

CHAPTER 7.0

LIQUID PHASE ODOR AND CORROSION CONTROL

This chapter summarizes the literature research findings for controlling hydrogen sulfide release by adding chemicals to the wastewater. Impacts to non-H₂S odors are also considered and summarized where information was found in the literature.

7.1 Literature Search Background Summary

We located one hundred papers providing pertinent information on liquid phase treatment in collection systems. Some covered multiple topics, comparing various liquid phase control approaches. The number of papers by topic are as follows:

- Aeration using either air or oxygen injection (9)
- Chlorine oxidation (8)
- Potassium permanganate oxidation (1)
- Hydrogen peroxide oxidation (18)
- Iron salts for precipitation (29)
- Nitrate inhibition (34)
- pH adjustment (16)
- Microbial inhibitors, enzymes, and bacterial treatments (17)

Figure 7-1 shows a distribution in terms of the percentage of literature identified.

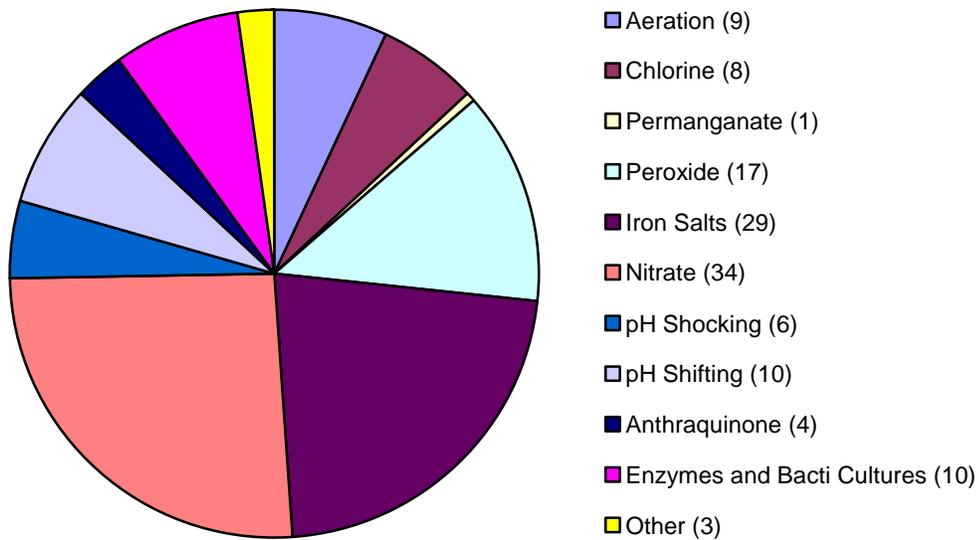


Figure 7-1. Distribution of Papers by Liquid Phase Treatment Topic

Virtually all liquid phase treatment topics were covered, but the bulk of the literature focused on either adding nitrates to inhibit sulfide formation, using iron salts to react with already formed sulfide, or adjusting pH for shocking slime layers and shifting dissolved sulfide species to ionic forms that are not released to the headspace.

Figure 7-2 shows the distribution of papers among published, peer-reviewed journal articles, conference proceedings, and gray literatures studies.

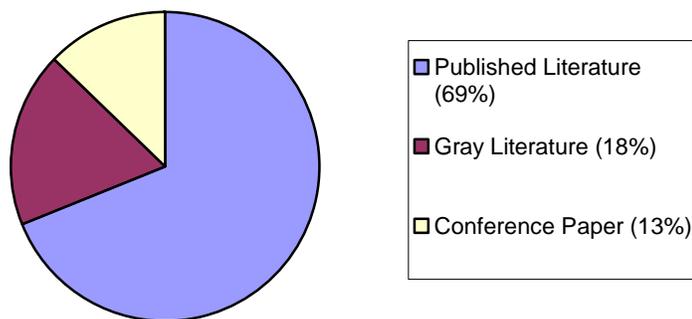


Figure 7-2. Literature Distribution by Source

The bulk of the identified literature (69 percent) came from published journal articles, with the remainder split nearly evenly between conference papers and gray literature. Papers and literature covered experiences as far back as 20 years.

Additional valuable information is available from well-established reference books and texts, such as the following:

- WEF (2004) Manual of Practice 25, *Control of Odors and Emissions from Wastewater Treatment Plants*
- WEF (1995) Manual of Practice 22, *Odor Control in Wastewater Treatment Plants*
- EPA (1985) Design Manual 625, *Odor and Corrosion Control in Sanitary Sewerage Systems and Treatment Plants*
- *Hydrogen Sulphide Control Manual* (Melbourne Water, 1989)

7.2 Introduction and Background

Although various organic and inorganic compounds can cause domestic wastewater odors, hydrogen sulfide was most often identified as the predominant odor- and corrosion-causing compound of concern, and as such, many liquid phase treatment articles focused on removing it.

Most articles focused on the collection system, but some discussed downstream impacts to the receiving wastewater treatment plant or the use of chemicals at the plant's entrance.

Hydrogen sulfide is often released into the gas phase when dissolved sulfide is present. Sulfide is generated within the slime layer attached to sewer pipe walls because of anaerobic biofilm activity. The bacteria responsible primarily for sulfide formation, "sulfate-reducing bacteria," use sulfate (SO_4^{2-}) as their terminal electron acceptor, reducing it to sulfide (H_2S , HS^- , and S^{2-}). The sulfide then diffuses through the biofilm to the bulk liquid phase. Once in the liquid stream, H_2S can volatilize into the gas phase, where it can become an odor and potential corrosion problem. Figure 7-3 is a schematic drawing of this process.

Liquid phase control is a method of odor and corrosion prevention by which chemicals are introduced into the wastewater to react with dissolved sulfides or prevent them from being formed, thereby preventing the release of H_2S into the vapor phase. Various chemicals are potentially suitable for liquid phase odor control. Table 7-1 summarizes generally established methods.

Wastewater characteristics and sewer configuration determine which methods are practical for a given situation. Important parameters include wastewater flow rate, temperature, pH, oxidation reduction potential (ORP), biochemical oxygen demand (BOD), process or sewer detention time, location of odor-releasing points (manholes, pump stations), and constraints imposed by downstream treatment processes. The type of odor-causing compound might also prove to be important.

Cost and practicalities will determine which method is selected. Factors influencing the cost of liquid phase treatment include chemical dose and regional chemical prices. Practicalities include chemical availability and difficulty of transporting, storing, and applying it. The following sections summarize each liquid phase odor control method and highlight the findings from the literature search completed for this study.

