CHAPTER 2.0

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2.1   Background

Problems associated with odors and corrosion in wastewater collection systems have become much more frequent in recent years from both public perception and infrastructure protection standpoints. Odor complaints, corrosion, and costly sewer rehabilitation projects are damaging public relations, degrading our wastewater facilities, and stressing already-limited collection system budgets. New research has revealed several seemingly unrelated factors that have combined to cause the increased collection system odor and corrosion problems we face today. This chapter reveals these factors and discusses their impact on collection system odor and corrosion. This chapter also unveils a new strategy for evaluating odor and corrosion control alternatives by interrupting the various physical, chemical and biological processes which produce hydrogen sulfide in sewers.

As odors have become more prevalent and corrosion more damaging, we find that many of the control strategies and technologies that worked well in the past cannot handle the increase, and many are no longer cost-effective. Recent advances in the understanding of odor and corrosion processes and the introduction of many new and innovative control methods and technologies necessitate this significant technical update. The information in this manual will be valuable for collection system managers, design engineers, operators, and others responsible for today's modern collection systems.

2.2   Introduction

The information presented in this manual has been authored by recognized experts in the field of wastewater odor and corrosion control and represents the most current information available. Technical details and case histories provide an in-depth analysis of real-world control alternatives applicable to modern collection systems. This Manual's authors believe, however, that the reader should first be familiar with some of the basic scientific concepts related to collection system odor and corrosion in order to fully utilize this material. The authors have therefore prepared this chapter to present some of the basic science that later chapters build upon. This chapter also discusses the common biological and chemical principles that users of this Manual will need to understand and apply the control measures discussed in later chapters.

2.3　Collection Systems Overview

As long as there have been sewers there have been sewer odors. The emission of "foul vapors" from sewer catchments and openings has been a common problem for developing civilizations throughout history. To compound this issue, sewers have demonstrated the unique ability to corrode, deteriorate, and sometimes collapse for seemingly unknown reasons. Over the past 80 years researchers have identified the primary cause of sewer odor and corrosion as hydrogen sulfide gas, although many other odorous compounds are also found in sewers. Hydrogen sulfide gas is the only substance produced in sewers that can cause damaging corrosion, and it is therefore provided some special attention in this chapter.

Recent studies have shown that hydrogen sulfide gas concentrations in sewers have been increasing since about 1985. While some municipalities have been affected more than others, owners and operators of all wastewater systems are now experiencing increasing odor and corrosion problems but are armed with outdated knowledge and technologies. This chapter presents the most recent developments concerning this increase in hydrogen sulfide, its role in odor and corrosion, and best methods for control.

Before we can control something we need to understand it. Something as simple and common as odor is no different. Collection system owners and operators must first know what "odors" are, some of their more important properties, and how they impact humans. We can then build a solid foundation for a sound, scientific approach to controls.

2.3.1　Odors in Sewers

Wherever you find them, odors are simply airborne (volatile) chemical compounds. When those volatile chemical compounds interact with certain protein receptors on cells in our nose, our brain registers an "odor." A well-known example of an odorous volatile chemical compound would be perfume, a volatile liquid that people apply to their bodies to make them smell more pleasant. Odors can play an important role in human psychology by directly affecting one's perception of their personal well being. When perfume molecules continuously release to the air, humans detect these molecules with their sense of smell, recognize them as pleasant and feel good about their environment. Volatile odor compounds found in collection systems are released and detected the same way; however, not many of them are likely to be recognized as pleasant.

The volatile odor compounds found in sewers generally have three basic origins: feces, chemical discharges into the system, and the products of biological and chemical reactions in sewers. Natural fecal odor compounds are produced in the human digestive system, dissolved into the wastewater, and released directly into the sewer airspace. Many other odorous compounds are discharged into sewers from factories, restaurants, industries, and rendering plants, for example.

The most important compounds related to odor and corrosion in sewers are generated in the sewer through biological and chemical interaction of the mixed sewage components. Odor compounds produced this way include hydrogen sulfide, which is a primary focus of this chapter.

2.3.2　Mechanisms of Sulfide Generation

The role of hydrogen sulfide in the sewer odor and corrosion process is so important that some time must be spent discussing how it is produced and how it reacts with other sewage components. As mentioned above, sulfide is generated in the wastewater collection system from

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the interaction of received wastes. Once formed, it can exist in one or more of several different chemical forms, each is important to the understanding of control strategies. The following is a brief step-by-step discussion of exactly how sulfide and hydrogen sulfide are formed in sewers.

Sulfide generation is a biological process that occurs only in the submerged portion of sanitary sewers. Fresh domestic sewage entering a wastewater collection system is usually free of sulfide. However, biological interactions in the wastewater quickly start producing sulfide. The primary sewer conditions which cause and accelerate sulfide generation are listed below.

1. High BOD_5 concentration (a measure of the strength of the wastewater;)

2. High wastewater sulfate concentration

3. Elevated wastewater temperature

4. Long hydraulic detention time in the collection system

5. Many pumping stations and long force mains

6. Low dissolved oxygen concentration in the wastewater

7. Sewer debris

2.3.2.1 Slime Layer

The first step in the sulfide production process is the growth of a thin layer of biological slime below the water level in a gravity sewer or force main. This layer is composed of bacteria and inert solids held together by a gelatinous slime and covers virtually all underwater surfaces. When this biological slime becomes thick enough, the side next to the pipe wall becomes anaerobic. Approximately 2 weeks is required to establish a fully productive slime layer in new sewers. Once formed, slime layers become permanent fixtures in sewers; virtually all sewers have a slime layer. Although formed from many different bacterial species, many of the slime layer organisms are in a symbiotic relationship, providing shelter, food and energy for each other. By living in close proximity and sharing resources, slime layer bacteria thrive in this artificial ecosystem. Figure 2-1 shows a typical sewer slime layer, the generation of sulfide and the release of hydrogen sulfide gas.

As mentioned above, many different species of bacteria reside in the slime layer. Some species can only be found in one of the slime layer "zones" whereas other species can live in more than one. Their survival depends upon their ability to adapt and carry out life processes under the conditions in each zone. One of the most important conditions controlling where organisms live is the presence of oxygen or oxygen-containing compounds. The oxidation-reduction potential (ORP) of a particular zone can be measured in millivolts (mV) and is a measure of the amount and type of oxygen available. Anaerobically produced odor compounds are generally more offensive to humans than aerobically produced odors, a concept that is explained further in the next section. Therefore, odors (and hence corrosion) generally get worse as the ORP of a biological system drops. Figure 2-2 presents a typical biological ORP scale.
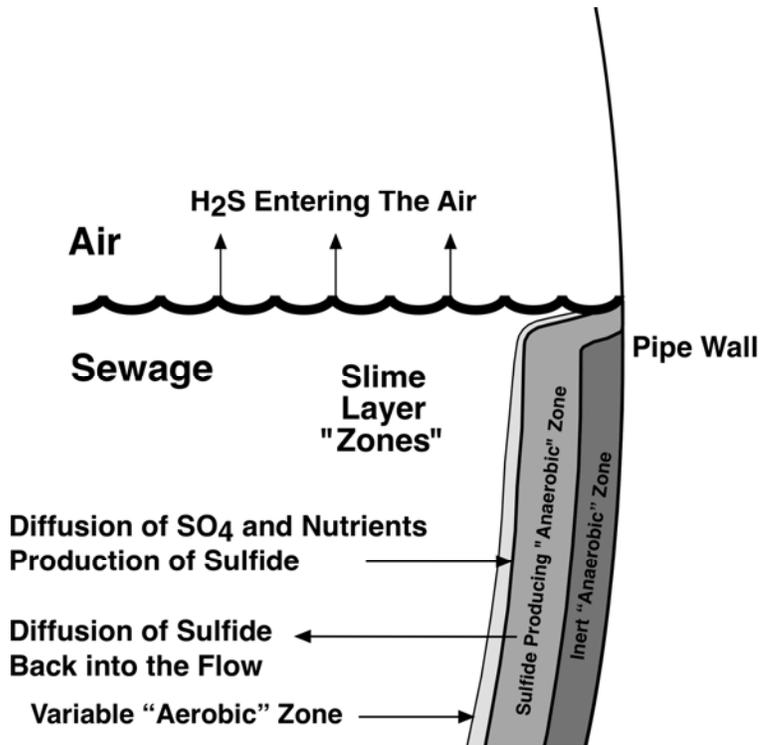
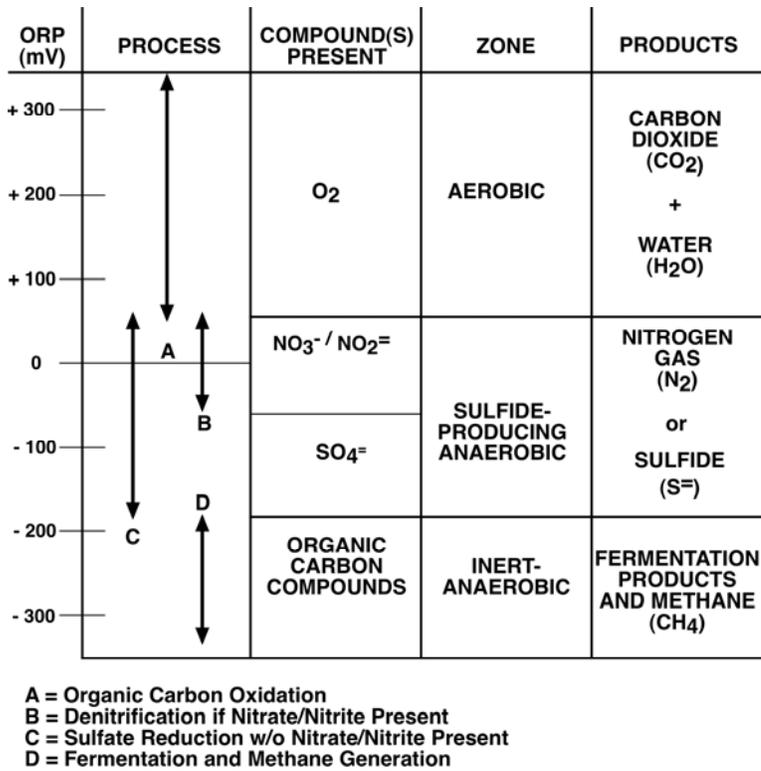Figure 2-1. Slime Layer Chemistry and Biology Illustration.

A = Organic Carbon Oxidation
B = Denitrification if Nitrate/Nitrite Present
C = Sulfate Reduction w/o Nitrate/Nitrite Present
D = Fermentation and Methane Generation

Figure 2-2. Biological ORP Scale

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The ORP values in Figure 2-2 are compiled from several references and represent an accurate averaging of variations which exist in the literature. The slime layer could be represented on this figure as having the highest (aerobic) ORP values at the outer surface nearest the wastewater and the lowest (anaerobic) values near the pipe wall.

As indicated in Figure 2-2, aerobic biological processes persist down to an ORP of around +50 millivolts (mV), at which point dissolved oxygen generally disappears. Between +50 and −200 is the range where only combined sources of oxygen are found. Bacteria under these conditions can use both nitrate and sulfate but prefer nitrate when present. It is this range of ORP values that dominates the slime layer biochemistry and is the primary cause of all sulfide-related odor and corrosion. Below −200 mV is the domain of the stick anaerobic and fermentative bacteria.

Many different species of bacteria reside in the slime layer. Some species can be found only in one zone, whereas other species can function in more than one. Their survival depends upon their ability to adapt and carry out life processes under the conditions in each zone.

2.3.2.2 Aerobic Zone

If the wastewater contains sufficient dissolved oxygen, the slime layer will be covered with an aerobic zone. The aerobic zone is characterized by the presence of dissolved oxygen (O_2), which penetrates a short distance into the biological slime. The bacteria that live in this zone use oxygen to break down organic compounds and carry out their life processes. Bacteria are able to get more energy from food sources when they use dissolved oxygen as opposed to combined sources of oxygen such as nitrate or sulfate. Some bacteria, called "strict aerobes," can use only oxygen; other bacteria, called "facultative bacteria," can use dissolved oxygen when it is present but can switch to combined sources of oxygen when O_2 is depleted. The primary byproducts of aerobic decomposition are carbon dioxide and water. The aerobic zone is usually very thin, if present at all.

The aerobic zone does not produce sulfide and is actually an active consumer of sulfide generated by the zone beneath it. When aerobic wastewater conditions permit the formation of an aerobic zone, the bacteria living there consume the sulfide and other odor compounds coming from below. Aerobic bacteria consider sulfide as a readily consumable food source and it is rapidly oxidized to sulfate and other harmless products.

2.3.2.3 Sulfide-Producing Anaerobic Zone

After all the oxygen has been removed from the aerobic zone (if present,) bacteria in the sulfide-producing anaerobic zone use combined sources of oxygen such as nitrate (NO_3^-), nitrite (NO_2^-), sulfite ($SO_3^=$) and sulfate ($SO_4^=$) to carry out their life processes. When these bacteria use nitrate and nitrite they produce nitrogen gas (N_2) which has no odor, and when they use sulfite and sulfate they produce sulfide ($S^=$) and hydrogen sulfide gas.

When compounds containing combined oxygen (such as nitrate and sulfate) are converted to compounds without oxygen (such as nitrogen gas or hydrogen sulfide) they are said to be "reduced" because they lose oxygen. When sulfide is converted back to sulfate in the aerobic zone, it is said to be "oxidized" because it gains oxygen. Some of the bacteria in this zone can use nitrate and are called nitrate-reducing bacteria, or "nitrate reducers," whereas some can use sulfate and are called "sulfate-reducing bacteria" (SRB). In general, bacteria can extract more energy from nitrate than from sulfate. Therefore, when nitrate is present in the wastewater,

nitrate-reducing bacteria in this zone become active and dominate the slime layer, even consuming the sulfide being produced by their neighbors. Since nitrogen gas is produced, this process generates no odor. However, nitrate and nitrite are rarely present naturally in domestic wastewater and so must be artificially added (see Chapter 7). However, sulfate is almost universally found in drinking water, and concentrations are always high enough in domestic wastewater to produce sulfide.

It is important to note that even if an aerobic zone or an artificial nitrate dominated zone is present on the outer surface of the slime layer, sulfide production still continues below. Sulfate can migrate through the aerobic and nitrate dominated zones completely unaffected and enter the sulfide producing zone where it is converted to sulfide. However, any sulfide produced under these circumstances would be quickly oxidized back to sulfate as it diffuses back out of the slime layer resulting in zero or near zero release of sulfide. It will appear as if the addition of oxygen or nitrate "stopped" the production of sulfide, which is technically incorrect. The sulfide is still produced but is actually being reoxidized to sulfate.

2.3.2.4 Anaerobic Zone

This zone does not directly produce sulfide and has historically been called "inert" for this reason. However, it plays an important role in sulfide production and is not actually inert. The food (BOD_5) that penetrates all the way to this zone is converted anaerobically to fermentation products. Fermentation products are small organic compounds left over after anaerobic bacteria are finished. Strict anaerobic bacteria that live here can only break down organic compounds to the two or three carbon atom stage even though there is energy left in them. Only aerobic bacteria or bacteria in the sulfide-producing zone can break them down further to retrieve energy. As these fermentation products migrate back up through the sulfide-producing zone, bacteria use them to convert sulfate to sulfide. Although this is not the only source of food for the SRBs, it can be a significant contribution to sulfide production.

