reportedly works by pH shifting to keep already-formed sulfides in solution, sulfide binding with magnesium cations, and pH inhibition of the slime layer. It is also reported to have beneficial downstream impacts by providing alkalinity to the treatment plant processes. Dosing can be either direct to the wastewater or as an intermittent spray coating on the crown of gravity collection systems. Typical dosing requirements range from 25 to 100 gallons per million gallons of wastewater treated.

pH stabilization requires storage and feed equipment similar to those in other liquid feed systems. Magnesium hydroxide is nonhazardous and safe to handle. It is applied as a slurry and requires mixing equipment.

2.3.   Liquid Phase Biological Treatment Methods

Liquid phase biological treatment methods that seek to modify microbial metabolism, change microbial populations, or otherwise affect the microbes responsible for generating odors in wastewater collection systems are broadly classified as liquid phase biological treatment methods. These are distinct from liquid phase chemical treatment methods, which seek chemical reactions with odor-causing compounds to convert them to nonodorous species.

Two main types of biological treatment methods have been marketed and applied with varying degrees of success. One method, bioaugmentation, seeks to deluge a collection system with bacteria specially bred to oxidize sulfide as it is generated, thereby reversing the natural anaerobic conversion of sulfate to sulfide. The second method, enzymatic treatment, uses substances that either interrupt the bacterial metabolic process that converts sulfate to sulfide or enhance enzymatic activity of microbes that oxidize sulfide. One of the best-known enzymatic treatment methods is anthraquinone, an aromatic ketone reported to block metabolic pathways for sulfate-reducing bacteria. Anthraquinone binds with a protein that is unique to sulfide-reducing bacteria and interrupts sulfate reduction by interacting with the cytochrome c3 location in the cytoplasmic membrane. Studies reported that anthraquinone dosed at 10 mg/L inhibit sulfide generation in laboratory tests, but follow-up field batch dosing of up to 480 mg/L provide no reduction in dissolved or gaseous sulfide on collection systems. Based on several reviews, the effectiveness of biological treatment methods is unclear at best and requires further investigation. Pilot testing would be required in all cases.

3. Dosing Summary

Table 3 summarizes dosage information for each liquid phase odor and corrosion control method. Some chemicals have a wide dosage range. This is representative of the varying results of field- and bench-scale studies. Closer estimates of chemical doses needed for certain applications should be obtained by running a bench-scale test on actual wastewater. If possible, jar and bench-scale testing of representative wastewater samples is highly recommended before proposing design.

Table 3. Dosage Information for Liquid Phase Odor Control Methods

Chemical	Concentration (% by weight)	Solution Density (lb/gal.)	Dose (lb/lb of Sulfide Removed) Low	Dose (lb/lb of Sulfide Removed) High
Pure O_2	95	gas	Not directly comparable to other chemicals	
Cl_2 gas	100	gas	4	15
NaOCl	15	9.7	10	15
H_2O_2	50	10.0	1	4
$KMnO_4$	5	8.7	6	7
$NaMnO_4$	20	9.8	7	8
$FeCl_2$	30	10.0	4	12
$FeSO_4$	6	10.0	5	14
$FeCl_3$	40	10.8	3	7
$Ca(NO_3)_2$	60	12.1	4	15
NaOH	50	11.4	Doses must be compared to other methods on a case-by-case basis as they are not directly related to sulfide concentration alone	
$Mg(OH)_2$	63	13.3		

4. Cost Comparison

The range of costs to install and operate the gas and chemical injection systems for wastewater odor control vary significantly depending on physical and chemical characteristics of wastewater, location, topography and forcemain geometry and material. Table 4 lists approximate Opex and Capex ranges for a 10,000-feet 8-inch diameter PVC SDR 26 forcemain in the continental USA.