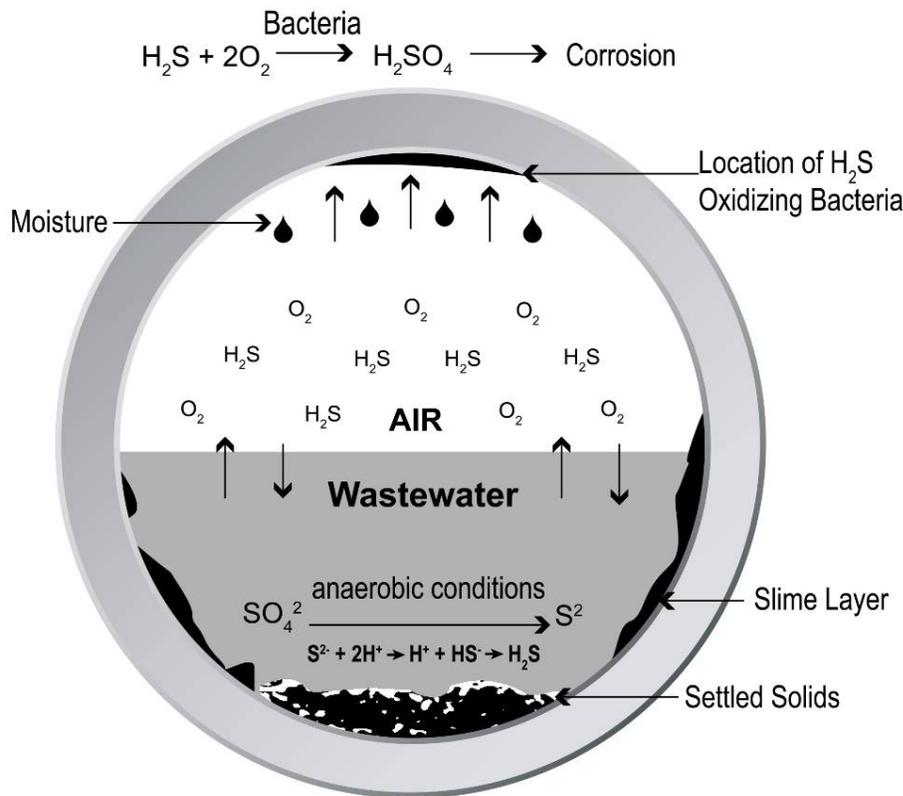


Figure 7-3. Sulfide Transformations in a Gravity Sewer

Table 7-1. Liquid Phase Odor Control Methods

Method	Description
Oxygenation and aeration	Ambient air or pure oxygen is injected into the waste stream to oxidize sulfides or to maintain an aerobic biofilm.
Chemical oxidation	Chemical oxidizing agents are added to the waste stream to oxidize dissolved sulfide to sulfate, which remains in solution.
Sulfur precipitation	Metal salts are added to the wastewater stream to form a metal sulfide precipitate with the dissolved sulfide, thus removing it from the waste stream.
Nitrate addition	Nitrate salts are added to the wastewater stream, displacing sulfate as the preferred electron acceptor for anaerobic bacteria and preventing sulfide formation.
pH adjustment	The pH of the waste stream is changed to inhibit growth of H ₂ S-producing bacteria or to drive volatile H ₂ S to soluble ionic HS ⁻ .
Biological treatment	Process changes or microbial cultures are used to affect the ability of bacteria to produce H ₂ S.

7.3 Oxygenation and Aeration

7.3.1 Technology Background

Oxygenation and aeration prevent odors by maintaining a layer of aerobic bacteria on the sewer pipe walls and in the wastewater itself. If a sufficient amount of dissolved oxygen is present in the bulk liquid phase, then the outermost layer of the biofilm can support aerobic

bacteria capable of biologically oxidizing sulfide as it diffuses outward through the biofilm. Because of biological oxidation, sulfide would not tend to diffuse into the bulk liquid stream.

However, when dissolved oxygen concentrations within the bulk phase are close to zero, sulfide generated in the biofilm is able to accumulate in the bulk liquid. In addition to preventing sulfide from leaving the anaerobic layer, dissolved oxygen in sufficient amounts can oxidize the sulfide in the bulk wastewater stream. At dissolved oxygen concentrations greater than 1.0 mg/L, oxidation can reportedly keep pace with sulfide production and prevent sulfide buildup (EPA, 1985).

Methods of adding air or oxygen include the following:

- Direct air injection into force mains
- Use of Venturi aspirators in side streams to lift stations or force mains
- Use of air lift pumps
- U-tube aeration
- Pressure tank injection into gravity lines
- Use of downflow bubble contactors (Speece Cones) in side streams to force mains or gravity sewers

7.3.2 Air Injection

Figure 7-4 is a schematic concept for injection of air or oxygen into a force main. Reports of required air injection rates vary greatly depending on wastewater characteristics, temperature, and pressure in the lines. Very simplistic “rules of thumb” for force mains suggest ranges of 1 to 2 cfm per inch diameter of pipe (EPA, 1985), but the true demand can be very site specific, require relatively complete characterization of the wastewater and the conveyance system, and potentially include the need to model the collection system.

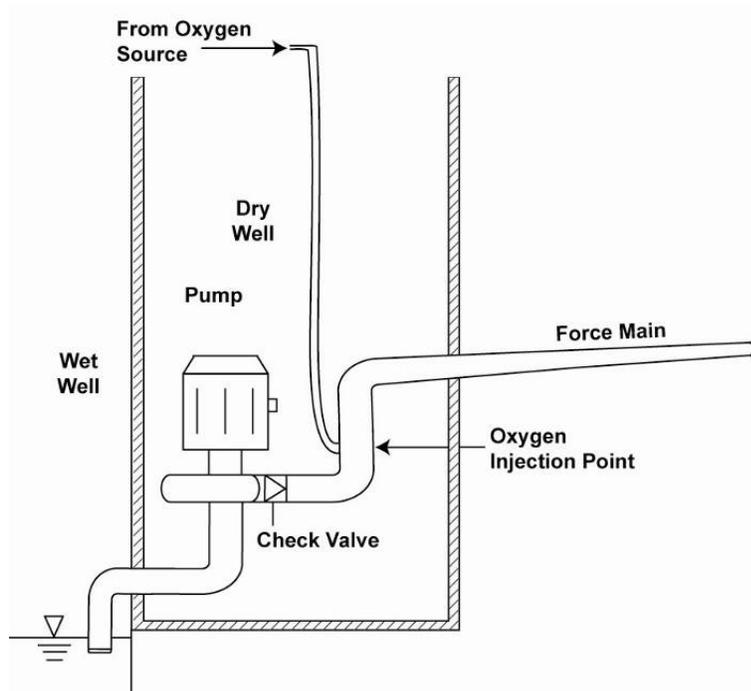


Figure 7-4. Force Main Air Injection

7.3.2.1 Air-Injection Dosing

Rule-of-thumb recommendations reported by WEF (2004) range from 0.1 to 6.3 cfm per inch of pipe diameter, or on a wastewater flow basis, 0.02 to 0.88 ft³ of air per gallon of wastewater, with typical reported values between 0.1 and 0.3 ft³ per gallon.

Soluducha (1989) reported several relatively successful attempts to use air injection in force mains in northern Virginia. In one instance, 25 cfm was injected into a 3-mgd force main with a 2.5-hour detention time, dropping dissolved sulfide from 2.2 down to 0.1 mg/L; this equates to only 0.01 ft³ per gallon. A second case required 78 cfm in a 4.5-mgd force main to get similar results; this equates to only 0.03 ft³ per gallon. Soluducha (1989) also reported intermittent maintenance problems with air release valves because of grease buildup plugging the release mechanism actuator of the valves. Maintaining the pressure release valves was reported to be maintenance intensive and problematic.

The air injection approach used a direct stub into a pipe without a diffuser. Air injection rates were calculated using the following equation:

$$V = (mgd \times 8.34 \times Co)(0.232 \times 1,440 \times 0.075) \quad (7.3.2.1-1)$$

where:

V = volume of injection air (scfm)

mgd = pumping discharge rate (millions of gallons per day)

8.34 = mass density of water (lbm/gal)

0.232 = mass fraction of oxygen in air

1,440 = unit conversion (min/day)

0.075 = mass density of air (lbm/ft²)

C_o was determined by using the force main residence time at typical flow and an estimated oxygen uptake rate of 10 mg/L per hour. This resulted in 25 scfm, which in this case is sufficient to drop the dissolved sulfides to 0.1 ppm. It should also be noted that this approach assumes 100 percent oxygen transfer, which may or may not have been achieved in this particular force main application. The force main pressure in this application was reported to have been approximately 85 psi, which may have resulted in a transfer efficiency of nearly 100 percent.