From the discussion above, we can see that the rate at which sulfide is produced by the slime layer depends on a variety of environmental conditions including the concentration of organic food source (BOD), dissolved oxygen concentration, presence of nitrate, sulfate concentration, and the submerged surface area of the pipe as well as other factors.

2.3.2.5 Preventing Sulfide Generation

It follows from the above discussion that sulfide generation in wastewater collection systems could be reduced or minimized by some or all of the following:

1. Minimize or reduce wastewater BOD concentration, particularly soluble BOD sources such as sugars, soluble lipids and readily hydrolysable proteins.

2. Minimize or reduce the sulfate concentration of wastewater if possible through industrial discharge controls.

3. Minimize or reduce elevated temperature discharges.

4. Minimize or reduce hydraulic detention time in the collection system.

5. Minimize the use of force mains and consider twinning force mains for future capacity as opposed to a single larger main.

6. Minimize or reduce sediment and debris in sewers through regular assessment and cleaning as required.

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7. Hydraulically scour and remove a portion of the slime layer from force mains by periodically allowing the wet well to fill and turn on all pumps. High velocity water will remove some of the bacteria responsible for sulfide generation. Required on a weekly routine or more often as needed.

Regardless of the rate of sulfide generation, when oxygen and nitrate are not present, there is no mechanism to reoxidize sulfide on its way out of the sulfide-producing zone. Under these conditions, sulfide is released back into the wastewater stream, where it quickly comes into chemical equilibrium between four different forms of sulfide: the sulfide ion ($S^=$), the bisulfide (or hydrosulfide) ion (HS^-), aqueous hydrogen sulfide ($H_2S_{(aq)}$), and hydrogen sulfide gas ($H_2S_{(g)}$). This chemical equilibrium and the properties of each sulfide chemical in it are critical to understanding the control of sulfide in wastewater collection systems. Each of the sulfide chemical species is briefly described below.

Sulfide ion ($S^=$). The sulfide ion carries a double negative charge, indicating that it reacts primarily by giving up or sharing two electrons from the outer shell. It is a colorless ion in solution and cannot leave wastewater in this form. It does not contribute to odors in the ionic form.

Bisulfide ion (HS^-). The bisulfide (or hydrosulfide) ion carries a single negative charge. This is because one of the negative charges of the sulfide ion is taken up by a positively charged hydrogen ion. The hydrogen ion (H^+) was taken away from a water molecule (H_2O), leaving one hydroxide ion (OH^-) behind. The hydroxide ion increases the alkalinity (pH) of the wastewater and serves an important function to be discussed later. The bisulfide ion is a colorless, odorless ion that can exist only in solution. It also does not contribute to odors in this form.

Hydrogen sulfide (aqueous) ($H_2S(aq)$). Hydrogen sulfide can exist as a gas dissolved in water. The polar nature of the hydrogen sulfide molecule makes it moderately soluble in water. In the dissolved (aqueous) form, hydrogen sulfide does not cause odor; however, this is the only sulfide compound that can leave water to exist as a free gas. The rate at which hydrogen sulfide leaves water is governed by Henry's law, how turbulent the wastewater is, and the pH of the solution.

Hydrogen sulfide (gaseous) ($H_2S(g)$). Once hydrogen sulfide leaves water and becomes a gas, it can cause odor and corrosion. Hydrogen sulfide gas is a colorless but extremely odorous gas that can be detected by the human sense of smell in concentrations as low as 0.0005 parts per million (ppm), although 0.002 ppm is probably more near the average threshold. It is also very hazardous to humans in high concentrations and can cause a number of health-related problems and even death. In concentrations as low as 10 ppm it can cause nausea, headache, and eye irritation. Above 100 ppm it can cause serious breathing problems and loss of the sense of smell along with burning of the eyes and respiratory tract. Above 300 ppm death can occur within a few minutes. Because it can deaden the human sense of smell in concentrations above 100 ppm, it is particularly dangerous, making victims think that it is no longer present. Hydrogen sulfide is the cause of death in numerous wastewater accidents every year. A generally accepted hydrogen sulfide odor and toxicity spectrum is presented in Figure 2-3.

DETECTION ──────────▶
RECOGNITION ────────▶
(ROTTEN EGG
ODOR ALARM)

ODOR THRESHOLD — 0.0005 ppm

— 1.0

OFFENSIVE ODOR

— 10

HEADACHE, NAUSEA,
THROAT AND EYE IRRITATION

— 50

THRESHOLD OF ─────────▶
SERIOUS EYE INJURY

EYE INJURY

LOSS OF SENSE OF ─────────▶
SMELL, LIFE THREATENING

— 100

CONJUNCTIVITIS RESPIRATORY TRACT
IRRITATION OLFACTORY PARALYSIS

IMMINENT LIFE ─────────▶
THREAT

— 300

PULMONARY EDEMA

— 500

STRONG NERVOUS SYSTEM
STIMULATION, APNEA

IMMEDIATE COLLAPSE ─────────▶
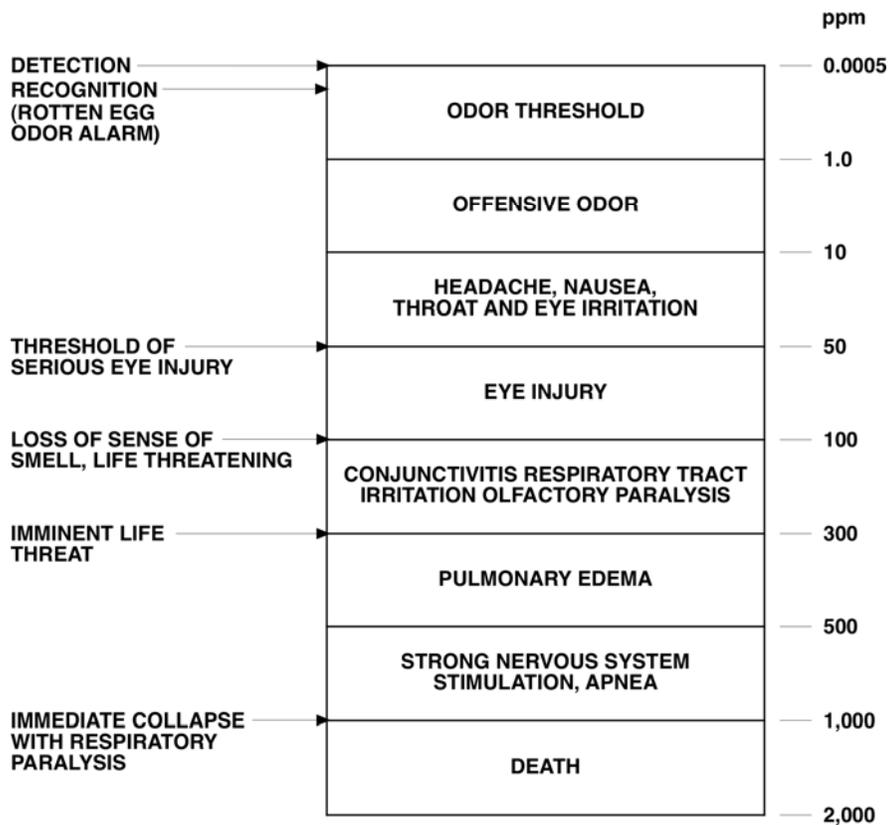WITH RESPIRATORY
PARALYSIS

— 1,000

DEATH

— 2,000

Figure 2-3. Generally Accepted Toxicity Spectrum for Hydrogen Sulfide Gas.

Due to the continuous production of sulfide by the slime layer, hydrogen sulfide gas rarely, if ever, re-enters the liquid phase. Sulfide continuously produced by the slime layer replaces that which is lost to the atmosphere as hydrogen sulfide gas in the collection system. In addition, once the hydrogen sulfide gas is released it usually disperses throughout the sewer environment and never reaches a high enough concentration to be forced back into solution.

The four sulfide chemical compounds are related according to the following equilibrium:

$$H_2S(g) \rightleftharpoons H_2S(aq) \rightleftharpoons HS- \rightleftharpoons S= \qquad (2.3.2-1)$$

As indicated by the equilibrium equations, once dissolved hydrogen sulfide is released into the gas phase, the bisulfide ion is immediately transformed into more aqueous hydrogen sulfide to replace that which was lost. Concurrently, sulfide ion is transformed into bisulfide to replace that lost to aqueous hydrogen sulfide. The equilibrium shift is very rapid and sensitive to the pH of the wastewater.

2.3.3 Relationship Between Turbulence and Sulfide Stripping

Turbulence is a critical parameter to consider in preventing hydrogen sulfide gas release from wastewater. The effects of sulfide odor and corrosion are increased significantly at points of turbulence. Turbulence, splashing and hydraulic outfalls generate water droplets which dramatically increase the surface area of the liquid. Any action that serves to increase the surface area of the liquid also increases the rate of H_2S gas transfer from the liquid to the gas phase.

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Unnecessary turbulence should be avoided in collection systems whenever possible. If turbulence is unavoidable due to drops, steep slopes or outfalls, the effects of odor and corrosion should be mitigated during design before they cause a problem.

The quantitative relationship between two of the most important sulfide species (HS$^-$ and H$_2$S$_{(aq)}$) is controlled by the pH of the wastewater as shown in Figure 2-4. This figure indicates that the proportional relationship between these two sulfide species is approximately 50/50 at a pH of 7.1. This means that at the pH of normal wastewater, half of all sulfide exists as the bisulfide ion and the other half exists as aqueous hydrogen sulfide (H$_2$S$_{(g)}$—a dissolved gas). Therefore, half of all sulfide in normal domestic wastewater is in a form that can leave the liquid phase to exist as hydrogen sulfide gas. If the pH of the wastewater is lowered, more of the sulfide exists as hydrogen sulfide gas.
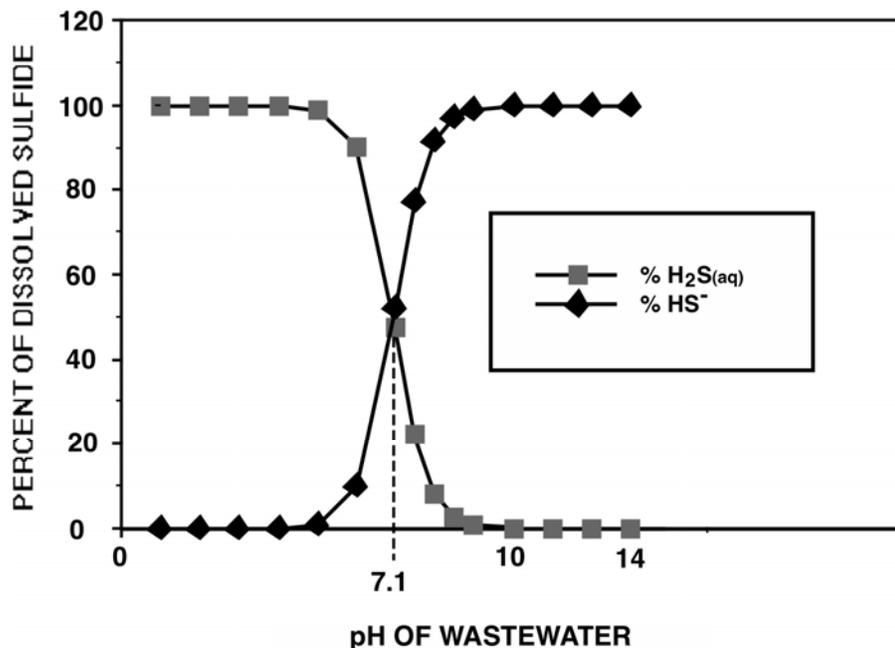

Figure 2-4. Effect of pH on Dissolved Sulfide Form

The sulfide equilibrium is extremely delicate and can shift rapidly with changes in temperature, barometric pressure, agitation, and particularly pH. As illustrated in Figure 2-4, the relationship curves between these two sulfide species is very steep near neutral pH. This means that a small shift in pH can translate into a large difference in hydrogen sulfide gas release. This fact has both negative and positive consequences. Low-pH discharges can cause increased localized release of hydrogen sulfide gas, which in turn causes increased odors and corrosion. On the other hand, artificially increasing the pH of wastewater to prevent hydrogen sulfide release is sometimes a viable sulfide control alternative. In one case, shifting the wastewater pH from 6.8 to 8.2 reduced hydrogen sulfide gas concentrations over 90 percent at a wastewater treatment plant headworks.

2.3.3.1 Preventing Sulfide Release

It follows from the above discussion that sulfide release from wastewater collection systems could be reduced or minimized by some or all of the following actions:

1. Minimizing or reducing wastewater turbulence in manholes, wet well entrances, and sewers through careful design and hydraulic modification.

2. Using contained-drop pipes for drop structures to minimize droplet formation and offgassing.

3. Inspecting and cleaning sewers where debris accumulation could occur or is suspected to have occurred. Debris in sewers can cause turbulence as well as increased sulfide generation.

4. Considering raising industrial discharge pH limits to allow higher wastewater pH and reducing sulfide-stripping potential.

2.4   Odorous Compounds in Wastewater

There are many odorous substances found in wastewater collection systems in addition to hydrogen sulfide gas. Hydrogen sulfide gas is inorganic, meaning it does not contain carbon. Hydrogen sulfide and ammonia are two examples of inorganic odor compounds found in wastewater collection systems. However, there are many more organic odorous compounds that can be produced in wastewater. All organic odor compounds contain carbon in one form or another. In addition, almost all of these organic odor compounds contain sulfur in some form. Some of the more common odor-causing substances, along with their chemical formula and odor threshold concentration, are listed in Table 2-1. All of these compounds can be produced naturally from domestic wastewater and sludge. Hydrogen sulfide, ammonia, and sulfur dioxide, which are inorganic, are included in Table 2-1 for comparison of their odor characteristics.

Table 2-1. Odorous Compounds in Wastewater

Name	Formula	Characteristic Odor	Detection Threshold (ppm)
Hydrogen sulfide	H_2S	Rotten eggs	0.0005
Ammonia	NH_3	Irritating, pungent	17
Skatole	C_9H_9N	Fecal, nauseating	0.001
Indole	$C_6H_4(CH)_2NH$	Fecal, nauseating	0.0001
Methylamine	CH_3NH_2	Putrid, fishy	4.7
Allyl mercaptan	$CH_2=CHCH_2SH$	Disagreeable, garlic	0.0001
Amyl mercaptan	$CH_3(CH_2)_4SH$	Unpleasant, putrid	0.0003
Benzyl mercaptan	$C_6H_5CH_2SH$	Unpleasant, strong	0.0002
Ethyl mercaptan	C_2H_5SH	Decayed cabbage	0.0003
Dimethyl sulfide	$(CH_3)_2S$	Decayed cabbage	0.001
Trimethylamine	$(CH_3)_3N$	Pungent, fishy	0.0004
Sulfur dioxide	SO_2	Pungent, irritating	2.7
Methyl mercaptan	CH_3SH	Decayed cabbage	0.0005
Thiocresol	$CH_3C_6H_4SH$	Skunk, irritating	0.0001
Thiobismethane	CH_3SCH_3	Rotting meat	0.0011

Note: Different threshold values are reported in the literature, particularly for hydrogen sulfide and ammonia. Odor thresholds are included here to give the reader a general idea of human sensitivity and odor concentrations which could potentially cause complaints. Ammonia for example is reported in ranges from 2.8 ppm to 17 ppm.

