

Chapter 4

Hydrogen Sulfide and Sulfuric Acid Estimation Techniques

SULFIDE GENERATION IN SEWERS

Sulfide generation is a bacterially mediated process occurring in the submerged portion of sanitary sewers and force mains. Fresh domestic sewage entering a wastewater collection system is usually free of sulfide. However, a dissolved form of sulfide soon appears as a result of the following conditions:

- Low dissolved oxygen content
- Long detention time in the collection system
- Elevated wastewater temperature

The root cause of odor and corrosion in collection systems is sulfide, which is produced from sulfate by bacteria residing in a slime layer on the submerged portion of sewer pipes and structures. Once released from the wastewater as hydrogen sulfide gas, odor and corrosion problems begin. Another type of bacteria utilizes hydrogen sulfide gas to produce sulfuric acid that causes the destruction of wastewater piping and facilities. Operation and maintenance expenditures are required to correct the resulting damage caused by this sulfuric acid. In severe instances, pipe failure, disruption of service and uncontrolled releases of sewage can occur.

Fresh domestic sewage entering a wastewater collection system is usually free of sulfide. When certain conditions exist within the collection system, dissolved sulfide soon begins to appear. These sulfide producing conditions are low dissolved oxygen content, high-strength wastewater, long detention times, extensive pumping and high wastewater temperatures. The first step in this bacterially mediated process is the establishment of a slime layer below the water level in a sewer pipe or force main. This slime layer is composed of bacteria and inert solids held together by a biologically secreted protein "glue" called zooglea. When this biofilm becomes thick enough to prevent dissolved oxygen from penetrating it, an anoxic zone develops within it. Approximately two weeks is required to establish a fully productive slime layer in pipes. Within this slime layer, sulfate reducing bacteria use the sulfate ion ($\text{SO}_4^{=}$), a common component of wastewater, as an oxygen source for the assimilation of organic matter in the same way dissolved oxygen is used by aerobic bacteria. Sulfate concentrations are almost never limiting in normal domestic wastewaters. When sulfate is utilized by these bacteria, sulfide ($\text{S}^{=}$) is the by-product. 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, temperature, wastewater velocity, and the area of the normally wetted surface of the pipe.

As sulfate is consumed, the sulfide by-product is released back into the wastewater stream where it immediately establishes a dynamic chemical equilibrium between four forms of sulfide; the sulfide ion ($\text{S}^{=}$), the bisulfide or hydrosulfide ion (HS^{-}), aqueous hydrogen sulfide ($\text{H}_2\text{S}(\text{aq})$), and hydrogen sulfide gas ($\text{H}_2\text{S}(\text{g})$).

Sulfide Ion ($\text{S}^{=}$)

The sulfide ion carries a double negative charge indicating that it reacts primarily by giving up two electrons in 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. It is a colorless, odorless ion which can only exist in solution. It also does not contribute to odors.

Hydrogen Sulfide (Aqueous)

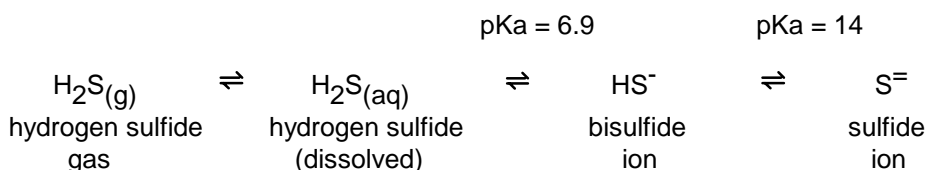
Hydrogen sulfide can exist as a gas dissolved in water. The polar nature of the hydrogen sulfide molecule makes it soluble in water. In the aqueous form, hydrogen sulfide does not cause odor; however, this is the only sulfide specie that can leave the aqueous phase to exist as a free gas. The rate at which hydrogen sulfide leaves the aqueous phase is governed by Henry's Law, the amount of turbulence of the wastewater and the pH of the solution.