7.3.3 Venturi Aspirators

Venturi aspirators create a high-velocity flow through a nozzle of decreasing diameter, which creates a suction pressure that can be used to aspirate air into a flowing pipeline. The turbulence in the line mixes the air and water. Fong (1992) reported on full-scale field research in southern California using a Venturi aspirator to inject oxygen in the side stream of a gravity sewer line. Approximately 10 percent of the flow was side-streamed using a pumping system through a Venturi. Figure 7-5 is a schematic of this type of system.

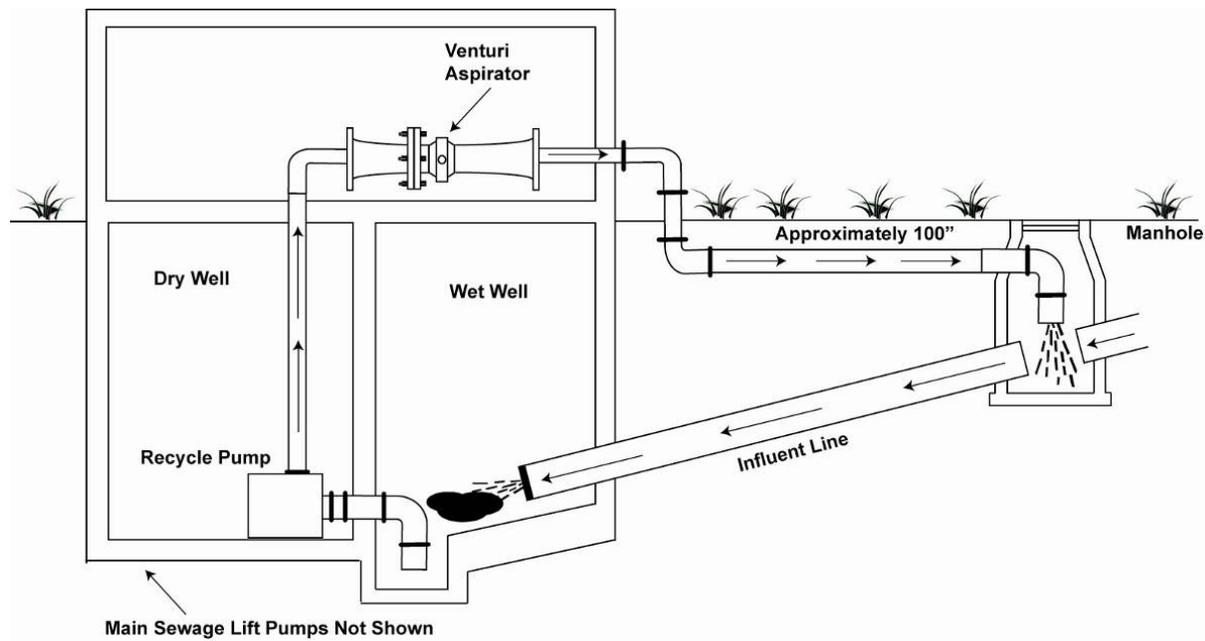


Figure 7-5. Venturi-Style Recycle System

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

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

With these settings and under these conditions, 80 percent oxygen transfer efficiency was achieved. This approach reduced the liquid phase sulfides by 90 percent and the gas phase H₂S by 70 percent.

O'Brien et al. (1994) reported the use of a similar system to side stream and recycle a portion of a septage storage tank flow in order to reduce odors from the septage before it was released into the collection system. Two 25-hp pumps were used to recycle 1,000 gpm back into a 100,000-gpd septage-receiving facility providing a 25- to 40-minute recycle time on the reaerated flow. This was done using a vendor-supplied system called a Hydro-Vac. This approach reportedly allowed the facility to stop using \$2,000 worth of liquid phase chemicals a day. A similar system is also produced under the supplier name HydroFlo.

7.3.4 Air Lift Pumps

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

7.3.5 U-tube Aeration

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

7.3.6 Pressure Tank Air Injection

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

7.3.7 Hydraulic Fall Injection

Oxygenation can be done using an intentional hydraulic fall when transitioning from a force main into a gravity line. This helps downstream in the gravity line but can release large amounts of H₂S gas at the point of turbulence. However, no recent published literature about using this approach was identified.

7.3.8 Downflow Bubble Contactors

In this case, air or oxygen is injected into the top of a downflowing cone that widens as the flow goes downward. The tendency for the bubbles to be carried downward with the flow is resisted by the bubbles' natural buoyancy, which tries to keep them moving upward. The long bubble contact time provided in the cone promotes high oxygen transfer. Figure 7-6 is a schematic diagram of this type of system.

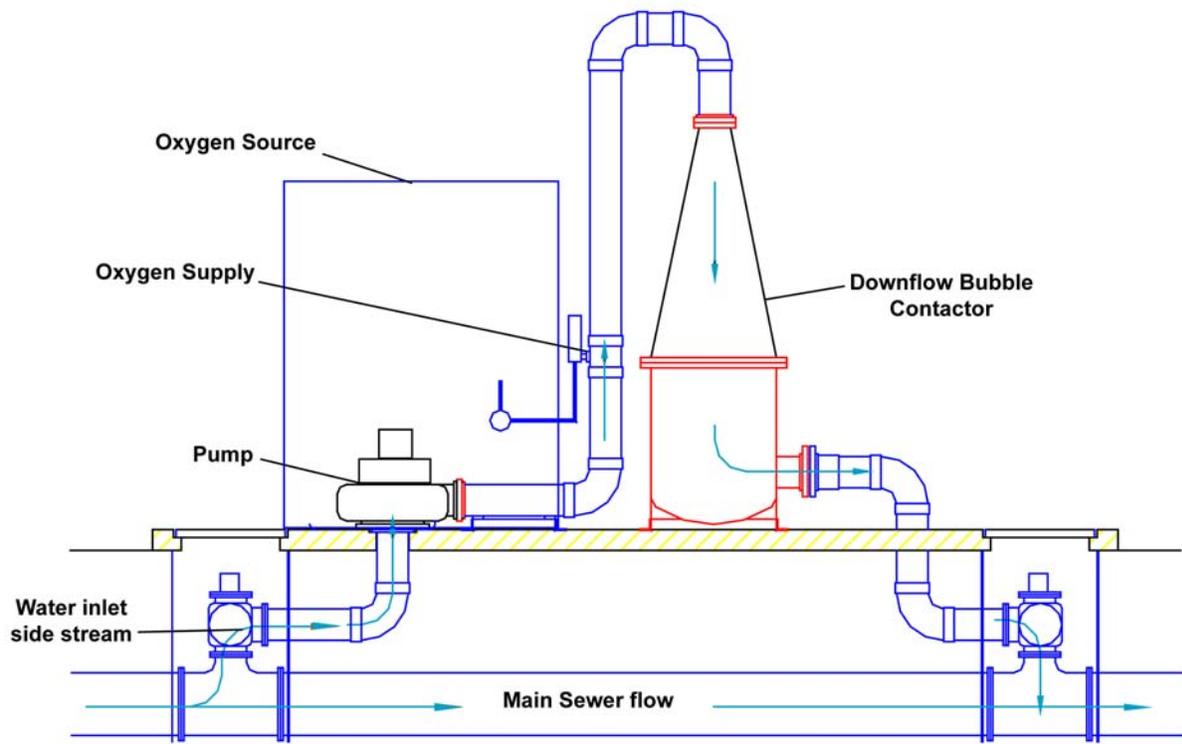


Figure 7-6. Downflow Bubble System Schematic

Early versions of this device are reported as having been provided by a supplier called Liquid Air and having had up to a 50 percent transfer efficiency (Melbourne Water, 1989). Speece et al. (2005), McGinnis et al. (1998), Moore (2003), and Little et al. (2001) report laboratory and field use of Speece Cones to raise collection system oxygen levels as well as dissolved oxygen levels in lakes by treating side streams of flow in a recycle mode. Theoretical oxygen transfer efficiencies as high as 93 percent were reported. Publications on this type of system in collection systems were limited. “Similar” mixing chamber-style versions of these side stream systems are also provided under the brand name Hydroflo. These systems differ in that the contact chamber relies on mixing baffles rather than downflow bubble contact.