Because Henry's law also applies to organic compounds, the potential for stripping of these compounds is increased at points of turbulence within collection systems and treatment processes.

Although numerous odor compounds are produced in wastewater and released into sewer systems, the most common compound associated with odor complaints is hydrogen sulfide. This is due partly to its universal presence in wastewater collection systems and partly to the human

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ability to detect the gas at extremely low concentrations. If air containing hydrogen sulfide gas and organic odor compounds escapes a collection system, hydrogen sulfide gas will typically dominate the odor as it disperses into the environment. However, the escaping air will also contain organic odor compounds that can cause complaints when hydrogen sulfide is absent.

Since human reactions to odor chemicals in the air are subjective and vary from person to person, odors cannot be easily measured or quantified with a straightforward analytical approach. The problem then becomes, How do I measure the impact of odor from my facilities? It is possible to sample air directly for some of the odor-causing compounds. Many regulatory authorities establish odor regulations and compliance criteria based upon the measured concentration of certain odor compounds (most often hydrogen sulfide gas). Many sampling methods and analytical techniques have been developed to measure specific odor compounds released from wastewater (see Chapter 4).

Odors also have different characters, with varying degrees of offensiveness, called the Hedonic tone of the odor. Hedonic tone is a very important parameter for odors and explains why some odors can produce serious complaints at very low concentrations whereas others can be tolerated by humans well beyond their odor threshold concentrations. Knowing which odors are more likely to produce complaints is important when considering which odor sources to control with limited budgets. To gain insight into the nature of odors and what makes them different from each other, it is necessary to briefly look at how the human brain recognizes and reacts to odors.

2.4.1 Odors 101

As discussed above, odor compounds are simply volatile chemical compounds in the air that have an unpleasant character. Volatile chemicals with a pleasant odor character are called "perfumes" instead of odor compounds. Whether pleasant or unpleasant, a volatile chemical in the air that can be detected with the human sense of smell is called an "odorant." It is important to note that at any given time there could be hundreds if not thousands of volatile chemicals (odorants) in the air around you, depending upon where you are. Only a very few of these chemicals are recognized by the human brain as unpleasant or offensive. How are these volatile chemical compounds recognized, and why are only some of them offensive to humans?

The human sense of smell is a very sensitive, broad-spectrum chemical analyzer with a direct link to the brain. The effect that volatile chemicals (both pleasant and unpleasant) can have on the human brain is controlled by the sensitivity of the sense of smell, which varies from person to person. However, there are certain traits of the human sense of smell (the olfactory sense) that are common to all individuals. Understanding a little about how the human olfactory system and brain work together to recognize odors will help us better understand which compounds might require priority attention and how best to control them.

Imagine that you are walking down a path in a quiet forest on a warm, sunny spring day. The air is filled with hundreds of odorants of many types and forms. There are volatile chemicals being released by the growing leaves, bark, and flowers on the trees and the decaying leaves from the previous fall; flowers are releasing pollen and insect-attracting chemicals, molds are releasing spores, insects and animals are releasing pheromones, and fungi on the rotting logs you occasionally step over are releasing many volatile decay products. However, your olfactory sense is telling your brain that the air smells fresh with earthy aromas and has a generally pleasant

character, so you are at ease with your environment. No unusual, dangerous, or extraordinary odors have been detected so your brain does not bother to bring them to your conscious attention.

Now imagine that you come across the rotting carcass of an animal along the path. Before you see it, your olfactory sense picks up the chemical, recognizes it as being associated with a potentially unhealthy environment and sends a warning to your brain. Your brain immediately brings the odor to your conscious attention, prompting you to look for the source of the odor in order to avoid contact with it. Your brain is acting solely on the odor input to protect you from what it perceives as a potentially dangerous situation. If you can identify the source and avoid contact with it, then your olfactory senses and brain have done their job and you can return to enjoyment of the day. However, if the source of the odor cannot be identified or avoided (one or both are often the case with wastewater odor complaints) your brain remains in a state of alert and you are not at ease with your environment.

What is the difference between these two situations? Why does your brain tolerate hundreds of volatile chemicals and conclude that you are in a pleasant environment but cause significant distress at the presence of one or two particular chemicals?

The volatile chemicals you recognized as pleasant, earthy fragrances were generated by aerobic processes and the unpleasant decaying odor was generated by anaerobic bacteria. We live in an aerobic environment where oxygen is plentiful. We are exposed to the products of aerobic life on a daily basis, we eat mostly aerobically produced foods and we are familiar with them. Our bodies have very little to fear from aerobic environments or the products of aerobic systems. Therefore, aerobic decay products are similarly not harmful to us and humans have not developed olfactory warning systems for most aerobic compounds.

However, some chemical compounds are automatically recognized by the human olfactory system and brain as dangerous or threatening. These compounds are produced by anaerobic processes in environments which could be potentially harmful to us. Our bodies do not tolerate anaerobic conditions well and we cannot eat most anaerobic things without becoming ill. Our feces as well as the feces of most animals is anaerobic and unhealthy, prompting us to recognize these odors and avoid contact. Many gasses produced by anaerobic processes (swamp gas) are poisonous to humans. Once recognized by the brain, anaerobic odors produce an immediate "flight" response which does not require conscious thought. The detection of these compounds is "pre-wired" into the human brain to protect us from potential environmental dangers.

One of these compounds is hydrogen sulfide gas. Because hydrogen sulfide can be deadly to humans, we are automatically programmed to detect and be repelled by the characteristic "rotten egg" odor. This protects humans against possible health impact and death.

Many *organic* (carbon-containing) odor compounds are produced by anaerobic decay and are also characterized as being "rotten" or "decaying." This response also protects us against biological hazards by warning us not to eat or get near certain things. Humans rely on the link between their sense of smell and taste to warn them of contaminated, rotten or spoiled foods which could cause them harm. In the rare case that an individual were not able to distinguish the difference between fresh and rotting food, they would likely not live long enough to pass this defective trait to offspring.

The olfactory detection of an odor compound that our brain recognizes as a potential threat to our health causes stress at the primal (subconscious) level of our brain. That means that

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olfactory signals bypass the logic and reason processing centers of our brain to illicit the "flight" response. There are many other factors which affect the severity of human responses to environmental odors. The concentration of the odor chemical in the air, its duration, and its frequency of occurrence (which are not discussed here) all affect the human reaction to environmental odors. This brief discussion only serves as an introduction to explain why some odor compounds cause a negative human perception and others do not. Knowledge of how odors impact humans can help identify odor sources deserving priority attention from those of lower impact and priority. This knowledge also helps us select more appropriate and cost effective odor treatment systems and technologies.

2.4.2 Sulfuric Acid Production

Hydrogen sulfide gas is not only the most common cause of odor complaints from wastewater collection systems; it is also responsible for 99 percent of all sewer corrosion. There is another type of aerobic bacteria that commonly colonizes pipe crowns, walls, and other surfaces above the waterline in wastewater pipes and structures. These bacteria have the ability to consume hydrogen sulfide gas, oxidize it for use as an energy source and excrete sulfuric acid. This process can take place only where there is an adequate supply of hydrogen sulfide gas (>2.0 ppm), high relative humidity, carbon dioxide gas, and atmospheric oxygen. These conditions exist in the majority of wastewater collection systems for at least some portion of the year. The pH of surfaces exposed to severe hydrogen sulfide environments (>50 ppm in air) have been measured as low as 0.5, which is approximately equivalent to a 7 percent sulfuric acid solution.

The simplified and balanced equation for the biological metabolic process which converts hydrogen sulfide to sulfuric acid is presented below:

Thiobacillus bacteria

$$H_2S(g) + 2O_2 \rightarrow H_2SO_4 \qquad\qquad (2.4.2\text{-}1)$$

hydrogen sulfide, atmospheric, sulfuric

gas, oxygen, acid

2.4.3 Concrete Corrosion

The effect of sulfuric acid on concrete surfaces exposed to the sewer environment can be devastating. Sections of collection interceptors and entire pump stations have collapsed due to loss of structural stability from sulfide-related corrosion. We have all seen the photographs of cars being swallowed by streets opened by the loss of a section of large-diameter sewer (and also water main breaks). The process of concrete corrosion, however, is a step-by-step process that can sometimes give misleading impressions. The following briefly describes the biochemical process of concrete corrosion in the presence of hydrogen sulfide in a sewer atmosphere.

Freshly placed concrete has a pH of approximately 12 or 13, depending upon the amount of cement in the mix design. This high pH is the result of the formation of calcium hydroxide [Ca(OH)$_2$] as a byproduct of the hydration of cement. Calcium hydroxide is a very caustic crystalline compound which can occupy as much as 25 percent of the volume of concrete. Any surface with a pH of 12 or 13 will not allow the growth of any bacteria, because these very high pH values will dissolve the protein in the cell walls. However, the pH of the concrete is lowered over time by the effect of carbon dioxide (CO_2) and hydrogen sulfide gas (H_2S). These gases are both known as "acid" gases because they form relatively weak acid solutions when dissolved in water: CO_2 produces carbonic acid, and H_2S produces thiosulfuric and polythionic acids. These
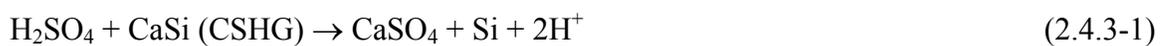
gases dissolve into the water on the moist, high-pH concrete surfaces above the sewage flow and react with the calcium hydroxide to slowly reduce the pH of the surface. Eventually the surface pH is reduced to a level which can support the growth of bacteria (pH 9 to 9.5).

The time it takes to reduce the initial high pH of fresh concrete is a function of the concentration of carbon dioxide and hydrogen sulfide in the sewer atmosphere. It can sometimes take years to lower the pH of concrete from 13 to 9; however, in some severe situations it can be accomplished in a few months.

Once the pH of the concrete is reduced to around 9, biological colonization can occur. Over 60 different species of bacteria are known to regularly colonize wastewater pipelines and structures above the water line. Most species of bacteria in the genus *Thiobacillus* have the unique ability to convert hydrogen sulfide gas to sulfuric acid in the presence of oxygen. Because each species of bacteria can survive only under a specific set of environmental conditions, the particular species inhabiting the colonies changes with time. Since the production of sulfuric acid from hydrogen sulfide is an aerobic biological process, it can occur only on surfaces exposed to atmospheric oxygen above the waterline in sewers.

As a simplified example, one species of *Thiobacillus* grows well only on surfaces with a pH between 9 and 6.5. However, when the sulfuric acid waste product they excrete decreases the pH of the surface to below 6.5, they die off and another species that can withstand lower pH takes up residence. The succeeding species grows well on surfaces with a pH between 6.5 and 4. When the acid produced by this species drops the pH below 4, a new species takes over again. The process of successive colonization can continue until species take over which can survive under extremely low pH conditions. One such species is *Thiobacillus thiooxidans*. This organism has been demonstrated to grow well in the laboratory while exposed to a 7 percent solution of sulfuric acid. This is equivalent to a pH of approximately 0.5.

Sulfuric acid attacks the matrix of the concrete, which is commonly composed of calcium silicate hydrate gel (CSHG), calcium carbonate from aggregates (when present), and unreacted calcium hydroxide. Although the reaction products are complex and result in the formation of many different compounds and minerals, the biogenic corrosion process can be generally illustrated by the following three reactions:

$$H_2SO_4 + CaSi\ (CSHG) \rightarrow CaSO_4 + Si + 2H^+ \tag{2.4.3-1}$$

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2CO_3 \tag{2.4.3-2}$$

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2\ H_2O \tag{2.4.3-3}$$

The primary product of concrete decomposition by sulfuric acid is calcium sulfate ($CaSO_4$), more commonly known by its mineral name, gypsum. From experience with this material in its more common form of drywall board, we know that it does not provide much structural support, especially when wet. It is usually present in sewers and structures as a pasty white mass on concrete surfaces above the water line. In areas where diurnal or other high flows intermittently scour the walls above the water line, concrete loss can be particularly fast.

It is generally believed by most investigators that the surface coating of gypsum paste somewhat protects underlying sound concrete by providing a buffer zone through which freshly produced sulfuric acid must penetrate. Because *Thiobacillus* bacteria are aerobic, they require free atmospheric oxygen to survive. Therefore, they can live only on the thin outer covering of any surface. This means that acid produced on the surface must migrate through any existing

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gypsum paste to reach sound concrete. By washing off the "protective" coating of gypsum with high diurnal or wet weather flows, fresh surfaces are repeatedly exposed to acid attack, which accelerates the corrosion process. Sewer-cleaning practices and equipment should be checked to determine the degree of gypsum layer loss during cleaning and the effects of such cleaning on the ultimate pipe life. Frequent high-pressure cleaning of concrete sewers under the influence of hydrogen sulfide could accelerate the corrosion process.

2.4.4 Metal Corrosion

Concrete is not the only material which can fall prey to the corrosive effects of hydrogen sulfide gas and sulfuric acid. Most metals, including many stainless steel alloys, can also be attacked and destroyed by exposure to sulfuric acid. Metals, however, are offered two routes of attack: acidic decomposition by exposure to sulfuric acid produced by *Thiobacillus* bacteria and direct chemical attack. Most common metals can exist as divalent cations, meaning that they carry two positive charges and react primarily by gaining two electrons in their outer shell (M^{++}). The sulfide component of hydrogen sulfide gas supplies these two electrons, resulting in a metal sulfide and two free hydrogen ions.

$$M^{++} + H_2S \rightarrow MS + 2H^+ \qquad\qquad (2.4.4\text{-}1)$$

The metal has a much stronger affinity for the sulfide than for the hydrogen, resulting in the formation of a stable sulfide-metal product and the release of two free hydrogen ions. In a moist or wet environment the hydrogen ions lower the pH of the water and increase the rate of corrosion. By reacting with sulfide, the metal is converted from the strong metal-metal bonding into a much weaker metal–sulfide product, and at the same time is exposed to the acidic effect of the free hydrogen ions. Most wastewater professionals have witnessed the corroded rungs of steel manhole steps, corroded and weakened manhole covers and rings, and have seen brass and copper fittings turned dark bluish-black, the color of nickel and copper sulfide.

2.5   Trends in Sulfide Production

Operators know that the production of hydrogen sulfide in wastewater collection systems has been increasing over the past 15 or so years. There are now significant scientific data to confirm that sulfide generation, odor, and corrosion are increasing in today's wastewater collection systems. A summary of some of the seemingly unrelated reasons for this increase is presented below, along with implications for collection system operators.