Hydrogen Sulfide (Gaseous)

Once hydrogen sulfide leaves the dissolved phase and enters the gas phase 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 very low concentrations. In high concentrations, it is also very hazardous to humans. In concentrations as low as 10 ppm it can cause nausea, headache and conjunctivitis of the eyes. 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. For these reasons, the Occupational Safety and Health Administration (OSHA) has established an 8-hour, time-weighted, personal exposure limit of 10 ppm (U.S. EPA, 1985).

Due to the continuous production of sulfide in wastewater, 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 species are related according to the following equilibrium:



As indicated by the equilibrium equations, once hydrogen sulfide is released into the gas phase, bisulfide ion is immediately transformed into more aqueous hydrogen sulfide to replace that which is lost. Concurrently, sulfide ion is transformed into bisulfide to replace that lost to aqueous hydrogen sulfide. Through this type of continuously shifting equilibrium it would be possible to completely remove all sulfide from wastewater as hydrogen sulfide gas through stripping. This is generally not recommended or advantageous due to odor releases and the accelerated corrosion which can take place.

The quantitative relationship between the four sulfide species is controlled by the pH of the wastewater. The sulfide ion (S⁼) does not exist below a pH of about 12 and as indicated by the pKa, is in a 50/50 proportional relationship with the bisulfide ion (HS⁻) at a pH of 14. Since the normal pH of wastewater is far lower, the sulfide ion is rarely experienced. The pKa of much greater importance is the one controlling the proportional relationship between the bisulfide ion and H₂S(aq). Most domestic wastewater has a pH near 6.9. This means that at the pH of normal

wastewater, half of all sulfide present exists as the bisulfide ion and the other half exists as aqueous hydrogen sulfide (a dissolved gas). Since the concentration of dissolved gases in solution are primarily controlled by the specific Henry's Law coefficient for that gas, they can be released from solution to exist as the free gas form. Once subjected to turbulence or aeration, wastewater can release the dissolved gas as free hydrogen sulfide gas, and more bisulfide ion is transformed into the dissolved gas form to replace that lost to the atmosphere.

Settleable Solids

Periods of low flow in the collection system correlate to lower average wastewater velocities. Low flow velocities allow material, usually grit and large organics, to settle in the collection system piping. This increases the mass and surface area of material in the collection system upon which sulfate reducing bacteria (slime layer) can grow, and can lead to an increased conversion of sulfate to sulfide.

Collection systems with sedimentation problems can experience sulfide concentration spikes during the historically high flow, cool temperature months. This phenomenon occurs when significant sand or grit accumulations exist and the particles are covered by an anaerobic slime layer that contains sulfate-reducing bacteria. Only the bacteria on the surface of the grit pile receive a continuous supply of sulfate because they are exposed to the wastewater. The buried sulfate-reducing bacteria are not exposed to a continuous supply of sulfate. This forces them to exist in a semi-dormant, anaerobic state with very low cell activity (but they are not dead). When a high flow event occurs, with sufficient velocity and shear force to re-suspend the sediment, this enormous surface area of sulfate reducing bacteria is suddenly exposed to ample sulfate and they rapidly convert it to dissolved sulfide. This causes a relatively short duration, high sulfide event with resulting hydrogen sulfide gas release, odor and corrosion.

The grit particles and their attached sulfate-reducing bacteria that were semi-dormant are suspended and exposed to a tremendous quantity of sulfate and quickly begin producing sulfide. The interaction between a large quantity of bacteria and an almost unlimited food source will create dissolved sulfide spikes that are subsequently released in areas of high turbulence. This trend is common and well documented in many cities with similar grit deposition problems such as Boston, Los Angeles, St. Louis, and Houston.

Temperature

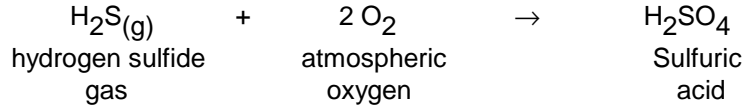
In addition to the factors described above, summer conditions result in an increase of wastewater temperatures. Greater wastewater temperatures increase the metabolic activity of the sulfate reducing organisms, causing faster conversion of sulfate to sulfide and increased dissolved sulfide concentrations. It has been estimated that each incremental 7 degree C (12.5 degree F) increase in wastewater temperature doubles the production of sulfide.