7.3.9 Oxygen Injection

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

Prewitt (2000) reported the use of a pressure swing absorption system in Kentucky. In this instance, 90 percent pure oxygen was generated onsite and injected into a force main. Oxygen demand was based on the assumption of 4.8 lb of oxygen per pound of sulfide; this was reported as effective in controlling sulfide formation.

Advantages of oxygen injection are the following: (1) A preventative residual can be maintained, (2) oxygen may be injected far upstream of the odor problem, (3) ambient air can be used for some applications with pressure swing systems, (4) chemical costs are reduced, and (5)

no harmful byproducts are formed. The same mass of oxygen is provided with one-fifth the volume of gas compared to air.

Disadvantages are the following: (1) Effectiveness may be limited by oxygen solubility, (2) oxygen injection *may* cause gas binding in force mains, (3) it may increase air release valve maintenance costs, and (4) it may not be cost-effective for treating gravity sewers, because injected gas could volatilize out of solution and be wasted. This would depend on how efficiently oxygen is dissolved and distributed.

7.3.9.1 Oxygen Dose

The stoichiometric demand for oxygen depends on which chemical reaction path is assumed. Researchers report a wide variety of chemical reactions promoted by either biological activity or by a non-biologically driven chemical reaction. Which reaction dominates is dependent on pH and the initial ratios of sulfide to oxygen (Melbourne Water, 1989). The most typical and conservative reaction depicted below reacts stoichiometrically at a ratio of 1.9 lb of oxygen per pound of hydrogen sulfide:



Oxygen demand can, however, be driven by more than just the need to react with sulfide, resulting in a higher “effective stoichiometric” demand. The total oxygen requirement demand includes the concentration of dissolved sulfide; the nonsulfide BOD of the wastewater, such as organics and nitrogen-ammonia; and oxygen demand in the slime layers on the collection system walls and in any sedimentation on the bottom of slow-moving collection systems.

Temperature and time in conveyance are important because oxygen is consumed faster at higher temperatures (and oxygen solubility is lower). As such, long-contact-time force mains in relatively high-temperature environments can quickly go anaerobic and begin producing sulfides.

Typical oxygen uptake rates reported for domestic wastewater range from 5 to 15 mg/L/hr (Jordan et al., 2003). Fong (1992) reported oxygen uptake rates of 2 to 15 mg/L/hr. Fong also indicated that the majority of the oxygen reaction is achieved biologically rather than by chemical oxidation paths.

Field trials and collection system modeling were evaluated for a collection system in California by Moody and Riek (1999), who found the typical oxygen dose to be 2.2 lb of oxygen per pound of sulfide removed. Jordan et al. (2003) reported that 4.8 mg/L of oxygen was required to biochemically oxidize each 1 mg/L of sulfide.

Various sources report different levels of background dissolved oxygen required to prevent sulfide formation and buildup. Melbourne Water (1989) reports various researchers’ values ranging from as low as 0.5 mg/L to as high as 2.0 mg/L. Tanaka and Takenaka (1994) reported that maintaining 1 mg/L of dissolved oxygen in the terminal point of the force main was sufficient to control sulfide formation.

The applicability of oxygen injection will depend on the BOD exerted over the detention time of the force main and the solubility of oxygen for conditions inside the force main. If more dissolved oxygen is consumed than can be dissolved during the detention time, then oxygen injection may not work without additional injection points.

A variety of equations for calculating oxygen demand and consumption in force mains and collection systems is provided in the literature (e.g., WEF, 1995, 2004; Melbourne Water, 1989; EPA, 1985).

Various collection system models that can calculate the oxygen demand also exist. These are discussed in Chapter 5.

Oxygen solubility can be calculated on the basis of the pressure inside the force main as

$$DO_{\max} = P f_O K_H \quad (7.3.9.1-2)$$

where

P = absolute pressure inside the force main (atm)

f_O = fraction of oxygen in the gas to be injected (for air, 0.21 g O₂ / 1 g air)

K_H = Henry's law constant (mg/L/atm) at the wastewater temperature

The Henry's law value for oxygen in water varies as a function of temperature (Figure 7-7).

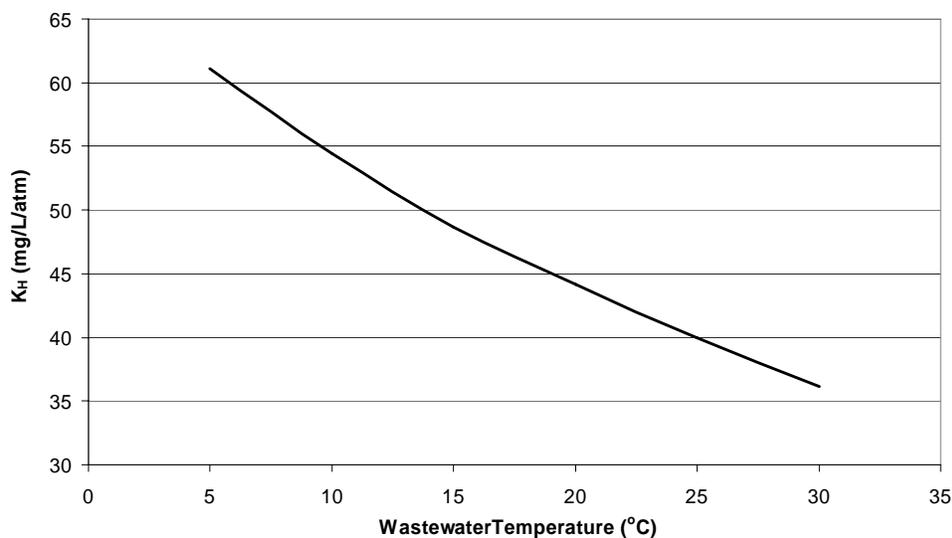


Figure 7-7. Henry's Law for Oxygen as a Function of Water Temperature

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

The required gas injection rate can be calculated as

$$\dot{G} = (Q DO_{\text{in}}) / (\eta_{\text{diff}} f_O) \quad (7.3.9.1-3)$$

where

\dot{G} = gas injection rate (g/s)

Q = wastewater flow rate (m³/s)

DO_{in} = required dissolved oxygen concentration at the injection point (mg/L)

η_{diff} = diffuser efficiency (gas dissolved/gas injected)

f_o = fraction of oxygen in the gas to be injected (for air, 0.21 g O₂ per 1 g air).

7.3.9.2 Treatment Effectiveness

Although it is consistently reported in the literature that keeping residual oxygen levels above 1 mg/L can control sulfide formation and odors, few data were identified showing the specific effectiveness of this approach on *non*-H₂S odors. Even data on effectively controlling H₂S seemed somewhat limited. This was particularly the case regarding gas phase concentrations of H₂S and other odorants.