2.5.1 Clean Water Act

The Federal Water Pollution Control Act Amendments of 1972 (PL 92-500), as supplemented by the Clean Water Act (CWA) of 1977, mandated that the nation's water supplies be protected through a variety of mechanisms. One such mechanism was to require cleaner wastewater discharges from our publicly owned treatment works. One concern with treated wastewater discharges was the bioaccumulation of heavy metals in the environment. Certain metals, such as lead, copper, mercury, chromium, and zinc, were shown to have toxic effects to animals and plants in high concentration. Some of these metals passed through wastewater treatment plants and entered the receiving stream where they could be bioaccumulated to dangerous concentrations. As a result, the EPA required municipalities to implement industrial pretreatment programs where heavy metals and other contaminants from industrial sources were identified. Before 1980, a common source of heavy metals in wastewater was industrial discharges from steel mills, electroplating operations, photo-finishing, and electronics and

computer chip manufacturing. In 1995, all such operations were required to begin pretreating their wastewater to remove metals prior to discharging the wastewater to a publicly owned treatment work.

Sulfide in the dissolved forms (bisulfide ion and sulfide ion) has a strong affinity for metals. In fact, one of the most common methods used to remove sulfide from wastewater is to add metal salts (usually ferrous iron compounds) to combine with sulfide and precipitate metal sulfide, which is very insoluble. The substitution of iron for other heavy metals does not violate the industrial pretreatment standards since iron is essentially not regulated and is abundant in nature. Most iron sulfide is removed at the treatment plant as sludge, but iron is typically not a permitted discharge constituent. Sulfide will combine with almost all metals; therefore, removing a source of metals in wastewater also removes a potential sulfide-removal mechanism.

It has also been noted that the targeted heavy metals exhibited a toxic effect on the slime layer bacteria that produce sulfide. Toxicity or inhibition of the sulfate-reducing bacteria in the slime layer naturally reduced their health and activity, which in turn reduced sulfide production. Removing the source of the toxicity allowed the slime layer bacteria to flourish and produce even more sulfide. In 1989, congress commissioned a study to assess the impact of the industrial pretreatment program on sulfide odor and corrosion. The study concluded that both of the above mechanisms were responsible for a general increase in sulfide concentrations in domestic wastewater. Figure 2-5 represents data taken at the Hyperion Wastewater Treatment Plant, in Los Angeles, California.
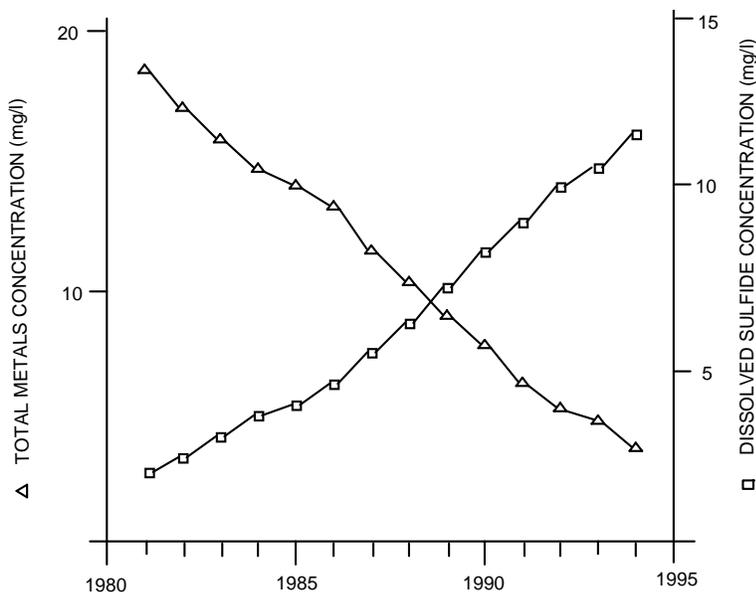

Figure 2-5. Metals-versus-Sulfide Relationship

Over a period of several years, influent wastewater was analyzed for several constituents, including sulfide and total metals concentrations. As the data dramatically indicate, influent sulfide to the plant increased at the same time total metals concentrations decreased. This trend began in 1980 and continues to this day; it can therefore be concluded that industrial pretreatment has resulted in an increase in sulfide concentrations in wastewater and thus in increased odor and corrosion.

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2.5.2 Water Conservation Practices

Over the last 15 years, utilities and water purveyors have recognized the benefit of promoting water conservation practices. Prompted by water shortages around the country, water conservation practices were shown to not only preserve a precious resource but also save utilities money by delaying planned expenditures for plant upgrades, system capacity increases, and storage facilities. Although cost-efficient and practical for the water industry, water conservation has caused an increase in wastewater system dissolved sulfide concentrations.

Reduced wastewater flows from water conservation practices cause reduced flow velocities and longer residence times, or the time wastewater spends in the collection system. This allows more time for the reduction of sulfate and therefore higher dissolved sulfide concentrations. It also increases the general septicity of the wastewater. Since less dilution water is entering the wastewater collection system, the strength of the wastewater in terms of BOD_5 increases. This increases the biological activity of the slime layer and causes the faster consumption of dissolved oxygen. Increasing septicity causes the production of organic acids that drop the pH of the wastewater. Since a small shift downward in the pH of the wastewater can cause a dramatic increase in hydrogen sulfide gas release (see Figure 2-4), the anaerobic drop in pH can also increase the release of odor-causing hydrogen sulfide. Although water conservation has increased the dissolved sulfide concentration of wastewater, there is little evidence to suggest this alone increases total sulfide mass. Increased sulfate or BOD_5 would be required to cause this effect. However, the Henry's law coefficient governing the release of hydrogen sulfide gas from wastewater is highly dependent upon sulfide concentration in the liquid phase. Therefore, any increase in the dissolved sulfide concentration of wastewater will increase the likelihood of hydrogen sulfide gas releases along with the associated odor and corrosion.

2.5.3 Regionalization of Wastewater Treatment Facilities

Over the past several years, wastewater agencies have been regionalizing wastewater treatment facilities, building larger plants or upgrading others while closing smaller, less-efficient plants. This action follows from the realization that a few larger plants are less costly to operate than many smaller ones. Also, improving many small plants to keep up with tightening regulatory requirements is much more expensive than upgrading one or two larger plants. The usual method of regionalizing wastewater treatment is to build a pumping station at the site of the small treatment plant, pump the wastewater to a larger or newer plant and demolish the small plant. This requires the use of pumping stations and force mains that have a 360° slime layer, have an increased detention time, do not allow reaeration, and are excessive producers of sulfide. The sulfide produced in the force mains is released when it is exposed to the atmosphere.

In addition, municipalities are sewering larger and more extensive areas of their districts in an effort to minimize the use of septic tanks. This is an effort to protect local groundwater supplies. Usually, the wastewater piping is oversized in anticipation of larger future capacities; this causes low velocities, long residence times, and excessive sulfide production.

2.5.4 Culture and Environmental Awareness

One of the reasons for increased odor problems is a general increasing awareness of odor and a lowering of the intolerance for it. Many years ago in the United States, and still in some other countries, odor was a given fact of life and was considered an acceptable price to pay for progress and prosperity. This was before an increasing general awareness of the environment in

the late 1960s and 1970s. As people became more aware of the environment and its workings, odor became a less and less accepted part of everyday life. It was perceived that if offensive odors are detectable, there must be something environmentally wrong. And when that odor had something to do with wastewater collection or treatment, then the environment, or at least people's health, must surely be threatened.

2.5.5 Urbanization

As population grows, land becomes more intensively used. This is particularly true of the areas near wastewater treatment plants and other wastewater facilities. Utilities often go to great lengths to locate treatment plants and other facilities as far away as possible from developed areas. Unfortunately, developers recognize the benefit of readily available roads, power and water lines installed to support the plant. Add to this the ready availability of sewer access and the land leading to and around the treatment plant is soon filled with new homes. This scenario happens all too often. Intensifying land use near wastewater facilities does not increase sulfide production, but it does make life difficult for wastewater professionals, increases capital and O&M budget expenditures for odor control measures, and can be a significant public relations problem.

The fact that wastewater no longer contains the natural control afforded by metals in industrial discharges, and that stronger wastewater is now traveling farther than ever to get to its final treatment destination is sufficient reason to be concerned with odors from wastewater systems. Add to this the fact that people are living closer to wastewater facilities and are no longer willing to put up with odors, and it is no small wonder that we are now faced with even greater odor and corrosion challenges for the future.

2.6   The Sulfur Connection

We have seen above how odors and corrosion in wastewater collection systems cause complaints from citizens and damage our wastewater infrastructure. We have also found that the principal chemical compound implicated in both cases is hydrogen sulfide gas. We know that it is produced in the collection system through the interaction of bacteria and the waste products in the sewer. We know that a great amount of money is spent each year in attempts to control this compound. How can a simple, plentiful compound like sulfur cause such damage? We must first investigate the "sulfur connection" to see how hydrogen sulfide is formed. This will allow us to identify our options for controlling odor and corrosion in collection systems.

2.6.1 In Nature

Sulfur is one of the most common elements on earth. It is abundantly present in rocks, minerals, soil, and water. Because sulfur is soluble in most of its forms, groundwater and surface water can contain considerable quantities of sulfur, depending upon local geology. In addition, seawater contains high concentrations of sulfur as sulfate, as well as sulfide and sulfite. The ocean is also a huge repository for organic sulfur accumulated from aquatic life processes such as seaweed and plankton deposits. Undersea volcanic activity also spews thousands of tons of sulfur into the oceanic abyss every hour. Sulfur in one or more if its forms is intimately connected with life on Earth.

As an element in nature, sulfur can exist in a wide variety of chemical forms. Because of the configuration of the outer electron shell for sulfur, it is capable of giving up, receiving, or sharing electrons in a variety of combinations. It is therefore able to combine with many other

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elements and compounds and has become widely distributed in nature. As a result of its wide natural distribution, sulfur has become an integral part of our ecosystem and biosphere. Most living things require sulfur in some form to carry out their life processes. It serves important biochemical functions in many plants and animals. It is an essential component of many proteins and a critical component of blood plasma.

Some species of bacteria have evolved to use sulfur as the primary component in their life cycle. Some bacteria require certain sulfur compounds to be present before their metabolism can function, while others can use only certain specific sulfur compounds as terminal electron acceptors. In extreme environments (such as undersea volcanic fumaroles), entire ecosystems have even evolved that use inorganic sulfur as a total energy source, without reliance on energy from the sun. Needless to say, the life processes of thousands of different types of bacteria are centered on sulfur in one or more of its various forms.

Almost any good textbook on environmental chemistry will contain a figure similar to Figure 2-6, which depicts the sulfur cycle and its many transformations in nature.
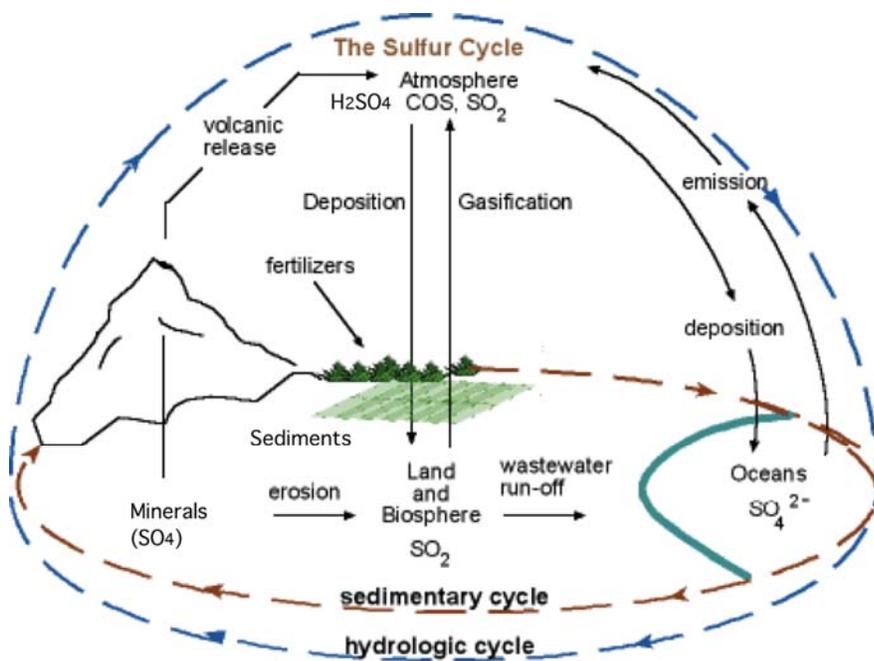

Figure 2-6. The Sulfur Cycle

The sulfur cycle is an important tool for learning about the overall environmental, chemical, and biological significance of sulfur, but it does not readily explain the small but important environmental niche that exists for sulfur in municipal wastewater collection systems.

2.6.2 In the Sewer

Civilization has created a very specialized environmental niche we call "the sewer." This niche consists of a complex biochemical environment that is populated by many different life forms. It also exhibits a specific and definable, semiclosed biological and chemical cycle of sulfur that can be identified and observed. The cycle is based upon the biological and chemical transformation of sulfate into sulfide and sulfide into a variety of ionic and gaseous forms,

ending in the biological transformation of hydrogen sulfide gas to sulfuric acid and then neutralization of the acid back to sulfate. This is the cycle that generates sulfuric acid and is responsible for billions of dollars of damage each year to wastewater collection and treatment systems. It clearly and simply illustrates a problem that has long been recognized but has only recently become a serious widespread concern. It is therefore important to understand the basics of the "sewer sulfide cycle" before we can scientifically apply control measures.

Figure 2-7 is a basic schematic diagram of the sewer sulfide cycle that shows the important interactions between sulfur and the natural biochemistry in a sewer. Since the reactions of sulfur take place both in the water and in the air, the processes are divided into liquid phase and vapor phase. In this way, the diagram also takes on the general form of a gravity sewer with the liquid phase processes taking place at the bottom and the vapor phase processes on the top.
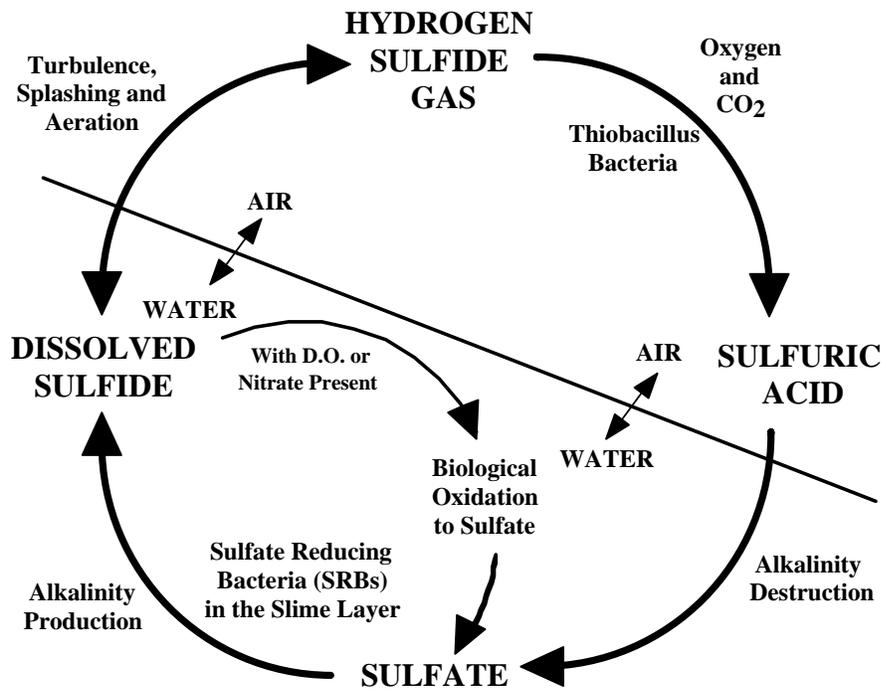
Figure 2-7. The Sewer Sulfide Cycle

This sewer sulfide cycle effectively represents the chemical, physical, and biological processes occurring in sewers that involve all the various forms of sulfide. The actual biochemical processes it represents are complex and dependent upon many variables, but the process pathways illustrated in Figure 2-7 are common to all sewers.