Sulfuric Acid Production

Thiobacillus aerobic bacteria, which commonly colonize pipe crowns, walls and other surfaces above the water-line in wastewater pipes and structures, has the ability to consume hydrogen sulfide gas and oxidize it to sulfuric acid. This process can only take place where there is an adequate supply of hydrogen sulfide gas (>2.0 ppm), high relative humidity and atmospheric oxygen. These conditions exist in the majority of wastewater collection systems for some portion of the year. A pH of 0.5 (which is approximately equivalent to a 7 percent sulfuric acid solution) has been measured on surfaces exposed to severe hydrogen sulfide environments (>50 ppm in air).

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

Thiobacillus Bacteria



Turbulence Reduction

Turbulence is a critical parameter to consider in preventing hydrogen sulfide gas release from wastewater. The effects of sulfide odor and corrosion are increased by orders of magnitude at points of turbulence. Henry's law governs the concentration of gas over a liquid containing the dissolved form of the gas. Henry's law states in effect:

The concentration of a gas over a liquid containing the dissolved form of the gas is controlled by the partial pressure of that gas and the mole fraction of the dissolved gas in solution.

Since this law governs the relationship between the dissolved form and gaseous form of sulfide over a given surface area, any action which serves to increase the surface area of the liquid also increases the driving force from the liquid to the gas phase.

The most common form of increased surface area is turbulence. In turbulent areas, small droplets are temporarily formed. When this happens, the forces governing Henry's law (partial pressure) quickly try to reach equilibrium between the liquid and atmospheric phases of the gas. The result is often a dramatic release of sulfide from the dissolved to the gaseous form. Structures causing turbulence should be identified and measures should be taken to protect and/or control the subsequent hydrogen sulfide gas releases. This same release mechanism is exhibited whenever wastewater containing dissolved sulfide is aerated.

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 been known to collapse due to loss of structural stability from corrosion. The process of concrete corrosion, however, is a step-wise process which can sometimes give misleading impressions. The following briefly describes the general process of concrete corrosion in the presence of a sewer atmosphere.

Freshly placed concrete has a pH of approximately 11 or 12, depending upon the mix design. This high pH is the result of the formation of calcium hydroxide [Ca(OH)₂] as a by-product 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. A surface pH of 11 or 12 will not allow the growth of any bacteria; however, the pH of the concrete is slowly lowered over time by the effect of carbon dioxide (CO₂) and hydrogen sulfide gas (H₂S). These gases are both known as "acid" gases because they form relatively weak acid solutions when dissolved in water. CO₂ produces carbonic acid and H₂S produces thiosulfuric and polythionic acid. These gases dissolve into the water on the moist surfaces above the sewage flow and react with the calcium hydroxide to reduce the pH of the surface. Eventually the surface pH is reduced to a level that can support the growth of bacteria (pH 9 to 9.5).

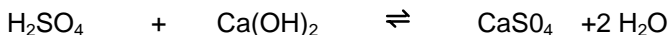
The time it takes to reduce the pH is a function of the concentration of carbon dioxide and hydrogen sulfide in the sewer atmosphere. It can sometimes take years to lower the pH of concrete from 12 to 9, however, in some severe situations it can be accomplished in a few months.

Once the pH of the concrete is reduced to around pH 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 only survive 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 only occur on surfaces exposed to atmospheric oxygen.

As a simplified example, one species of *Thiobacillus* only grows well 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 below 6.5, they die off and another species takes up residence which can withstand lower pH ranges. The succeeding species grows well on surfaces with a pH between 6.5 and 4. When the acid produced by these species drops the pH below 4, a new species takes over. The process of successive colonization continues until species, which can survive in extremely low pH conditions, take over. One such species is *Thiobacillus thiooxidans*, which is sometimes known by its common name, *Thiobacillus concretivorus*, which is Latin for "eats concrete". This organism has been known 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 un-reacted calcium hydroxide. Although the reaction products are complex and result in the formation of many different compounds, the process can be generally illustrated by the following reactions:



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 occur rapidly. The surface coating of gypsum paste can protect 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 only live on the thin outer covering of any surface. This means that acid produced on the surface must migrate through any existing gypsum paste to reach sound concrete. When the gypsum is washed off fresh surfaces are exposed to acid attack and this accelerates the corrosion.