7.4 Chemical Oxidation

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

7.4.1 Chlorine Gas

7.4.1.1 Technology Background

The first reported chlorine application is described by Melbourne Water (1989), whose text reports that in 1854, chloride of lime was used by the First English Royal Sewage Commission to deodorize London wastewater. Today chlorine is still used in a variety of forms. Chlorine treatment can come from several sources, including chlorine gas, sodium hypochlorite (bleach), and sodium chlorite.

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

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

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

7.4.1.2 Dose

Chlorine is very reactive with many compounds found in raw domestic wastewater, including hydrogen sulfide. Chlorine and sulfide react as shown by the following:



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

However, since chlorine indiscriminately oxidizes any reduced compound in wastewater, competing side reactions also influence the required effective dose.

Field studies have shown that, depending upon pH and other wastewater characteristics, 4 to 15 parts by weight of chlorine are often required for each part of sulfide. Moody and Riek (1999) reported typical demands in the range of 5 to 15. Ten to 15 parts by weight is not, on the basis of EPA (1985) guidance, unusual, but higher-strength waste may require even higher dosing. For example, Wolf et al. (2000) reported unusually high demands on a high-strength industrial food waste force main. In that study, with a 700 to 1,200 BOD, waste dosing as high as 25:1 was required to sustain effective odor control. This points out the importance of following jar testing with pilot testing to determine the true dosage requirement for a given wastewater and wastewater collection system.

7.4.1.3 Equipment and Handling

Chlorine gas is shipped and stored in tanks containing liquid chlorine under pressure. The gas is drawn off the tank headspace and mixed into a side stream with a chlorinator before being injected into the wastewater. Regulators and diffusers are also required for chlorine injection. Chlorine gas is poisonous and requires special precautions for storage, including containment and scrubbing facilities in case of a leak. Effective mixing is also reported to be very important in full-scale applications (EPA, 1985; WEF, 2004).

7.4.2 Sodium Hypochlorite

7.4.2.1 Technology Background

Sodium hypochlorite (NaOCl) is the chemical commonly found in bleach home-cleaning products. In typical odor control applications, industrial strength hypochlorite—approximately triple the strength of home-cleaning products—is used.

Hypochlorite is essentially 18 to 20 percent caustic with chlorine injected into it, resulting in a 10 to 15 percent solution of chlorine stabilized in caustic as hypochlorite. The high-pH caustic stabilizes the chlorine and acts as the carrier. Hypochlorite performs comparably to chlorine gas but is preferable for safety reasons related to potential chlorine gas release.

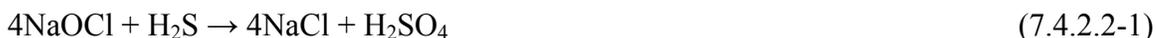
Chlorine gas tends to acidify any solution it is added to, whereas hypochlorite tends to make solutions more basic, owing to the presence of the caustic carrier solution. Generally, hypochlorite is much safer to use and is preferred over chlorine gas for collection system applications.

Its advantages are that the equipment required is inexpensive and widely available and that it has a long record of effectiveness.

Its disadvantages are that (1) reactions may form toxic and carcinogenic byproducts, some of which are regulated; (2) it may inhibit downstream biological treatment; and (3) it degrades slowly, thus complicating long-term storage.

7.4.2.2 Dose

Hypochlorite is a strong oxidizing agent. It reacts stoichiometrically with hydrogen sulfide in wastewater at a theoretical ratio of 8.8 lb of sodium hypochlorite per 1 lb of hydrogen sulfide:



It is, however, also sensitive to pH, with stoichiometric demand rates similar to those of chlorine gas injection under acidic conditions.

Since hypochlorite reacts indiscriminately with other wastewater constituents, the required effective dose is often higher than stoichiometric. In practice, the required dosage is often reported to be in the range of 10 to 15 lb of sodium hypochlorite per 1 lb hydrogen sulfide (EPA, 1985). However, field experience indicates that significantly lower or higher values can also be observed. Jar testing specific wastewaters is therefore recommended to determine true demand.

7.4.2.3 Equipment and Handling

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

7.4.2.4 Treatment Effectiveness

Generally, chlorine is reported to be very effective at reducing H_2S , although the effect can be limited with distance downstream of the dosing point. Non- H_2S odors are also generally reported as being controlled (Choudray, 2000), although hard data on specific non- H_2S odorants was seldom reported.

“Shock dosing” has been attempted using hypochlorite but with short-lasting results. Hamilton et al. (1992) reported that hypochlorite shocking at up to 115 mg/L for as long as 60 minutes on a 4-mile-long collection system achieved a downstream residual of 3 mg/L and did impact dissolved sulfide during the shocking, but within 35 minutes of dosing being stopped, concentrations were back to normal at the downstream end of the reach.

Lamb Technical Services (1998) reported attempts to use hypochlorite shocking in Arizona, where hypochlorite dosing was maintained on a 2-mile reach. In this instance sulfide also dropped during the shock dosing, but once dosing was stopped the system rapidly returned to previous liquid and gas phase H_2S levels.

Waltrip and Snyder (1985) reported on continuous dosing evaluations of the force main injection of chlorine in Virginia. Although the information provided is insufficient to determine the dose rate that was used, chlorine was reportedly dosed in a force main carrying 12 to 20 mg/L of dissolved sulfide. Dosing effectively elevated the ORP to +200 and removed the sulfide, but within 1 to 2 miles downstream of the application point, sulfide began to increase again, and

within 5 miles sulfide was back up to the initial background levels of 15 to 18 mg/L. This indicates that chlorine can be effective but only for relatively limited periods and that intermediate dosing stations may be needed.

Although chlorine control of odors and corrosion is well established in the literature, few data were identified showing the specific effectiveness of this approach on non-H₂S odors. Even data on H₂S control effectiveness were limited. This was particularly the case with regard to gas phase concentrations of H₂S and other odorants.

7.4.3 Sodium Chlorite

Sodium chlorite (NaClO₂), which is produced by Basic Chemical (formerly Vulcan) as a 25 percent solution, is an alternative source to chlorine sometimes used in sludge applications but not reported in the literature for collection systems. At the time of this writing, sodium chlorite is distributed in the U.S. by Siemens Corporation under the product name VX-456. It reportedly reacts with H₂S as follows:



Chlorite is used much less often than hypochlorite because it costs more and there is less knowledge of its application. It reportedly reacts with sulfide selectively, so it may have a longer residual than other forms of chlorine. A chemical supplier reported that 4 to 6 lb of NaClO₂ per pound of sulfide removed was sufficient to decrease sulfide concentrations to below detectable levels (Rio Linda, 1996).

7.4.4 Permanganate

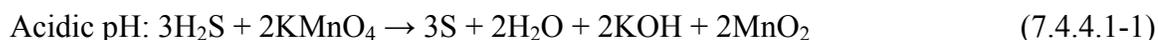
Sodium and potassium permanganate are strong oxidants that can be used to remove sulfide and other odor- and corrosion-causing compounds. Sodium permanganate is more soluble, whereas potassium permanganate is less expensive, but both are more expensive than other chemicals. Permanganate sometimes is used to treat sludge because it reacts preferentially with sulfide and can be cost effective in this type of application. It is not generally the most cost effective approach on the full flow of a typical wastewater plant collection system.

Permanganate is available in both concentrated liquid and crystal forms. It is most often used as a crystal to make a 3–6 percent solution. The solution is then blended with the waste stream. In crystal form the concentration as permanganate is high—97 percent. Also available is a liquid product at approximately 12.5 percent concentration that typically comes in drum-size carboys or drums for small applications.