There are four major segments of the cycle: the generation of sulfide, the release of sulfide, the conversion of hydrogen sulfide gas to sulfuric acid, and reaction of acid on sewer walls. Each segment comprises biological and chemical processes that fulfill that segment's particular function in the overall sulfide cycle. The four segments are linked by arrows representing the major pathways through which all sulfide processes must pass. These pathways provide us with an opportunity to interfere with the processes and thus reduce or stop the cycle of sulfide generation in sewers. The following describes each of the pathways in detail and illustrates how they can be used to control sulfide.

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2.6.2.1 From Sulfate to Dissolved Sulfide

The cycle starts when sulfate ($SO_4^=$) in the wastewater is consumed by anoxic slime layer organisms to produce sulfide ($S^=$). Sulfide produced by the slime layer immediately attracts hydrogen atoms from water to form dissolved sulfide ($HS^- + H_2S(aq)$). When a hydrogen atom is taken from a water molecule it forms one hydroxide ion (OH^-). Hydroxide ions are alkaline since they can react with acids. Therefore, the creation of one hydrogen sulfide gas molecule generates alkalinity in the form of two hydroxide ions. This process occurs only underwater in the slime layer and the wastewater.

If the wastewater contains sufficient dissolved oxygen or nitrate, some or all of the sulfide can be reoxidized to sulfate to restart the process. This process occurs in the outer slime layer, which recycles the sulfur between sulfide and sulfate, as represented by the small arrow cycle back to "sulfate."

2.6.2.2 From Dissolved Sulfide to Hydrogen Sulfide Gas

The next pathway of the cycle represents the release of a dissolved gas ($H_2S(aq)$) into the sewer to exist as a free gas ($H_2S(g)$). It should be noted that as with almost all gasses that exist in nature, hydrogen sulfide gas would naturally be released from water containing the dissolved gas in an attempt to establish equilibrium with Henry's law. The rate of this release is dependent upon the surface area of the air–water interface.

For example, if we fill a beaker half-full with a solution containing exactly 1.0 mg/L of dissolved sulfide and then immediately seal it, some of the dissolved hydrogen sulfide gas would naturally be released from the water to exist as the free gas. Assuming that the pH of the solution remains neutral (7.0) and the dissolved sulfide concentration stays constant at 1.0 mg/L, the airspace in the beaker will eventually contain close to 300 ppm of hydrogen sulfide gas (well into the deadly range for hydrogen sulfide!). This concentration just happens to be the equilibrium point for hydrogen sulfide with Henry's law at 1.0 mg/L dissolved sulfide. If we place the sealed beaker in a quiet area and leave it totally undisturbed it may take many months or even years for this equilibrium to stabilize. However, if we vigorously shake the sealed beaker (again assuming that the pH of the solution remains neutral and the dissolved sulfide concentration stays constant at 1.0 mg/L), we will achieve our 300-ppm airspace concentration in about 30 seconds.

The reason we can cut the equilibrium time from several years to 30 seconds is surface area. In the undisturbed sample, the surface area of the air–water interface is fixed and easily determined. In the violently shaken sample, the air and water are mixed intensely so that all of the air exists as very small bubbles that are in constant contact with water. The combined surface area of the bubbles (total air–water interface) is many hundreds of times larger, which means that the equilibrium forces can now operate across the entire bubble–water surface area and reach equilibrium very quickly.

Note that this is the only pathway which has an arrow going in both directions. Although it rarely happens in sewers, if hydrogen sulfide gas concentrations are very high it could force some of the gas back into solution. The dispersing and dilution of gas throughout the sewer and the continuous production of sulfide by the slime layer will keep the dissolved concentration high enough to prevent reabsorption of the gas. The double-arrowed pathway represents this possible but unlikely event.

2.6.2.3 From Hydrogen Sulfide Gas to Sulfuric Acid

The next process of the sulfide cycle shows that hydrogen sulfide gas can be oxidized by *Thiobacillus* to produce sulfuric acid or can be released to the atmosphere. Once secreted by the bacteria on the sewer walls, the acid either reacts with the concrete and metal in the sewer to cause corrosion or runs down the sewer walls back into the wastewater where it is neutralized. Wherever atmospheric oxygen, carbon dioxide gas, water vapor and hydrogen sulfide gas (>2 ppm) are present, *Thiobacillus* bacteria can exist. This pathway occurs only on the abovewater surfaces in sewers.

2.6.2.4 From Sulfuric Acid to Sulfate

The last pathway completes one full cycle of transformation when unreacted sulfuric acid runs down the pipe wall and is neutralized in the wastewater flow. When it contacts the wastewater, the acid destroys the alkalinity (OH⁻) that was produced when the original sulfate was reduced to sulfide. Therefore, there is no net change in wastewater pH from the generation of acid from hydrogen sulfide gas in sewers. It is also important to note that when sulfuric acid is neutralized by reacting with alkalinity in the sewage, sulfate is the product. This sulfate is once again available for uptake and conversion to hydrogen sulfide gas as shown. Through this ever-repeating, self-sustaining cycle, sulfur and sulfate are in a constant state of change in a sewer.

Figure 2-7 explains in basic terms the transformation pathways of sulfate and sulfide in sewers. However, it is most useful when technically evaluating and selecting sulfide control measures for a particular sewer system.

2.7 Using the Sulfide Cycle to Evaluate and Select Control Measures

The sulfide cycle and its pathways explain how one part of the cycle is dependent upon another. As mentioned above, we need to look at only the four major process pathways, each feeding the next step, to realize that interrupting one or more of these pathways could stop the cycle and thus stop sulfide odor and corrosion. By knowing how these pathways are related and some general information on sulfide control mechanisms, we can evaluate the various methods of sulfide control and prepare a short list of feasible alternatives.

All sulfide-related odor and corrosion control alternatives for collection systems fall into one of three basic control strategies: design and operational activities, chemical–liquid phase operations, and ventilation/vapor phase operations. Knowledge of the interdependent relationships of sulfate concentration, slime layer biochemistry, turbulence conditions, and *Thiobacillus* requirements allows an investigator to evaluate how any particular sulfide control alternative would work in any particular collection system.

As an example, let's assume that we want to interrupt the cycle in a 925-mm (36-inch) diameter gravity sewer where sulfate is biologically reduced to sulfide in the slime layer.

(Note that stopping sulfate reduction in the slime layer is an interesting place to start since it requires clarification of a small but important detail of sulfide generation in sewers: Technically, there is no way to completely stop the reduction of sulfate by the slime layer short of physical or chemical removal the slime layer itself. Even when wastewater contains high concentrations of dissolved oxygen, sulfate still penetrates through the aerobic zone to be reduced to sulfide. When this sulfide migrates back up through the aerobic zone, it is oxidized to sulfate with no net effect on wastewater sulfide concentrations. Although no sulfide is being released back to the wastewater from the aerobic zone on top of the slime layer, sulfide is still being generated in the zone beneath.)

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2.7.1 Interrupting the First Pathway

In our example, we will evaluate ways to stop the first pathway (reduction of sulfate to sulfide), as illustrated in Figure 2-8. Table 2-2 lists by category the options available for interrupting this pathway.
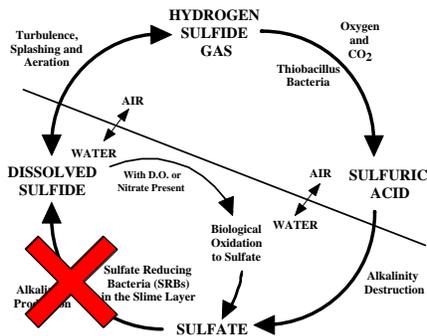

Figure 2-8. Interrupting the First Pathway of the Sulfide Cycle

Table 2-2. Strategies for Interrupting the First Pathway

Category	Strategy	Method(s)
Design and operational	Physically remove the slime layer	Pigging Water jetting
	Physically remove sulfate from wastewater	Ultrafiltration/nanofiltration (not practical) Sewer-use ordinances (regulate sulfate discharge)
Chemical and liquid phase	Chemically remove the slime layer	Caustic slug dosing
	Chemically stop sulfate reduction in the slime layer	Addition of anthroquinone (metabolic inhibitor)
	Chemically remove sulfate from wastewater	Barium precipitation (not practical)
Ventilation/vapor phase	None	None

2.7.1.1 Design and Operational Methods

In our example, physically removing the slime layer would stop sulfate reduction and can be accomplished by pigging in force mains or high-pressure water jetting in gravity sewers. Pigging involves forcing a "pig" the same diameter as the pipeline through the pipe to scrape off the soft biological slime layer. Pigging is not feasible in a gravity sewer, and high-pressure jetting of a sewer every few days would be cost prohibitive and might accelerate pipe deterioration. Neither of these physical removal methods is in widespread use due to high labor requirements and regrowth of the slime layer in 3–7 days.

Removing sulfate from wastewater means controlling sulfate in all discharges to a collection system, which is very difficult, if not impossible, because sulfate is found almost universally in all waters and is very soluble in most of its forms. One conceptual physical method of sulfate removal is to regulate or control the discharge of sulfate through sewer-use ordinances. There are only a few instances where sulfate discharges have been regulated, and in these cases the intent was to reduce extremely high discharge concentrations to levels closer to background. Sulfate can also be physically rejected using certain membrane processes (ultrafiltration and nanofiltration) but the process is expensive and not practicable on a large-scale basis.

2.7.1.2 Chemical and Liquid Phase Methods

Chemical removal of the slime layer can be accomplished through caustic shock dosing, a chemical method. By killing all of the bacteria that make up the slime layer, the reduction of sulfate is stopped. Neither physical nor chemical removal of the slime layer is used very much since it can grow back in 3–10 days, depending upon BOD and temperature.

Chemically stopping sulfate reduction can be accomplished by adding the chemical anthroquinone to wastewater. This chemical interferes with the metabolism of sulfate-reducing facultative organisms, rendering them useless. The chemical is not very soluble at typical wastewater pH, which limits its usefulness.

Barium is the only element which reacts with sulfate under normal conditions to form an insoluble precipitate. Barium is also toxic to humans and is not practicable for use in wastewater.

2.7.1.3 Summary

We have just evaluated all of the potential alternatives for preventing the reduction of sulfate to sulfide in our example sewer. Additional detailed knowledge of our sewer would provide the data necessary to put costs to feasible methods and arrive at the least costly alternative for stopping sulfate reduction in the slime layer. In actual practice, prevention of sulfate reduction is rarely considered or evaluated except in the case of a few very high sulfate concentration industrial discharges, and then only to reduce the concentration and not eliminate sulfate. Sulfate is generally assumed to be present in all wastewaters and it is rarely feasible to remove it.

2.7.2 Interrupting the Second Pathway

Let's now consider interrupting the second sulfide cycle pathway in our sewer. In this case, we are allowing sulfide to be generated in the slime layer but will try to prevent its release to the sewer atmosphere.

In this example we will evaluate ways to interrupt the second pathway of the sulfide cycle (Figure 2-9); Table 2-3 lists by category the options available for interrupting this pathway.
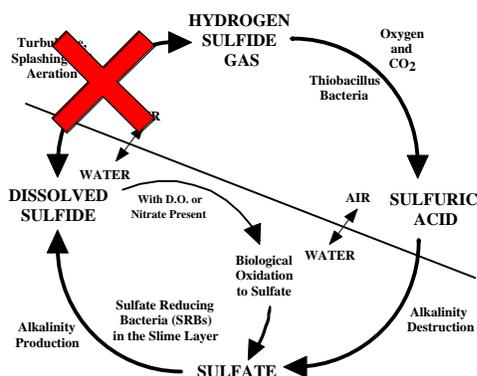
Figure 2-9. Interrupting the Second Pathway of the Sulfide Cycle

Interrupting the second pathway of the sulfide cycle is much more common, and there are many potential alternatives which can do this. We must first list the alternatives to stop this pathway and categorize them once again into design and operational activities, chemical–liquid phase operations, and ventilation/vapor phase operations; most of the alternatives in this category

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are chemical and liquid phase methods and there are no ventilation alternatives to prevent the release. Ventilation controls become effective only after hydrogen sulfide gas is released in the next pathway of the cycle.

Table 2-3. Strategies for Interrupting the Second Pathway

Category	Strategy	Method(s)
Design and operational	Physically prevent turbulence	Sewer velocities/hydraulic jumps
		Drop structure/drop manhole modifications
		Modify/design force main terminations for turbulence reduction
		Controlled release of sulfide from wastewater (stripping—requires vapor phase treatment for odor control)
Chemical and liquid phase	Oxygen injection/ addition	Air injection/diffusion
		Pure oxygen injection
	Chemical addition	Chemical oxidants (chlorine compounds, hydrogen peroxide, potassium permanganate)
		Precipitants (ferrous and ferric chloride and sulfate)
		pH adjustments (caustic addition, magnesium hydroxide addition)
		Bioactive oxidants (nitrate/nitrite)
Ventilation/vapor phase	None	None

As we can see in Table 2-3, it is in interrupting this pathway where most of the current sulfide controls operate. We saw above that preventing the transformation pathway of sulfate to sulfide in sewers is very difficult, if not impossible. Therefore, we must try to remove the sulfide immediately after it emerges from the slime layer but before it can be released to the air. Because of the high number of sulfide control methods focused on this pathway of the sulfide cycle, descriptions will be brief.

2.7.2.1 Design and Operational Methods
Since preventing sulfide release is the goal and since turbulence controls stripping, we could focus on turbulence reduction to reduce the release of sulfide. Sewers can be designed to avoid excessive slope/velocity changes and hydraulic jumps. Drop structures and manholes should be designed with drop pipes to handle wastewater smoothly and without agitation. Force mains should discharge below a standing body of water whenever possible to absorb the kinetic energy of the discharge without splashing or turbulence. At the outer range of possibilities is the intentional stripping of sulfide and removal from the air as hydrogen sulfide gas. Although stripping seems counter to the goal of preventing release of hydrogen sulfide gas, if the release can be accomplished in a location where facilities have been designed to handle the conditions, this effectively prevents release from downstream facilities.