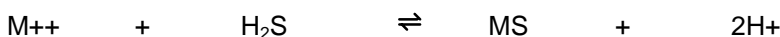
The color of corroded concrete surfaces can be various shades of yellow caused by the direct oxidation of hydrogen sulfide to elemental sulfur. This only occurs where a continuous high concentration supply of atmospheric oxygen or other oxidants are available. The upper portions of manholes and junction boxes exposed to high hydrogen sulfide concentrations are often yellow because of the higher oxygen content there. This same phenomena can be observed around the outlets of odor scrubbers using hypochlorite solutions to treat high concentrations of hydrogen sulfide gas.

Another damaging effect of sulfuric acid corrosion of concrete is the formation of a mineral called "ettringite". The chemical name for ettringite is calcium sulfoaluminate hydrate. It is produced by a reaction between calcium sulfate and alumina, which is found in virtually all cements. It forms at the boundary line between the soft calcium sulfate layer and the sound, uncorroded concrete

surface. Ettringite is damaging because it is an expansive compound which occupies more space than its constituents. When ettringite forms, it lifts the corroded concrete away from the sound concrete and causes a faster corrosion by continually exposing new surfaces to acid attack. Although the rate of concrete loss is dependent upon a number of factors including ettringite formation, it is not uncommon to see concrete loss of 1 inch per year in heavy sulfide environments.

Metal Corrosion

Concrete is not the only material that can be affected by the corrosive action of hydrogen sulfide gas. Most metals, including stainless steel, can also be attacked and destroyed by exposure to the strong mineral acid, sulfuric acid. Metals can be corroded by two means, acid decomposition by exposure to sulfuric acid produced by *Thiobacillus* bacteria, and direct molecular attack. Most free metals are bi-valent 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.



The metal has a much stronger affinity for the sulfide than hydrogen causing the release of two free hydrogen ions. In this manner, the metal is converted from a strong metal-metal bonding arrangement into a much weaker metal sulfide product. At the same time metals are exposed to the acidic effect of the free hydrogen ions. This condition results in missing rungs of former manhole steps, the corroded and weakened manhole covers and rings, and brass and copper fittings turned dark bluish-black, the color of nickel and copper sulfide.

Trends in Sulfide Production

Hydrogen sulfide has always existed in wastewater. Recent trends of water conservation, industrial pretreatment, and design deficiencies can significantly increase sulfide generation. This increase in sulfide generation leads to additional odor and corrosion problems.

Water Conservation Practices

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 dissolved sulfide concentrations in wastewater systems.

Reduced wastewater flows from water conservation practices can cause reduced velocities and longer residence time in the collection and transmission systems. These conditions allow more time for the reduction of sulfate, creating higher dissolved sulfide concentrations and they also increase the general septicity of the wastewater. Since less water is entering the wastewater collection system while the organic load remains the same, the strength of the wastewater in terms of BOD_5 also increases. This increases the biological activity of the slime layer and causes the faster consumption of dissolved oxygen and the creation of anaerobic conditions. Anaerobic conditions also cause the production of organic acids, which 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, the anaerobic drop in pH can also increase the release of odor-causing hydrogen sulfide gas.

Although water conservation has increased the dissolved sulfide concentration of wastewater, little evidence suggests a general increase in total sulfide mass. However, the Henry's Law coefficient governing the release of hydrogen sulfide gas from wastewater is dependent only upon sulfide concentration in the liquid phase, not mass. Therefore, any increase in the dissolved sulfide concentration of wastewater will increase the release of hydrogen sulfide gas.