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

7.4.4.1 Dose

Potassium permanganate (KMnO₄) is a strong chemical oxidizing agent that reacts with hydrogen sulfide according to the following equations:



In practice, several reactions ranging between these two may take place to produce elemental sulfur, sulfate, thionates, di-thionates, and manganese sulfide depending upon local wastewater chemistry. Field studies have indicated that between six and seven parts of KMnO_4 are required for each part of sulfide. A major vendor reports that for sludge streams typical dosing can run as high as 100 mg/L. This often equates to the demand for approximately 7 lb of permanganate per 1 lb of sulfide.

Permanganate reportedly reacts preferentially (first) with sulfide. However, permanganate, like chlorine or peroxide, can be considered an indiscriminate oxidant if sufficient contact time and exposure is provided. As such, dosing requirements can depend on how it is applied.

Very little experience was identified where permanganate is used in collection systems. This appears due primarily to its relatively high cost and complexity of the mixing and delivery systems.

As such, permanganate odor control appears to be substantially limited to side streams in wastewater treatment plants rather than to an entire treatment plant's flow (Lloyd, 1997).

7.4.4.2 Equipment and Handling

Potassium permanganate is typically available and used in dry form and must be mixed with water to an approximately 3–6 percent solution (with a density of 8.7 lb/gallon) before being used. Mixing with water at temperatures below 40°F may be problematic because of its low solubility; accordingly, heating dilution water may be required. Sodium permanganate is more soluble and is sold in a 12–20 percent solution.

The equipment required for a typical potassium permanganate application consists of a dry feeder, mixing tank with mixer, metering pumps, control system, valves, and piping. Potassium permanganate typically is used in smaller applications because its cost makes it prohibitively expensive to treat large flows, such as the entire plant flow, on a continuous basis. It is most often used on liquid sludge stream applications.

When kept dry and cool, potassium permanganate is relatively stable. However, when contaminated with organics or acids, it can become unstable and decompose, causing potentially explosive conditions. Thus, sodium permanganate that is stored and transported in solution may be safer in this respect. Appropriate worker safety precautions must be followed when using the material, including use of rubber gloves, goggles, and a particulate breathing mask. Eyewash and shower stations and other safety equipment should be available.

7.4.5 Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a strong oxidizer that reacts with most reduced compounds in wastewater, including sulfide. It is typically available in bulk concentrations of 35 to 50 percent. It has the advantage of having harmless reaction byproducts, and the breakdown of excess H_2O_2 increases dissolved oxygen in wastewater; a disadvantage is that an H_2O_2 residual is very difficult to maintain (though reaction adds residual O_2).

7.4.5.1 Dose

Hydrogen peroxide oxidizes hydrogen sulfide to colloidal elemental sulfur (Melbourne Water, 1989). Under typical wastewater pH ranges, reactions proceed according to the following equation:



Field studies and bench-scale test reports indicate a required dose of one to four parts by weight of H_2O_2 per one part sulfide, depending on target sulfide concentration (Van Durme et al., 1987; Waltrip and Snyder, 1985). Larger doses are reportedly needed as the target sulfide concentration approaches zero. For example, a larger H_2O_2 /sulfide ratio is needed to achieve a dissolved sulfide concentration of 0.1 mg/L than is needed to achieve a dissolved sulfide concentration of 0.5 mg/L (Waltrip and Snyder, 1985). Because of the fourfold dose range, bench-scale tests on a wastewater sample from the source to be treated are recommended in order to verify the appropriate dose. A field test reported by Melbourne Water (1989) required a peroxide dose up to 40 mg/L for a 5-mile-long pressure main in order to reduce end-of-pipe dissolved sulfides to near zero.

The reaction between hydrogen peroxide and sulfide is relatively slow (reactions are very nearly complete in 30 minutes) when compared to those of other oxidants, which take seconds to minutes. EPA (1985) reports that 90 percent of the reaction occurs within 10 to 15 minutes and that reaction is essentially complete within 20 to 30 minutes. Therefore, adequate mixing and contact time must be provided. Melbourne Water (1989) appears to be slightly more conservative and reports up to 60 minutes being required for complete reaction in wastewater. Typical designs shoot for approximately 30 minutes' upstream contact time with good mixing. Melbourne Water (1989) also reports that peroxide reacts with mercaptans, disulfides, and other organic sulfides under acidic conditions in the presence of soluble iron catalyst.

Peroxide-Enhancing Product Ghosn and Cox (2006) report on a relatively new catalytic product that enhances the reaction time of peroxide and other oxidants. In their study, contact times were reduced to 3 to 5 minutes using the VTX-1 catalyst. This catalyst is reported to be a proprietary organic based metal (iron) complex that enhances the reactivity of the oxidant.

Peroxide Derivative Product Kotonarou et al. (1991) also report on an alternative salt derivative to peroxide called peroxymonosulfate (HOOSO_3^-). They report this as more reactive than peroxide but point out that at present there is no economic advantage to this approach owing to the cost of currently available salt products.

Solid Tabular Product Sodium percarbonate is distributed under the brand name Cellinite, which reportedly includes both a time released source of peroxide and that is spiked with bacteriological supplements. This product has been used in small lift stations and in animal waste lagoons for manure treatment (Turo et al., 1998).

Peroxide Regenerated Iron-Sulfide Control Peroxide dosing in combination with iron salts is also reported in the literature under the proprietary name Peroxide Regenerated Iron Sulfide Control. This approach integrates the use of iron salts and peroxide. The combination involves addition of an iron salt in the upper reaches of a collection system followed by injection of peroxide at intermittent downstream locations. The peroxide is used to regenerate the precipitated iron (FeS) recreating ferric and ferrous iron along with colloidal sulfur. The regenerated iron provides subsequent sulfide control.

This approach was reported as beneficial by Walton et al. (2003) in Orange County, California, where reactivation of iron salts at the treatment plant was also reported as beneficial. This report indicates that headspace H_2S in a collection system was reduced from 700 ppm to 20–125 ppm (80 to 95 percent reduction), and that 85 to 90 percent of the iron added in the

collection system could be regenerated at the treatment plant, thereby enhancing both odor control at the plant and settling in the primary clarifiers.

US Peroxide (2001) reported on work at two trunk lines in Orange County, California, and indicated that adding ferrous chloride in upper reaches followed by peroxide at intermediate locations (a 6-hour contact time) and just in front of the wastewater treatment plant dropped liquid phase sulfides from 9 to 12 mg/L down to below 0.5 mg/L.

7.4.5.2 Equipment and Handling

The type of peroxide storage and feed equipment required depends upon the dosage rate and the concentration of peroxide used. The maintenance and repair of hydrogen peroxide systems requires special training and procedures. Hydrogen peroxide is very reactive with organic materials, including grease and oil. When systems are installed or repaired, all wetted surfaces must be specially cleaned and prepared beforehand through a process called passivation. This consists of rigorous cleaning with a sequence of detergent, water, nitric acid, and water to avoid possibly dangerous reactions with contaminants. For this reason, hydrogen peroxide feed systems are sometimes contract operated by suppliers.

Worker safety issues must be addressed when using hydrogen peroxide. Gloves, goggles, and protective clothing should be worn when handling hydrogen peroxide solutions and contaminated equipment because skin, eyes, and other sensitive body parts can be damaged by exposure. Eyewashes and safety showers must be provided for workers. Adequate water supply should also be provided to dilute any spills.

7.4.5.3 Treatment Effectiveness

Peroxide has been reported as effective on both H₂S- and organic-based odor-causing compounds. Devai and Delaune (2002) reported that peroxide was effective in reducing both H₂S and organic compounds such as dimethyl sulfide, methanethiol (methyl mercaptan), and carbon disulfide in a sludge stream when tested on sewage sludge samples.