Table 4. Chemical Injection Equipment Installation Costs		
Chemical/Gas	**Capex, $1000**	**Opex, $1000/year**
Air	50-100	20-30
Oxygen*	200-250	15-20
Ozone*	220-260	20-25
Chlorine	60-100	6-10
Sodium Hypochlorite	60-80	5-10
Hydrogen Peroxide	50-100	8-15
Potassium Permanganate	50-90	9-17
Sodium Permanganate	50-90	9-17
Ferric Chloride	60-90	10-18
Ferrous Sulfate	40-90	10-15
Ferrous Chloride	60-90	10-18
Calcium Nitrate	60-80	5-8
Sodium Hydroxide	50-100	10-20
Magnesium Hydroxide	60-90	12-20

Note: * cost includes an onsite PSA

The slightly higher that others operating and maintenance expenditures for air injection entail blowers, air pressure tank and air distribution and release devices maintenance as well as increased electrical power usage. Normally, air injection systems require a separate vault or a temperature-controlled building. The high capital expenditure values for onsite oxygen and ozone production are due to higher equipment costs including pressure swing absorbers (PSA). The cost of biological methods cannot be approximated due to the lack of references.

5. Technology Ranking

The overall rating of the forcemain wastewater odor abatement technologies discussed in this paper is based on the following factors:

- Efficiency
- Conventionality
- Capex
- Opex
- Ease of operation
- Equipment footprint
- Environmental, health and safety (EHS) considerations
- Public perception
- Design firm's experience with system design
- Operator's experience with similar systems.

The overall rating in Table 5 is a sum of each criteria rated based on the numbers from 0 to 5 where 0 and 5 are the lowest and highest ratings, respectively. It is based on the author's experience which may be different than others'.

Table 5. Method's Overall Rating										
Chemical/Gas	Effic.	Conv.	Capex	Opex	Oper.	Area	EHS	Publ.	Exp.	City	Score
Air	3	5	5	0	5	0	5	5	4	4	36
Oxygen	5	5	1	2	5	4	1	3	4	4	34
Ozone	5	3	0	1	4	5	0	1	4	4	27
Chlorine	5	5	3	4	4	4	0	0	4	4	33
Sodium Hypochlorite	5	5	3	5	4	3	2	2	4	4	35
Hydrogen Peroxide	4	4	2	3	3	4	2	1	4	4	31
Potassium Permanganate	4	4	3	4	3	2	3	2	4	4	33
Sodium Permanganate	4	4	3	4	3	2	3	3	4	4	34
Ferric Chloride	4	5	3	3	4	3	3	2	4	4	35
Ferrous Sulfate	4	5	3	2	3	2	4	4	4	4	35
Ferrous Chloride	4	5	3	3	4	3	3	2	4	4	35
Calcium Nitrate	5	5	4	5	4	3	5	5	4	4	44
Sodium Hydroxide	4	4	2	3	4	5	1	2	4	4	33
Magnesium Hydroxide	2	4	3	3	3	1	5	5	4	4	34

According to this table, the lowest ranking technologies are ozone and hydrogen peroxide.

The ranking in this table do not necessary diminish the merits of such common technologies as hydrogen peroxide, chlorine and ferric chloride injection nor do they imply the superiority of the proposed methods over the others such as, for instance, ozone. For comparison, the oxidation reduction potentials of ozone, chlorine, and oxygen are 2.07, 1.36, and 1.23 Volts, respectively. Fluorine has an oxidizing power of 2.87 Volts and would immediately destroy H_2S. Unfortunately, due to it prohibitively high corrosive nature and toxicity, fluorine has very limited application.

A treatment chemical or gas dosage calculation needs to take wastewater age into consideration as well as gage pressure. Wastewater age is the wetwell storage plus pipe travel time. The latter varies depending on the pipe size, pumping rate and pump cycle time. Normally, a residential wastewater age of over 90 min requires odor control.

The efficiency of the proposed treatment method must be verified based on representative wastewater samples collected during a range of flow regimes. For instance, organic and inorganic pollutants in a typical residential wastewater are more concentrated during base flow

and less during peak flow. It is suggested that the biochemical oxygen demand (BOD), H_2S and total organic carbon (TOC) of wastewater are not linearly proportional to flow rate due to reactions taken place on pipe walls and inside the slime layer. For gravity sewers, the aqueous H_2S concentration depends on inputs from downstream sources, pipe material, air velocity and temperature, number of drop manholes and infiltration rate. For forcemains, it remains fairly constant along the length if no air is supplied by vacuum relief valves.

6. References

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