Industrial Pretreatment

Perhaps the greatest contributor to increased dissolved sulfide concentrations in municipal wastewater is industrial pretreatment (Public Law 92-500). The Clean Water Act, mandated that the nation's water supplies be protected through a variety of mechanisms. One such mechanism is to require cleaner wastewater discharges from our Publicly Owned Treatment Works (POTW). One concern with treated wastewater discharges was the bio-accumulation of heavy metals in the environment. High concentrations of certain metals, such as lead, copper, mercury, chromium, and zinc were shown to have toxic effects on animals and plants. Some of these metals can pass through a wastewater treatment plants and enter the receiving stream or water body where they could be bio-accumulated to dangerous concentrations. As a result, the U.S. Environmental Protection Agency (EPA) required municipalities to implement industrial pretreatment programs, under which heavy metals and other contaminants from industrial sources were identified and treated. Removing heavy metals removed a potential sulfide removal mechanism. Dissolved forms of sulfide (bisulfide ion and sulfide ion) have a strong affinity for metals. One of the most common methods used to remove sulfide from wastewater is to add metal salts, usually ferrous iron compounds. Metal salts combine with sulfide and precipitate an insoluble metal sulfide. Before 1980, a common source of heavy metals in wastewater was industrial discharges from steel mills, electro-plating operations, photo-finishing, and electronics manufacturing. As of 1995, all such operations pre-treat their wastewater to remove metals prior to discharge to a POTW.

The targeted heavy metals also exhibit a toxic effect on bacteria in the slime layer that produce sulfide. Toxicity or inhibition of the sulfate-reducing bacteria in the slime layer by the targeted heavy metals naturally reduced their health and activity, which reduced sulfide production. Removing the source of the toxicity allowed the slime layer bacteria to flourish and produce even more sulfide. In 1989, the United States Congress ordered a study to assess the impact of the industrial pretreatment program on sulfide generation. The study indicated that both of the above mechanisms were responsible for a general increase in sulfide in domestic wastewater.

Over a period of several years, influent wastewater at the Hyperion Wastewater Treatment Plant in Los Angeles, California, was analyzed for several constituents including sulfide and total metals concentrations. As the data in Table 4-1 dramatically indicate, influent sulfide to the plant increased at the same time that total metals concentrations decreased. This trend has continued since 1980 and is considered a direct effect of industrial pre-treatment. Therefore, industrial pretreatment has resulted in an increase in sulfide in wastewater.

Design Deficiencies

Wastewater and collection system facility designers often under state the increasing trend in sulfide odor and corrosion related problems and neglect to incorporate controls into their designs. Often the relatively complex relationships between wastewater characteristics, slime layer formation, sulfide production bio-kinetics, sulfide chemistry, corrosion biology, gas release, and ventilation dynamics are not fully understood are not fully understood.

Table 4-1. Dissolved Sulfide and Total Metals Concentration Trends at Hyperion WWTP, Los Angeles, CA (Joyce, 1998)

Year	Total Metals Concentration (mg/l)	Dissolved Sulfide Concentration (mg/l)
1981	19.0	1.0
1982	17.0	2.0
1983	16.0	3.0
1984	14.0	4.0
1985	13.0	4.5
1986	12.5	5.0
1987	11.0	7.0
1988	10.0	8.0
1989	8.0	10.0
1990	7.0	12.0
1991	6.0	12.5
1992	5.0	13.0
1993	3.5	13.5
1994	3.0	15.0

The following examples should be noted as potential odor and corrosion catastrophes and should be avoided:

- force mains routed on a downhill gradient can experience premature crown failure
- drop manholes with 4.5 to 6 meter (15 to 20 foot) hydraulic freefalls causing extreme turbulence and hydrogen sulfide release
- unlined, unprotected pipe conveying wastewater for distances up to 48 kilometers (30 miles)
- manifolded force main systems for distances up to 24 kilometers (15 miles), detention times of two or three days, and 360-degree slime layers producing dissolved sulfide with no chance of reaeration

Flushing Relationship to Hydrogen Sulfide Generation

Description of the Process

Wastewater, stormwater or riverwater can be collected and stored in chambers or upstream sewers for release as a flush wave. As the flush wave travels down the sewer, the shear forces applied to the upper layer of the sediments exceeds the bonding strength of the solids, and eroded particles are moved downstream with the flow. In the process of traveling down the sewer, the upper layer of solids are removed and moved downstream with the flush water.

Odor Producing Conditions

The following scenarios illustrate how flushing may produce odor conditions.