Moody and Riek (1999) reported the use of peroxide alone at 3.5 lb of peroxide per 1 lb of sulfide in a force main. This dosing level prevented sulfide from rising from 0.3 mg/L to 10 mg/L, observed without peroxide, and maintained the end-of-pipe sulfides to below a target of 0.5 mg/L.

Jefferson et al. (2002) reported on peroxide dosing to condition sewage upstream of a wastewater plant. Dosing of 1.8 mol of peroxide per 1 mol of sulfide at 30 minutes' contact time resulted in approximately a 64 percent reduction in dissolved sulfides. Increasing the peroxide dose up to 7.4 mol of peroxide per 1 mol of sulfide with 30 minutes' contact time resulted in an 86 percent removal of liquid phase sulfides. Increasing contact times up to as much as 145 minutes increased the control only up to approximately 88 percent.

In yet another instance, Nowak et al. (2004) reported using a combination of aeration and peroxide on septage before it was released to a collection system. This reduced by 90 percent overall odors as measured by D/T; however, required dose rates and reductions of specific odor-causing compounds were not reported.

Schmidt et al. (2000) reported on work studying dosing control methods to improve the efficiency of peroxide at the entrance of a treatment plant in California. The most effective feedback control was based on both flow rate pacing and headspace H₂S levels downstream, where the collection system flow hits the primary clarifiers. Without increasing overall chemical

dosing, the headspace H₂S was reduced by 67 percent by improving the feedback control approach to dosing.

Fong (1986) reported the use of peroxide in large-diameter sewer systems in southern California. At 5:1 and 6:1 doses of pounds of peroxide to pounds of sulfide, the systems achieved 90 percent liquid phase sulfide control but for only 30 to 60 minutes. Gas phase H₂S was reduced 60 to 100 percent, and “odors” were reduced 60 to 90 percent. At dissolved sulfide levels below 1 mg/L the peroxide reaction is reported as very slow, requiring higher dosing rates. Example installations showed a wide range in required dosing from 2.4:1 at a force main discharge for control to 18:1 in a gravity sewer for prevention. This points out that peroxide dosing to react with existing sulfide may take lower dosing rates than peroxide dosing to control downstream sulfide formation.

Van Durme and Berkenpas (1989) reported on work in an Arizona collection system where 3.3 kg of peroxide per 1 kg sulfide reduced odors but did not meet the 0.5 mg/L H₂S liquid phase goal.

7.5 Sulfur Precipitation

Various metal salts can combine chemically with dissolved sulfide to form relatively insoluble metal sulfide that precipitate from the wastewater, thus preventing the release of H₂S gas. Metal sulfide precipitates exist as soft black or reddish-brown flocs that usually do not settle in the collection system but can be removed at treatment plants. In fact, more-restrictive industrial source control programs have been credited with a tendency for increasing levels of sulfides over the years because of the associated lowering of metals in the wastewater (Padival, 1993). Effective metals might include iron, zinc, lead, chromium, cadmium, nickel, and copper, but iron is most typically used today owing to availability of the chemicals and the fact that other metals have become more restrictive in terms of allowable plant effluent and biosolids impacts. This is a potential concern because heavy metal concentrations could be regulated and make the solids difficult to dispose of.

Sulfur precipitation has several advantages, including the following: (1) long residuals can be maintained to precipitate sulfide as it is generated, which can result in sulfide control over very long collection system reaches; (2) iron salts can be used to treat sludge; (3) reaction byproducts are innocuous; and (4) precipitates are beneficial to downstream treatment processes.

The following are its disadvantages: (1) Precipitates can dissociate at pH less than 6.5, allowing sulfide to release back into the wastewater (EPA, 1985); (2) at typical wastewater pH, dissolved sulfide cannot be decreased to much lower than 0.2 to 0.5 mg/L; (3) anecdotal evidence suggests that precipitates form “clinkers” when iron-dosed biosolids are incinerated, and therefore this potential should be considered where sludge cake is incinerated; (4) iron salts can form a film on pipe walls, instrument sensors, and ultraviolet disinfection equipment; and (5) these precipitates can substantially increase sludge production at the treatment plant.

7.5.1 Reaction Mechanisms

Ferrous iron salts such as ferric chloride (FeCl₂) and ferrous sulfate (FeSO₄) are commonly available for sulfur precipitation. Ferrous iron reacts with each sulfide species as shown below:





These reactions indicate a stoichiometric dose of 3.8 lb of FeCl₂ per 1 lb of sulfide. However, effective doses for reducing the sulfide concentration to below 1.0 mg/L are reported from 4 to 12 lb of FeCl₂ per 1 lb of sulfide removed, depending on the target sulfide concentration (Slezak et al., 1994; Mohleji et al., 1992).

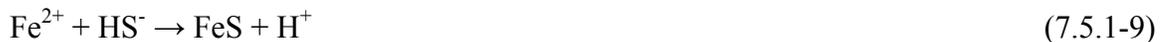
Ferric iron reacts similarly to ferrous iron:



These reactions indicate a “stoichiometric” dose of 3.3 to 4.9 lb FeCl₃ per 1 lb of sulfide. However, field and laboratory experiments indicate that the typical required dose to remove sulfide in domestic wastewater is between 3 and 7 lb FeCl₃ per 1 lb of sulfide removed (Jameel, 1989; Van Durme and Berkenpas, 1987).

Ferric iron solutions have a lower pH than does ferrous iron. Care should be taken that the wastewater is sufficiently buffered so that its pH is not lowered by ferric salts.

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



FeSO₄ and FeCl₃ in combination have been demonstrated to be more effective than either chemical alone. Field experience with reductions down to 0.2 mg/L dissolved H₂S have been reported. Typically, one part of ferrous FeSO₄ is used in combination with two parts ferric FeCl₃. The limitation of this approach is the requirement for separate chemical feed equipment for each chemical.

Another promising combination is iron salts followed by hydrogen peroxide. In a process sold as Peroxide Regenerated Iron Sulfide Control by US Peroxide, iron salts are used to complex with sulfide regenerated by means of downstream peroxide dosing. This chemical combination is discussed also in Section 7.4.5.

7.5.2 Dosing Requirements

Won (1988) reported on work done in large-diameter sewers in Los Angeles County, California, and indicates that the effective stoichiometric iron dose can be very dependent on the background concentrations of sulfide. For lower concentrations, higher ratios may be required. This paper reported that for wastewater with already low sulfide concentrations below 1 mg/L, up to 100 lb of iron might be needed for each additional pound of sulfide controlled whereas if the background sulfides were above 4 mg/L, the effective dose ratio was closer to 7:1.

Mohleiji et al. (1992) reported on ferrous chloride dosing into sewers in California. In this case ferrous dosing of less than 15 mg/L dropped dissolved sulfides to below the detection limits but left residual gas phase H₂S. Dosing of 20 mg/L was sufficient to drop both liquid phase and gas phase levels to below detection. Dosing in the range of 25 to 30 mg/L also lowered the gas phase mercaptan and dimethyl sulfide levels to below the detection limit. This is the only case found in the literature that reported iron salt impacts on non-hydrogen sulfide odors.

Richard et al. (1993) reported on the use of ferrous chloride in North Dakota collection systems where 8 lb of iron per 1 lb of sulfide was sufficient to reduce the dissolved sulfides to a target level of 0.5 mg/L. At this dosage, suspended solids increased 37 percent at the downstream treatment plant and the pH dropped by 0.2 units.