2.7.2.2 Chemical and Liquid Phase Methods
The vast majority of chemical and liquid phase sulfide controls operate by interfering with this pathway. They range from the powerful oxidants such as chlorine, hydrogen peroxide, and potassium permanganate to the precipitants like iron that work to precipitate sulfide as a metal sulfide. Some chemicals take advantage of the pH dependence of sulfide by raising the pH of the entire wastewater flow. This shifts the sulfide equilibrium from the releasable dissolved gas form to the nonreleasable bisulfide ion, as illustrated in Figure 2-4. It is in this category that we also find oxygen and nitrate chemicals, which we discovered earlier form an aerobic or nitrate-dominated zone on top of the slime layer.

There are many chemicals and liquid phase treatments available to interfere with this cycle pathway in many different ways. It would not be appropriate to try to discuss each of them here. A full technical description and analysis of each of these chemical treatments is discussed in detail in Chapter 7.

2.7.2.3 Summary

Controlling the second sulfide cycle pathway is the exclusive domain of chemical treatments and other liquid phase processes. Chemicals are the most common sulfide control technique and are used primarily to control odor complaints and not corrosion.

2.7.3 Interrupting the Third Pathway

To continue our example, let's now consider that we want to interrupt the third cycle pathway in our sewer. In this case, we are allowing sulfate to be reduced in the slime layer and released to the sewer atmosphere but will try to prevent its conversion to sulfuric acid.

In this example we are essentially interrupting the third pathway of the sulfide cycle (Figure 2-10); Table 2-4 lists the options available for interrupting this pathway.
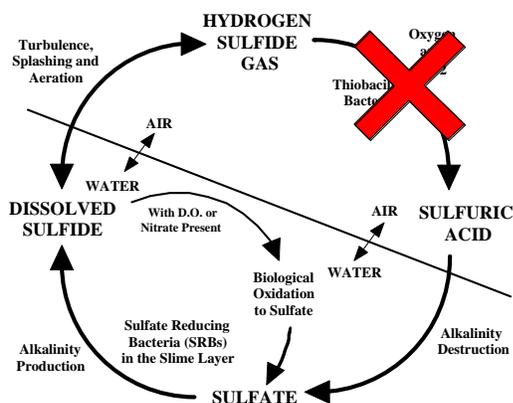

Figure 2-10. Interrupting the Third Pathway of the Sulfide Cycle

Interrupting the third pathway of the sulfide cycle involves preventing hydrogen sulfide gas from being oxidized to sulfuric acid. This means that we need to stop or limit the growth of *Thiobacillus* bacteria or otherwise interfere with the uptake of hydrogen sulfide gas and generation of acid.

Once again, if we list the alternatives to stop the sulfide cycle at this pathway (with the exception of preventing release of H$_2$S discussed above) we find that there are possibilities in two of the three categories: design and operational and ventilation/vapor phase alternatives but no chemical–liquid phase controls. This is because acid generation occurs on the abovewater surfaces in sewers and there is nothing that can be added to the wastewater that will affect this area of sewers.

Table 2-4. Strategies for Interrupting the Third Pathway

Category	Strategy	Method
Design and operational	Physically prevent acid generation	Surcharge sewers
Chemical and liquid phase	Chemically prevent acid damage	Crown spraying
Ventilation/vapor phase	Modify sewer environment to prevent *Thiobacillus* growth	Ventilate sewer and treat odorous air

2.7.3.1 Design and Operational Methods

One way to prevent oxidation of H_2S to sulfuric acid is to prevent the growth of *Thiobacillus* bacteria. Since these bacteria require three gasses in combination with high humidity and/or moist growing surfaces, we can try to eliminate one of these factors. Eliminating gasses from the sewer would require operating the sewer with no available headspace for air or required gasses like H_2S or CO_2. By operationally surcharging the sewer, the bacteria to not have access to the necessary gasses, and thus corrosion is effectively stopped. Caution should be given to "crown cutting," which affects surcharged pipes as discussed below.

It would typically be assumed that *Thiobacillus* corrosion would not be present in a full-flowing gravity sewer since full pipes typically do not allow gasses to be present. However, a phenomenon called "crown cutting" or "crown corrosion" has been found in concrete pipes which intentionally flow full. The process starts when entrained air bubbles in the flow coalesce on the pipe crown in a place where the bubble can remain stationary against hydraulic forces. This is typically at a joint in reinforced concrete pipe (RCP) or any high spot in the line where hydraulic shear cannot dislodge the air bubble. All of the conditions required for *Thiobacillus* will exist inside this bubble of air. As acid is generated on the above-water portion of this air pocket, the concrete corrodes upward, which makes the air pocket larger. Over time, acid production continues on the top surface and can even breach the crown of the pipe. The corrosion does not extend laterally beyond the limits of the bubble since it is continuously wet and not exposed to gasses. Figure 2-11 is a photograph of crown corrosion in a full-flowing concrete pipe.

Figure 2-11. Crown Corrosion

Crown spraying typically involves spraying a caustic or alkaline chemical on the exposed surfaces of sewers and structures to kill *Thiobacillus* bacteria and neutralize any acid that may be on the surface. (This process is discussed more in Section 2.7.4.) However, crown spraying

(most often used with magnesium hydroxide slurry) also functions to prevent the uptake of hydrogen sulfide gas by *Thiobacillus* bacteria. Floating "skids" or "boats" are used to transport a spray nozzle assembly down the sewer while pulling chemical supply hoses along and spraying slurry as it goes. The process is usually applied from one upstream manhole to the next downstream manhole and requires two crews. The skid is pulled through the sewer so that speed and therefore application rate can be controlled. The thick layer of alkaline slurry covers the above-water surfaces of sewers, effectively cutting off the food supply for *Thiobacillus*. In addition, the slurry reacts directly with hydrogen sulfide gas in the sewer to form a magnesium sulfide complex (blue or black in color). The high pH of the slurry surface also prevents *Thiobacillus* growth until the pH is naturally reduced to acceptable limits.

2.7.3.2 Ventilation/Vapor Phase Methods

The forced ventilation of sewers can be used to reduce the rate of corrosion and to stop corrosion in certain situations. Extracting air from a sewer with a fan will cause a similar volume of air to enter the system. This dilutes the concentration of hydrogen sulfide gas in the sewer which in turn reduces the mass of sulfuric acid being generated and thus reduces the corrosion impact. Similarly, the influx of outside air and its subsequent withdrawal will reduce the relative humidity in the sewer, which will change the moisture levels in the sewer and dry some of the pipe surface. A dry surface cannot support *Thiobacillus* bacteria, so sulfuric acid will not be produced. Additionally, the exchange of air will also change the air temperature in the sewer, which will affect the dewpoint and condensation on the interior sewer walls. All of these actions will serve to reduce the rate and extent of corrosion. It is important to point out that ventilation alone will not be as effective as when used in conjunction with one or more other control methods. Ventilation will never be able to stop corrosion completely.

2.7.3.3 Summary

Very few of the common sulfide control methods act to interfere with the generation of sulfuric acid from hydrogen sulfide gas. Those that do can rarely be 100 percent effective.

2.7.4 Interrupting the Fourth Pathway

Let's now consider that we want to interrupt the fourth pathway of the cycle in our sewer. In this case, we are allowing sulfate to be reduced in the slime layer, released to the sewer atmosphere, and converted to sulfuric acid but will try to prevent corrosion of materials before it runs back into the wastewater.

In this example we will evaluate ways to interrupt the fourth pathway of the sulfide cycle (Figure 2-12); Table 2-5 lists by category the options available for interrupting this pathway.

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Figure 2-12. Interrupting the Fourth Pathway of the Sulfide Cycle

Interrupting the fourth pathway of the sulfide cycle involves preventing sulfuric acid from contacting sensitive surfaces. Using this pathway for control of sulfide involves protecting sensitive corrosion-prone surfaces. This latter method could be used without odor treatment systems if the location is remote and there is no potential for complaints, although this situation is unlikely.

Once again if we list the alternatives to stop this pathway we find that there are design and operational alternatives but no chemical and liquid phase or ventilation/vapor phase controls. This is because acid generation occurs on the abovewater surfaces in sewers and there is nothing that can be added to the wastewater that will affect this area of sewers. Ventilation controls prevent oxidation of hydrogen sulfide to sulfuric acid through interruption of the third pathway only.

Table 2-5. Strategies for Interrupting the Fourth Pathway

Category	Strategy	Method
Design and operational	Use of inert construction materials	Plastics (PVC, HDPE, PE, PP, FRP)
		Coatings on concrete
		Cast-in-place liners on concrete (PVC, HDPE)
		Applied liners on concrete (PVC)
	Crown spray	Periodically spray crowns of sewers with caustic chemicals (sodium hydroxide, magnesium hydroxide)
Chemical and liquid phase	Crown spray	Periodically spray crowns of sewers with caustic chemicals (sodium hydroxide, magnesium hydroxide)
Ventilation/vapor phase	None	None

2.7.4.1 Design and Operational Methods

One way to prevent corrosion from even starting in the first place is to use acid-proof materials of construction. Selecting the proper pipe material for a new sewer must consider corrosion impacts. When corrosion resistance alone is considered, pipe material selection favors plastic materials such PE/HDPE, PVC, or various resin-based, composite materials such as polymer concrete, GRP, or FRP.

Inert pipe materials are still economical for pipe diameters less than about 72 inches, which comprises the vast majority of the total service area of the typical collection system. The vast number of plastic pipe types, formulations, and configurations makes a complete discussion

in this chapter impossible. However, care should be exercised to determine the specific formulation of plastic pipes since all plastics are not equal. For instance, PVC pipe is manufactured using a number of different filler materials. This is due to the cost of the resins used and the strength of each particular resin. Fillers are added to provide bulk and mass to the pipe and reduce excessive resin consumption. Some filler materials can be attacked by acidic conditions, which leach the fillers from the pipe and reduce the structural capacity.

Coatings. By far the most common method used to interrupt this pathway is protecting sensitive sewer surfaces from contact with acid. The most common protection method (also the one with the shortest effective lifetime) is applying a coating, specifically, a product applied to a concrete surface as a liquid or semisolid and then allowed to chemically cure. Coatings used in the wastewater industry are generally either epoxies or urethanes. Many different formulations of each are available. Coating formulations should be selected based upon the requirements of the service conditions and performance characteristics of the coating product. Coating products must be evaluated for use on a case-by-case basis. The successful application of coatings is very environmentally sensitive. It can be extremely difficult to successfully apply coatings under the temperature, humidity, and flowing water conditions found in sewers. These factors often cause microscopic holes (pinholes) to form in the coating even when it is applied under strict supervision and inspection. Pinholes and other defects found in coatings provide a direct route for acid produced on the surface to reach the concrete and cause attachment failure.

Liners. When the cost of producing such large-diameter (over 72 inches) inert material pipes is considered, it is quickly found that the cheapest material by far is reinforced concrete pipe (RCP). The relatively low cost and high-strength of concrete makes it economically attractive for large-diameter, deep sewers, but the corrosion resistance of concrete is minimal. Concrete is readily attacked and destroyed by strong mineral acids like H_2SO_4; hence the need for liners.

Cast-in-place liners have knobs, Ts, ribs, or some other type of protrusion from one side of the liner sheet that are embedded into concrete or grout during construction. When the liner is attached to the concrete formwork with the protrusions facing outward, the opposite smooth, acid-resistant side of the liner is exposed when the forms are removed. Brand-name examples are T-Lock (PVC) and Bekaplast, Studliner, and Agru Sure-Grip (all PE). These types of liners can be used for either new construction or rehabilitation, and although new construction is where they are most often used, some of these liners are gaining acceptance as viable rehabilitation methods due to advances in grouting technology and in-pipe construction techniques. Whether cast-in-place liners are used for new or rehabilitation service, they relieve hydrostatic and vapor pressure by providing a pathway for gas and water escape into the sewer without sacrificing corrosion protection. Since the anchors are the only part of the liner embedded in the pipe wall, the flat surface of the liner is held close against the concrete but not tightly adhered to it. This allows "weep water" and vapor pressure to equalize into the sewer between the embedments without creating an open airspace where gasses can accumulate. Figure 2-13 shows a typical T-type cast-in-place liner.
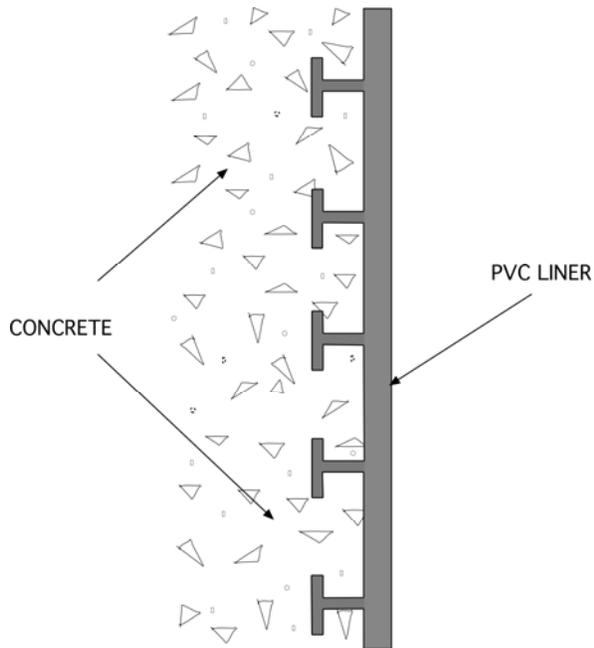
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Figure 2-13. Typical Cast-in-Place Liner Profile on Wall

Mechanically attached liners can be almost any material, although rigid (unplasticized) PVC and HDPE are most common. The most significant variation is the method of attachment, which can vary from small expansion-type anchors to stainless steel batten strips with epoxy grout anchors, as shown in Figure 2-14. The high degree of flexibility offered by mechanically attached liners makes them adaptable to a wide variety of conditions. Attachment systems can be designed to safely accommodate the anticipated hydraulic and hydrostatic forces. Liner thicknesses can also be easily varied for additional hoop strength to adjust to specific design needs. These liners have been used primarily for new construction, although numerous rehabilitations have been reported with equal success. Mechanically attached liners, like the cast-in-place liners, do not resist hydrostatic and vapor forces but pass them harmlessly to the sewer environment. Like the cast-in-place liners, the flat inner surface of the liner is held closely against the interior of the concrete pipe but not fastened to it. This allows water to flow harmlessly into the sewage and not create a localized high-pressure area, which could create a bulge and make the liner fail. Due to high flow failures in large-diameter sewers, mechanically attached liners are now used almost exclusively in structure protection where hydraulic forces can be controlled.
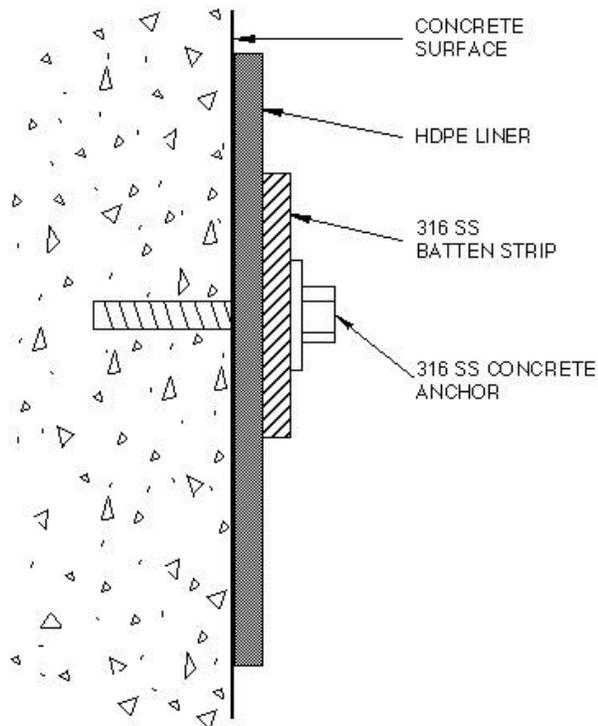
Figure 2-14. Mechanically Attached Liner Detail