- Remaining water in the pipe can contain high concentrations of dissolved sulfide. The turbulence associated with the flush wave may release peak concentrations of hydrogen sulfide gas at the downstream flushing terminus.

- Decomposing and hydrolyzing organic solids in the sewer materials can produce locally high soluble BOD concentrations in the matrix of the solids. Due to the presence of sulfate and sulfate reducing organisms in the matrix of the solids, it can be expected that high dissolved sulfide concentrations can exist in the upper layer of solids (approximately 2 to 6 centimeters). When this layer of solids is removed by a flush event, the dissolved sulfide present inside the matrix of the solids will be released into the flush water. Turbulence associated with the flush water will then cause release of the dissolved sulfide as hydrogen sulfide gas. This may cause odor and corrosion producing conditions.
- When flushing deep deposits, once a fresh layer of solids is scoured away the new surface of the solids will presumably be the solids previously buried deeper within the solids mass. The biological population in this freshly exposed layer of solids will likely be strict anaerobes. This class of bacteria also contains species that can reduce sulfate. Prior to being exposed to the flush event, these solids received very little flux of sulfate, since most sulfate was reduced to sulfide by the previous layer. Since the now exposed solids have been buried for some time, the anaerobic decomposition of organic matter can produce a rich mixture of organic acids and other short-chain carbon compounds. These organic acids and other anaerobic products make the soluble BOD of the mixture very high. Now that the freshly exposed layer is subjected to ample sulfate in the flush water flow, the metabolism of the sulfate reducing organisms is greatly accelerated and significant quantities of dissolved sulfide will again be formed. This newly formed sulfide is therefore available for release as hydrogen sulfide during the next flushing event.
- As the flush wave moves down the sewer at significant velocities, friction between the air and water creates a very large bowls of air traveling down the pipe with very high concentrations of hydrogen sulfide present. When this air arrives at the downstream flushing terminus, a peak spike of hydrogen sulfide odor may need controlling.

Invert Erosion

It is important to consider the effect of flushing on the condition of the partially corroded pipe. Will the high velocity water cause erosion of the partially corroded and pasty pipe walls? This may be a concern when flushing older pipe systems or new systems recently impacted by corrosion. The basis of this concern is a series of observations noted in 1997 in Phoenix, Arizona. The following is an excerpt from a recent investigation in Phoenix, Arizona noting the erosion of stones and aggregates on a downstream new interceptor system from upstream piping areas (OCTC, 1997).

Example of Invert Erosion: Phoenix, Arizona

During an investigation of the twin 1.8 meter (72 inch) diameter sewers entering the 91st Avenue Wastewater Treatment Plant (WWTP) on June 18, 1997, the flow in the pipe was approximately 0.9 meters (3 feet) deep at the invert and moving at an estimated 1.5 m/s (5 fps). This was a reduced flow condition from previous inspections in this sewer, and it allowed the inspector to physically make contact with the invert of the sewer. As the inspector stood on the bottom of the pipe, a groove, approximately 8 to 10 centimeters (3 to 4 inches) wide and 10 centimeters (3 inches) deep, was detected in the sewer invert. As the inspector probed the length and depth of the groove with his boot to determine the dimensions, a rock approximately 4 centimeters (1.5 inches) in diameter struck the toe of his boot with considerable force. The rock was retrieved, examined, and found to be a semi-round, river-gravel type silica rock with one fracture plane. The rock was relatively clean and did not have a slime layer attached. The rock resembled what could be used as concrete aggregate in upstream piping. The precise source of the rock could not be determined. During the 15 minutes that the inspector was in the pipe more than two dozen rocks were noted to travel down the pipe inside the groove in single-file fashion.

The groove was probed further and found to extend as far as the inspector could reach both in an upstream and downstream direction from the manhole. It is believed that the groove extends the entire length of the sewer in this reach. It was concluded that the groove is caused by the impacts caused by stones, rocks, and other hard debris traveling down the pipe with the flow. Because of the high wastewater velocity and hydraulic shear forces developed in the fast-flowing Salt River Outfall (SRO), it is suspected that all hard debris and rocks which enter the SRO (and pipes of similar hydraulic characteristics) produce invert erosion until they reach the 91st Avenue WWTP.

It could not be determined with certainty that the reinforcing steel has been severed by the groove; however, estimating from the depth of the groove and the normal reinforcing mesh coverage in reinforced concrete pipe (RCP), the steel reinforcing in the bottom of the pipe has most likely been compromised.

The source of the debris that is causing the invert corrosion cannot be definitely determined, although the type and size of the rocks are very similar to what would normally be used as concrete pipe aggregate. The pure silica, acid-proof, river-gravel stone aggregate historically used as concrete aggregate in the Phoenix area comes from the Salt River basin. The stones are crushed and screened to produce the proper gradation for concrete mix designs. The crushing operation produces very hard, sharp, angular pieces ideal for concrete aggregate. It is this type of aggregate that has been noticed during these inspections to be protruding from the surface of corroded pipes. The aggregate protrudes from the concrete matrix because silicate stones are inert to strong reducing acids such as the sulfuric acid produced by Thiobacillus bacteria from hydrogen sulfide gas. The concrete matrix (predominantly calcium silicate, calcium carbonate, and calcium hydroxide), however, is easily dissolved by sulfuric acid leaving the inert silicate stones protruding from the corroded concrete surface.

The older, shallow surface sewers of all SRO member communities are most likely the source of the rocks. The rocks move slowly or intermittently in these shallow sewers due to the lack of sustained flushing velocities. When moving slowly or intermittently the rocks do not tumble with great force and their impact locations are scattered across a large area of the bottom of the pipe. When these rocks enter the fast-flowing SRO or other large diameter sewers with sustained high velocities, the rocks are overwhelmed by the hydraulic forces and align themselves in single-file fashion as they move quickly down the pipe. This causes the impacts from all these stones to be concentrated in a very narrow band directly in the invert of the pipe. The combination of the mass (weight) of the stones, their velocity, tumbling action caused by asymmetrical shapes and the concentration of all impact sites directly at the invert of the pipe is causing the groove. If not addressed or corrected the erosion of the invert will continue to the point of pipe breach. Once this happens, the pipe bedding and surrounding soils will likely be liquefied and either moved or transported downstream. This will leave portions of the bottom of the pipe unsupported and promote pipe settlement, fracture, and eventual destruction of the pipe requiring replacement.

From a brief study of the physics of this erosion phenomenon, it can be determined that the greatest damage is caused by those stones and rocks having sufficient mass to impart a significant impact under the acceleration of gravity. As the stones tumble within the pipe they are continuously striking the bottom of the pipe, rebounding, being launched briefly a few inches above the invert, and then strike the invert again a short distance downstream. It can be determined that the larger stones and rocks cause the greatest damage; however, it can certainly be argued that the smaller stones also contribute to the phenomenon (less than #4 sieve) but to a much less degree.

Dissolved Sulfide Prediction Procedure

The dissolved sulfide estimation procedure used in the desktop analyses was developed by Montgomery Watson to estimate the amount of dissolved sulfide which can be produced by wastewater under a variety of gravity and force main situations and the corrosion which results from the release of dissolved sulfide to hydrogen sulfide gas. This procedure is used in conjunction with the solids deposition and erosion procedure noted earlier in this chapter. This procedure uses the classical Pomeroy/Parkhurst dissolved sulfide generation equations, with the exception that additional logic have been added to account for variables not anticipated in the original equations. The procedure consists of two parts: one for dissolved sulfide generation based on the Pomeroy equations, and a second part to estimate corrosion rates in wastewater collection systems. This second part estimates the corrosion rate of concrete, steel, brick, mortar and other materials subjected to hydrogen sulfide environments. This procedure is for use in gravity sewers, wet wells, junction boxes, siphons and force main discharge manholes downstream of sulfide producing sewers and force mains.