Chemically attached liners come in two basic forms: One type has protrusions on one side of a PVC sheet that are pressed into freshly applied epoxy mastic on the concrete. The mastic flows around the protrusions to provide secure attachment when cured. Another form of chemically attached liner is a flat PVC sheet that is pressed against a freshly applied polyurethane material as illustrated in Figure 2-15. A chemical additive on the PVC sheet causes chemical fusion and cross-polymerization between the urethane and the PVC, resulting in a very secure bond. These liners can be applied over new concrete; however, they are more commonly used in concrete rehabilitation projects. There are other, more-secure and more-economical methods for new construction than chemically attached liners. One of the potential pitfalls of a chemically attached liner is the requirement that it physically resist *all* hydrostatic and vapor pressure forces trying to push it off the wall. Since the liner is "glued" to the pipe wall with an epoxy or urethane mastic, the attachment of the epoxy or urethane to the pipe wall is critical to liner performance. The ability to resist anticipated hydrostatic and vapor pressures should be adequately demonstrated.
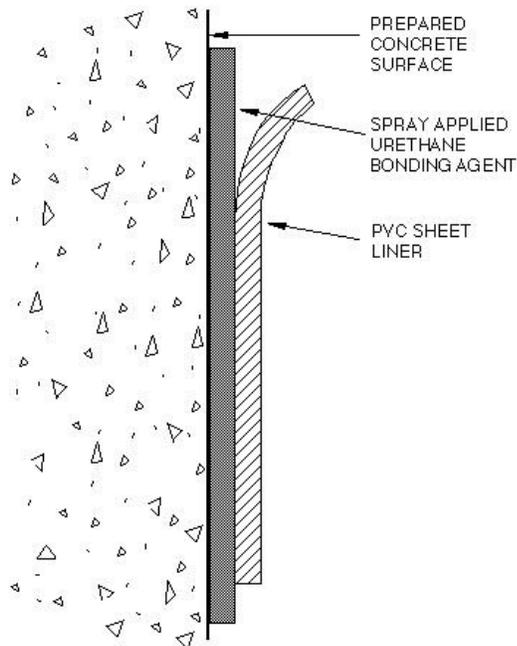
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Figure 2-15. Typical Chemically Attached Liner

Crown Spraying. This process involves spraying a caustic or alkaline chemical on the exposed surfaces of sewers and structures to kill *Thiobacillus* bacteria and neutralize any acid that may be on the surface. Floating "skids" or "boats" are used to transport a spray nozzle assembly down the sewer while pulling chemical supply hoses along. The process is usually applied from one upstream manhole to the next downstream manhole and requires two crews. The skid is pulled through the sewer so that speed and therefore application rate can be controlled. Sodium hydroxide was first used for this purpose, but it is hazardous to handle. This chemical has the consistency of water and any excess runs down into the wastewater. Magnesium hydroxide has been used more recently to provide the same effect without hazardous concerns. Magnesium hydroxide is also applied as a thick slurry, which puts more alkalinity on the crown and keeps it there. Depending upon the rate of corrosion and the condition of the pipe, crown spraying can cost effectively delay sewer rehab or prolong the life of pipes almost indefinitely.

2.7.4.2 Summary
The prevention of acid contact is the exclusive domain of inert materials, liners and coatings. When considering corrosion protection for new sewers, the increase in sulfide-related corrosion should be anticipated to continue and even more corrosive conditions will be experienced in the future. This would tend to favor inert materials and cast-in-place liners.

2.8   Corrosion Control Guidelines for Gravity Sewers, Force Mains, and Wastewater Collection Systems

Because wastewater flow itself plays a role in odor and corrosion within collection systems, those systems designed to reduce turbulence also minimize the effects of hydrogen sulfide, corrosion, and sewer ventilation in wastewater collection systems. The following design

guidelines should be used prior to and during preparation of the engineering alternatives analysis and design for wastewater facilities.

2.8.1 Sulfide Control Design Considerations

The following guidelines help minimize the production of dissolved sulfide and the release of hydrogen sulfide gas into wastewater collection systems.

2.8.1.1 Gravity Sewers

Sufficient wastewater velocity, if maintained in gravity sewers, can minimize the production of dissolved sulfide. An absolute minimum velocity of 2.0 fps at low flow is recommended to reduce the accumulation of sewer solids in the pipe and allow potential reaeration of the wastewater to prevent excessive production of sulfide.

Excessive velocities—generally those over 6.0 fps—cause turbulence in the wastewater and strip hydrogen sulfide gas and should be avoided, particularly downstream of sulfide sources such as force main discharges. The sulfide concentration in the wastewater to be conveyed by the gravity sewer should be considered before designing for velocities that could cause the stripping of hydrogen sulfide gas.

Turbulence at points of intercepted flow (manholes or wyes) should be minimized by smooth transitions. Hydraulic drops and outfalls should be avoided. The use of drop manholes should be minimized, and optional methods such as submerged-outlet drop pipes or contained drops should be considered for outfalls up to 20 feet to contain and minimize turbulence (Figures 2-16 and 2-17).

Avoid combining wastewater flows at a confluence angle greater than 90 degrees, and never join sewers with opposing flows (confluence angle of 180 degrees). Confluence angles of 45 degrees or less have been found to reduce sewer pressurization, turbulence, and corrosion (Figure 2-18).

Sudden or dramatic changes in direction (such as 90-degree bends) and sudden changes in slope or velocity should be avoided due to turbulence, pressurization, and ventilation concerns. The longest radius horizontal curves possible should be used.

Inverted siphons should be avoided whenever possible. When absolutely necessary, inverted siphons should be provided with adequate air jumper or odor treatment capabilities and positive corrosion control measures such as liners or inert materials.

Never allow a gravity sewer's diameter to decrease in the downstream direction even if hydraulically correct. This causes turbulence, dramatic ventilation effects, localized pressurization, and odor release. More money will be spent to correct the odor and corrosion problem than was saved in pipe material and construction costs.

2.8.1.2 Pump Stations and Force Mains

The use of pump stations and force mains should be avoided whenever gravity sewer designs are feasible and constructible.

Pump stations and force mains should be designed to minimize hydraulic detention time within the pipeline, thereby reducing dissolved sulfide production.

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MANHOLE OR ACCESS
STRUCTURE WALL

PVC, FRP
CROSS (TYP.)

316 SS STRAP
FOR SUPPORT

EPOXY ANCHOR
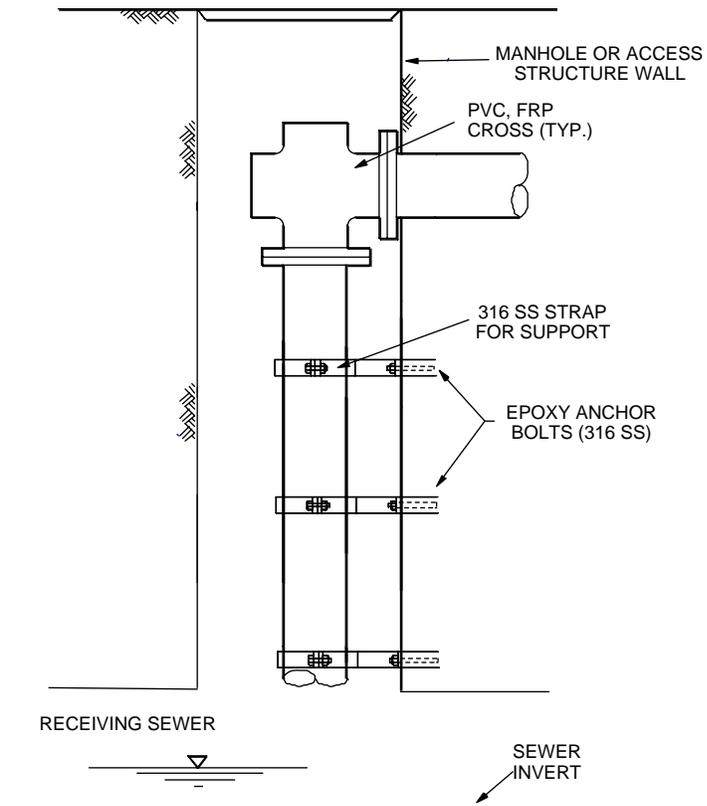BOLTS (316 SS)

RECEIVING SEWER

SEWER
INVERT

Figure 2-16. Inside Drop Structure to Minimize Turbulence of Gravity Drops
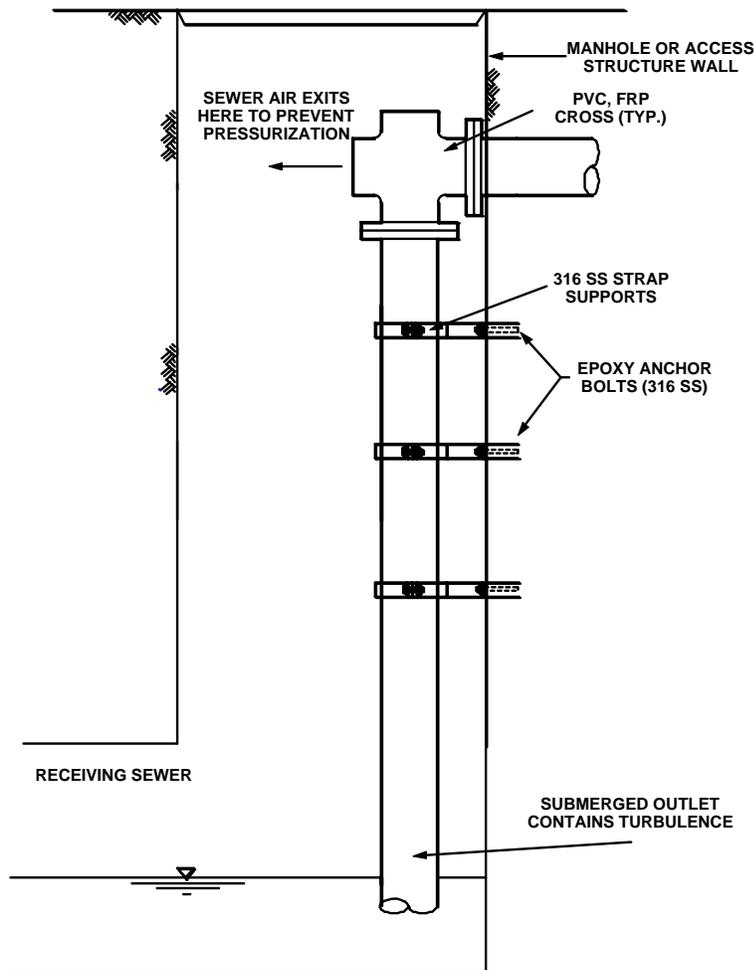
Figure 2-17. Submerged Inside Drop Structure

Force mains should be designed so that discharges directly into a wet well minimize turbulence and the stripping of hydrogen sulfide gas. Wherever possible, discharges should be submerged to completely absorb hydraulic energy (Figures 2-18 through 2-24). Back-siphoning tendency should be evaluated before implementing.

Gravity sewer entrances into wet wells should be designed to minimize free fall and turbulence. Turbulence reduction measures similar to those in Figures 2-22 and 2-23 can be used if adjusting water levels and sewer elevations are impractical. Pump stations should be designed so that free air movement through the sewer is not impeded by wet well water levels except at flows greater than peak dry weather flow.

The number of air/vacuum release points for force mains should be minimized through grade and slope control. Avoid partially full force main conditions at any point in the pipe. Force mains should always have a flat or continuously rising profile, never a downward profile or negative slope.
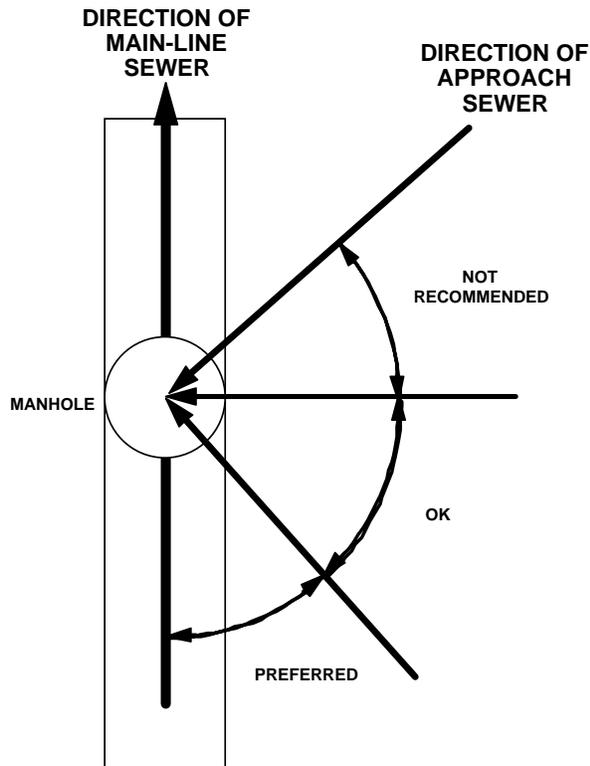
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Figure 2-18. Sewer Approach Angles for Reducing Turbulence and Controlling Ventilation

Consider the use of dual force main piping for new pump stations to maintain minimum velocities, provide for future capacity, allow redundancy of facilities, and reduce dissolved sulfide generation during early use years (if force mains can be drained by gravity).

Consider also programming the pump station controller to periodically surcharge the wet well to high levels and then call for all pumps to scour the slime layer from the pipe. This will minimize sulfide generation in the force main if done every 3 days.

Where the force main profile cannot be controlled and air/vacuum releases must be used, consider using variable-frequency drives on pump motors to maintain flow conditions and avoid excessive valve operation.

2.8.2 Corrosion Protection Design Considerations

The following guidelines have been prepared to assist in the reduction of corrosion potential in wastewater collection and treatment systems caused by exposure to hydrogen sulfide gas. In general, hydrogen sulfide gas concentrations below 2.0 ppm are not considered corrosive. Hydrogen sulfide gas concentrations between 2.0 and 5.0 are considered potentially corrosive, and sewers with concentrations averaging over 5.0 ppm should be 100 percent protected.