Sulfide Model Development

The dissolved sulfide generation rate is most affected by BOD and temperature. An increase in temperature increases the metabolic rate of the bacteria and the rate of sulfide production. The term "effective BOD" has been used as a convenient way to combine the temperature and BOD effects. The equation for this relationship is as follows:

$$(EBOD) = (BOD) \times (1.07)^{(T-20)}$$

Where:

EBOD = effective BOD, mg/l

BOD = standard BOD₅, mg/l

T = temperature, deg C

1.07 = empirical factor

The Pomeroy and Parkhurst equation noted below is used to predict dissolved sulfide buildup. This equation accounts for the various factors affecting sulfide buildup in typical municipal wastewater applications (Pomeroy, 1985). A common form of the equation is presented below (where D/4 represents the hydraulic radius):

$$S_2 = S_1 + (M) (t) [EBOD (D/4 + 1.57)]$$

Where:

S₂ = predicted sulfide concentration at time t₂, mg/l

S₁ = sulfide concentration at time t₁, mg/l

t = t₂ - t₁ = flow time in a given sewer reach with constant slope, diameter, and flow; hr

M = specific sulfide flux coefficient; m/hr

D = pipe diameter; ft

An M factor of 1×10^{-3} m/hr is generally reasonable for force mains in which conditions are favorable for sulfide buildup (ie: infrequent flow, low velocities, high temperatures, long retention times, very low dissolved oxygen, and moderate to high BOD). The default value for M in the sulfide generation procedure is 3×10^{-4} m/hr and has been found to be a good approximate value when all force mains and gravity sewers are considered. This value can be adjusted up or down to account for the specifics of each system to be modeled.

Dissolved Oxygen Effects

The Pomeroy/Parkhurst equations for prediction of sulfide buildup assume that little or no dissolved oxygen is present. One of the requirements for use of the equations is that less than 0.5 mg/l dissolved oxygen be present for the equations to be accurate. This is due to the sulfide oxidation effects of the aerobic zone on top of the slime layer. Typically, wastewater contains more than 0.5 mg/l dissolved oxygen. If the effect of this oxygen is ignored, the model will over-estimate sulfide production. Facultative bacteria are a type of common sewer bacteria that utilize dissolved oxygen, when available, but can also respire in its absence. These bacteria will utilize the available dissolved oxygen (D.O.) until it is depleted. Then, in the absence of dissolved oxygen, the bacteria will begin utilizing first nitrate and then sulfate as their oxygen source. Unprocessed municipal wastewater typically has a limited nitrate concentration. Once oxygen and any nitrate is depleted, the bacteria will begin to utilize sulfate as an oxygen source and produce sulfide. The time required for depletion of the DO should be accounted for in the determination of sulfide buildup so that the most accurate results are obtained.

To account for dissolved oxygen concentrations higher than 0.5 mg/l, the Pomeroy/Parkhurst equations have been modified to include logic which estimates the time for oxygen depletion. The time required for depletion of the dissolved oxygen is calculated with the following equation:

$$t_{DO} = \frac{DO}{SOUR (1/10^3) (VSS)}$$

Where:

t_{DO} = time required for bacterial dissolved oxygen depletion, hr

DO = initial dissolved oxygen concentration, mg/l

SOUR = specific oxygen uptake rate, mg O₂/g VSS-hr

VSS = volatile suspended solids concentration, mg/l (represents bacterial concentration)

Subtracting the time required for oxygen depletion from the detention time yields the time remaining for sulfide production. This assumes that sulfide accumulation does not occur during periods when dissolved oxygen concentrations are greater than 0.5 mg/l. Substituting the time remaining for bacterial sulfide production into the equation for prediction of sulfide buildup results in an equation which accounts for the presence of DO. The equation is expressed as follows for a force main or full flowing pipe:

$$S_2 = S_1 + (M) t_s [EBOD (D/4 + 1.57)]$$

Where:

S_2 = predicted sulfide concentration at time t_2 ; mg/l

S_1 = sulfide concentration at time t_1 ; mg/l

M = specific sulfide flux coefficient; m/hr

$t_s = t - t_{DO}$ = time remaining for sulfide accumulation; hr

D = pipe diameter; ft

If enough dissolved oxygen is present, many bacteria will not utilize sulfate as an oxygen source and therefore not produce sulfide, and other bacteria in the aerobic zone on the slime layer will oxidize sulfide produced in the anoxic zone and suppress sulfide release back into the wastewater.