2.8.2.1 Gravity Sewers

Pipe material and pipe liners used for wastewater collection system construction should be unaffected by contact with sulfuric acid solutions of pH 0.5 (approximately 7 percent sulfuric acid by weight).
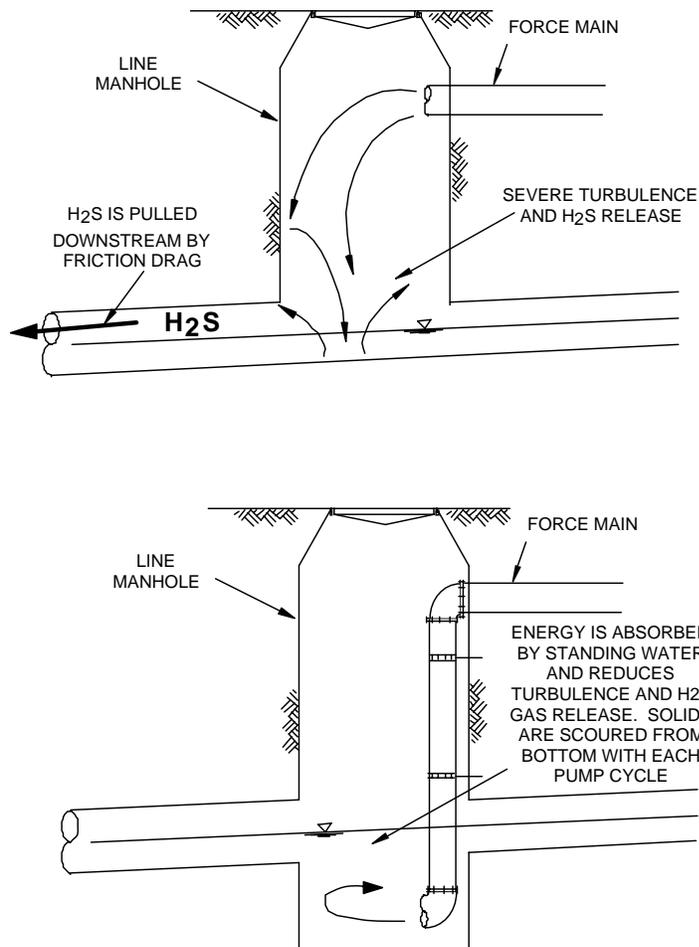
Figure 2-19. Force Main Turbulence: Before and After Reduction Using Modified Manholes

Cementicious concrete products of any type (calcium silicate, calcium aluminate) should not be used for the conveyance of wastewater without an appropriately designed corrosion protection system (liner). Coatings cannot provide the service life of liners, and coated pipes will require recoating periodically. Coatings are not recommended for concrete that cannot be readily visually inspected and easily repaired without entering the pipe.

Particular attention should be given to corrosion protection of existing unprotected concrete gravity sewer pipes and manholes in areas of increased turbulence (intercepted flows, 90-degree bends, slope changes, drop manholes, and force main discharge locations) for a distance of 300 sewer diameters downstream and 50 sewer diameters upstream.

2.8.2.2 Pump Stations and Force Mains

Pump station wet wells should be constructed of or lined with inert materials. Plastic liners provide a longer life than applied coatings. Exposed, unprotected concrete of any kind should not be used in pump station wet wells or other areas exposed to average concentrations of hydrogen sulfide gas greater than 5.0 ppm.

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Piping, valves, and fittings used inside pump station wet wells or areas exposed to significant concentrations of hydrogen sulfide should be constructed of, or lined with, inert materials. The only metal allowed is 316 stainless steel. Coated ductile iron is not acceptable.

Force mains should be constructed of inert pipe materials or factory-applied polyethylene-lined ductile iron pipe. Prestressed concrete cylinder pipe is not recommended for wastewater force main applications.

Pay particular attention to protecting structures downstream of turbulent force main discharge areas. Force main discharge manholes should be constructed from T-Lock concrete or inert materials only.
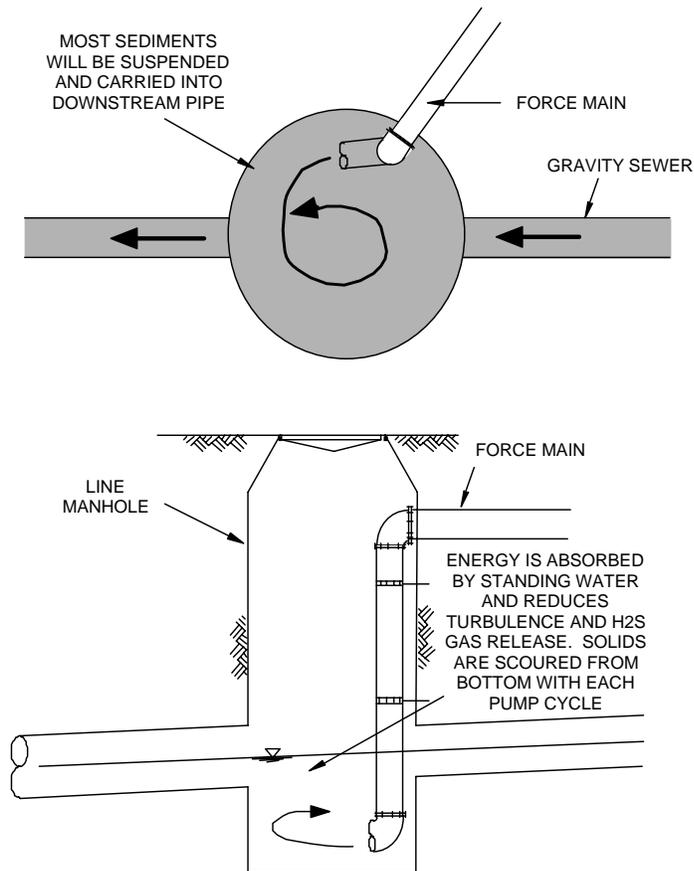

Figure 2-20. Force Main Line Manhole Turbulence Correction (Plan and Section Views)
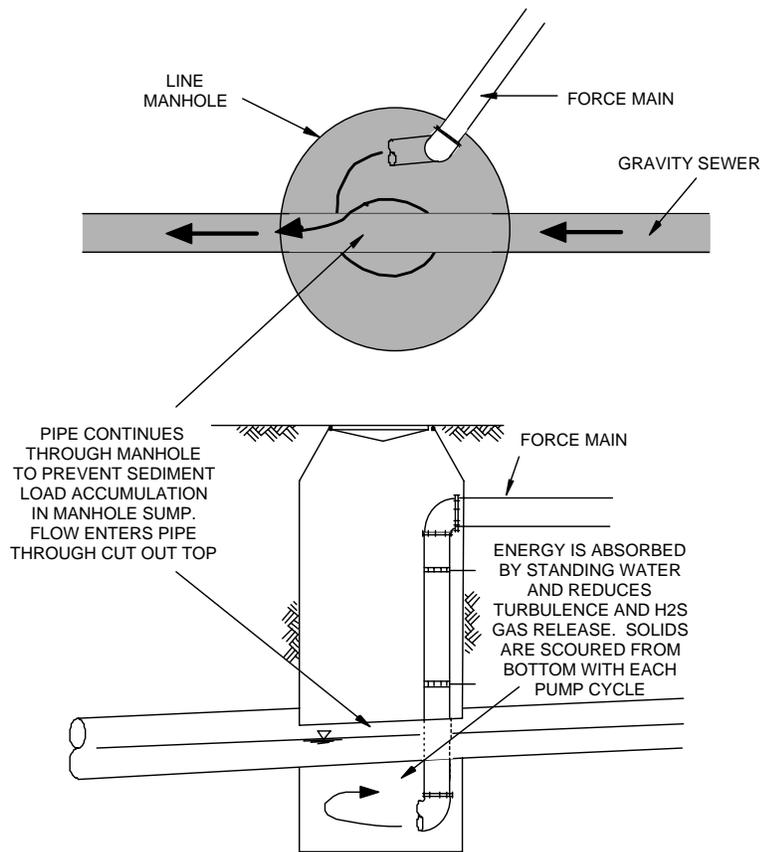
LINE
MANHOLE

FORCE MAIN

GRAVITY SEWER

PIPE CONTINUES
THROUGH MANHOLE
TO PREVENT SEDIMENT
LOAD ACCUMULATION
IN MANHOLE SUMP.
FLOW ENTERS PIPE
THROUGH CUT OUT TOP

FORCE MAIN

ENERGY IS ABSORBED
BY STANDING WATER
AND REDUCES
TURBULENCE AND H2S
GAS RELEASE. SOLIDS
ARE SCOURED FROM
BOTTOM WITH EACH
PUMP CYCLE

Figure 2-21. Line Manhole Turbulence Reduction Using Modified Manhole with Receiving Sewer Elevated (Plan and Section Views)
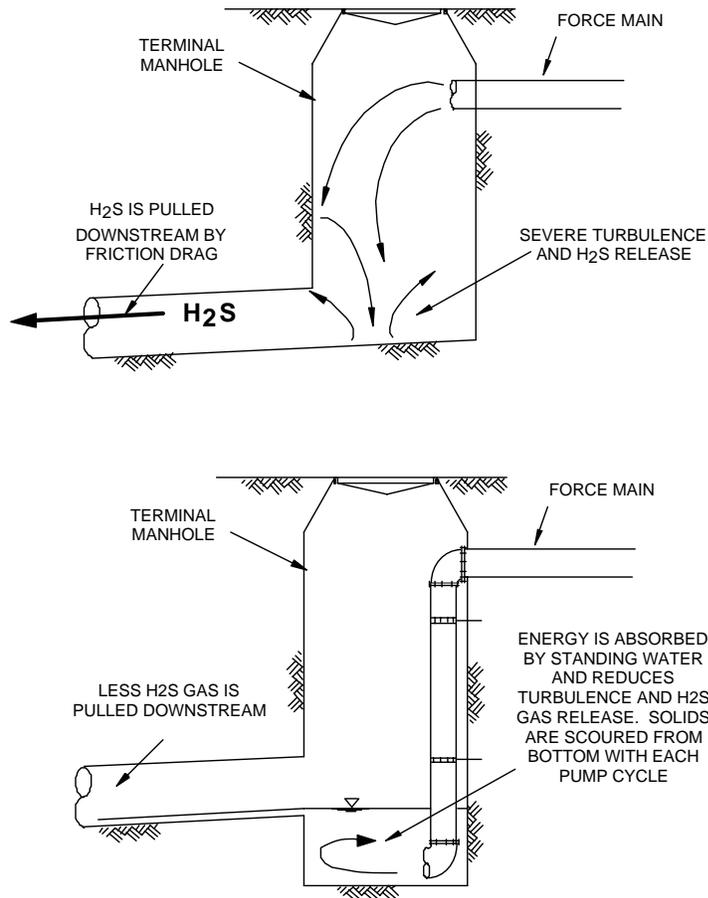
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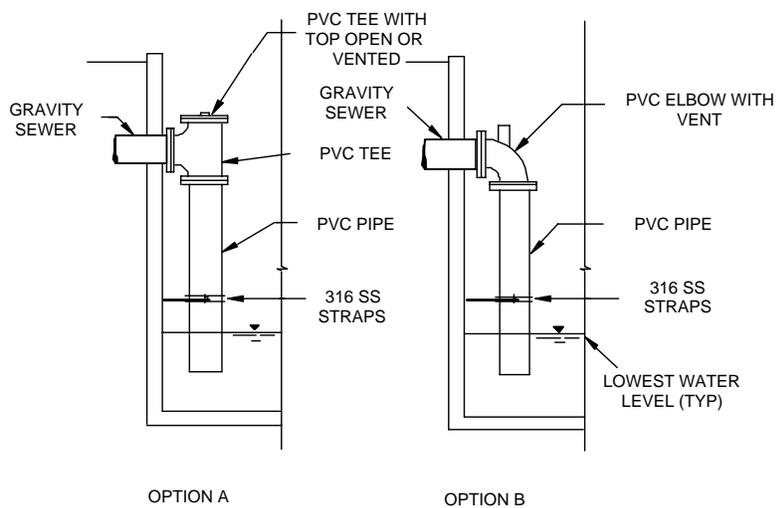Figure 2-22. Terminal Manhole Force Main Connection Turbulence Control

Figure 2-23. Conceptual Wet Well Turbulence Reduction by Modification of Influent Gravity Sewers
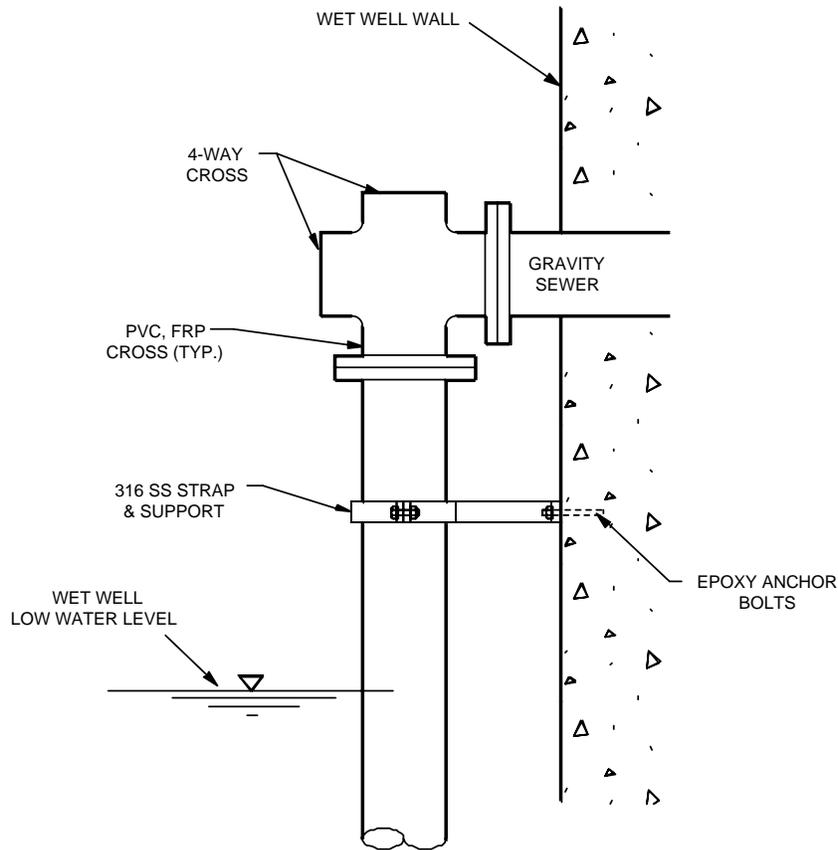
Figure 2-24. Wet Well Influent Sewer Turbulence Control Using Drop Pipe with Vent and Maintenance Access (Cross)

2.9   Summary

This chapter has explained what causes odors and corrosion in sewers, some of the important characteristics of the specific chemicals involved, and some of the methods available for interrupting the sulfide cycle. We have explained the general trends in wastewater sulfide generation and why the subject of collection system odor and corrosion control are important. We have also explained the basics of using the sulfide cycle to evaluate control mechanisms. As we have seen, some of the most common methods for sulfide odor and corrosion control would be rejected from use when evaluated with the sulfide cycle. The information contained in the remainder of this manual expands upon these control methods to provide the information necessary to evaluate any collection system and select viable sulfide control mechanisms.

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