Slezak et al. (1994) reported on the use of “pickle liquor,” an industrial waste acidic iron solution byproduct created by an acid-washing process in the steel industry. In this instance, the authority wanted to evaluate both the effectiveness of this low-cost iron source and the impact on the plant’s effluent streams, including liquid and biosolids waste. Dosing of 10 to 15 mg/L iron was found to be sufficient to keep sulfides below 0.5 mg/L. This demonstration study indicated that this approach might be feasible as long as pickle liquor-dosing locations in the collection system were controlled, and the effects on the plant were closely monitored. In this instance, it was the iron that was the concern rather than other regulated metals.

7.5.3 Using Iron Coagulated Sludge in Sewers

Several papers reported on attempts to use iron-coagulated sludge from drinking water plants to facilitate sulfide control in the collection system. Edwards et al. (1997) reported on recycling waste iron coagulated sludge in this manner and indicate that when plausible this can be a cost effective control method. They also reported that the effects of this method extended into the treatment plant, resulting in lower H₂S levels in digester gas.

7.5.4 Potassium Ferrate

Sharma (2002) provided a summary for an alternative iron product, potassium ferrate. Potassium ferrate (K₂FeO₄) provides iron (VI), a powerful oxidant that might be used for either disinfection or odor control. At neutral pH, it takes 1.51 K₂FeO₄ per 1 sulfide. Full-scale field application of this oxidant for odor control was not discussed.

7.5.5 Handling and Equipment

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

7.5.6 Treatment Effectiveness

Some literature suggests that iron control has a limit below which liquid phase sulfides cannot be controlled by iron salts alone. The achievable levels reported vary greatly. Nielsen et al. (2005a) reports that iron salts may not be able to lower the liquid phase sulfide below 0.2 mg/L. This same paper reports that iron reactions can be dependent on whether the iron is added under anaerobic or aerobic conditions and that aerobic conditions produced lower results. Sercombe (1995) reports on work by others that indicates iron salts could not drop the liquid

phase sulfide below 4 mg/L. Bielefeldt et al. (2002) reported on both lab-scale and full-scale testing results for ferric chloride in wastewater just upstream of a treatment plant and on the sludge. This paper suggests that control down to 0.5 mg/L of dissolved sulfide is possible with ferric iron salts.

Jameel (1989) reports successful treatment down to 0.5 mg/L dissolved sulfides on collection systems in Arizona. Required dosing used 6 gallons per hour of 40 percent ferrous chloride dosed into 9.5 mgd, an equivalent of approximately 23 mg/L. This was also reported as 4.3 lb of ferrous chloride per lb of sulfide removed.

Dewaters et al. (1999) reported on work in waste treatment lagoons that shows the effectiveness of the presence of oxygen enhancing the performance of iron salts, indicating that lower dissolved sulfide levels can be obtained if any oxygen is present. Without oxygen, iron's effective limit was 1 mg/L; with it, the iron sulfide precipitation dropped levels even lower.

Padival et al. (1995) reports iron salt dosing on a 44-km trunk sewer reach in Los Angeles. The impact on the upper 27 km was reduction of the average dissolved sulfides by as much as 94 percent. This required approximately 16 mg/L Fe dosing. A blend of 1.9:1 ferrous to ferric worked best, achieving a 97 percent reduction. Below the 27-km mark, the impacts appeared to be diminished. The paper suggests this was due to impacts of side streams. This is an effective example of how far-reaching iron control can be downstream of the dosing point.

Bielefeldt et al. (2002) reported on both lab-scale-testing and full-scale-testing results for ferric chloride on wastewater just upstream of a treatment plant. Ferric was shown to increase suspended solids, resulting in higher primary sludge blankets that became poorly defined (reportedly from pin floc in the primaries). Ferric was shown to create process impacts, including 50 to 95 percent reduction in sulfide in downstream wastewater plant anaerobic digesters. Reduced performance in belt filter press dewatering was also reported. Ferric doses below 4.5 mg/L helped reduce odors without impacting processes. Ferric dosing above 4.5 appeared to negatively impact sludge volume indices. Ferric dosing above 13.5 mg/L impacted belt filter press performance. Dosing at the full scale of as low as 2 mg/L reduced but did not get rid of odors (more was needed). An optimum range appears to be near 5 to 12 mg/L.

Wolstenholme and Jabloner (2004) reported that dosing of 8 mg/L of ferrous chloride reduced gas phase H₂S in a naval station's intermittent force main discharge from an average of 35 ppm to below 1 mg/L. In this instance, waste from naval ships (with high detention times) was being pumped through a force main and impacting the receiving collection system.

Padival (1993) reported on full-scale testing on trunk sewers in California to control dissolved sulfide level. Padival reported that 16 mg/L of blended Fe₃ and Fe₂ at a ratio of 1.9:1 provided a 97 percent reduction in the dissolved sulfides and a 79 percent reduction in the headspace H₂S. The blended ferrous and ferric worked better than they did alone. O₂ reportedly made Fe₂ as effective as Fe₃.

7.6 Nitrate Addition

Nitrate salts can be used to prevent the formation of sulfides by providing an alternative electron acceptor for sulfate-reducing bacteria, which preferentially reduce oxygen, nitrate, and sulfate in that order. Therefore, as long as enough oxygen or nitrate is in solution, sulfate conversion to sulfide will be minimized. Nitrate can also be used as an oxygen source to promote the biological oxidation of sulfide. Nitrate is available in both liquid and dry form as sodium

nitrate (NaNO_3) or, more commonly, as calcium nitrate ($\text{Ca}(\text{NO}_3)_2$). Both salts are quite soluble, and liquid solutions of between 40 and 60 percent by weight are usually used. Several products, such as Nutriox and Bioxide, are identified in the literature. Bioxide is a trademark for a calcium nitrate solution currently distributed by US Filter throughout the United States. US Filter also distributes Bioxide-AQ, which includes a slime layer bacteria inhibitor called anthraquinone. This will be discussed in the following section.

Nitrates have been used to control sulfides in collection systems, in sludge, and in treatment lagoons (Hobson and Yang, 2000; Einarsen et al., 2000; Wissenberger et al., 2004; Groleau et al., 2002; Watson et al., 2001). Einarsen et al. (2000) reported on using nitrate mixed into dewatered centrifuge cake to control residual cake odors; H_2S - and mercaptans-related odors were reduced.

Watson et al. (2001) reported success in pulp and paper treatment lagoons where dissolved sulfide levels were reduced from around 15 to 20 mg/L down to below 0.1 mg/L. This process reportedly took 1 to 2 weeks. This is considered indicative of the biological process changes that must occur with Bioxide. Collection system changes are also not instantaneous and can reportedly take from hours to days.

Nitrates are also created naturally as the side effect of nitrification. These naturally created nitrates can be used to inhibit sulfide generation. As an example, Delgado et al. (2004) reported on using residual nitrate present in plant effluent to control sulfide formation in long-contact-time force mains conveying reclaimed wastewater. Rodriguez-Gomez et al. (2005) reported similar work, where nitrate dosing was used to control sulfide formation in reclaimed water pipes. Coughenour et al. (2003) reported on work investigating the recycling of centrate discharge from dewatering to a dedicated activated sludge reactor for nitrification creating nitrate. Field trials of nitrate addition at the plant headworks reportedly dropped H_2S odor levels throughout the plant.

Nitrate addition has the following advantages: (1) It can maintain a long residual; (2) it is safe and does not require special handling or storage; and (3) reactions do not form hazardous byproducts. Its disadvantages are that nitrate (1) sometimes causes gas binding of long force mains with inadequate air relief valves and (2) may increase the cost and difficulty of denitrification at the treatment plant.

7.6.1 Dose

Nitrate addition reportedly controls dissolved sulfides by two methods, prevention and control. Prevention is based on nitrate's acting as the alternative electron acceptor and promoting the use of nitrate instead of sulfate by the facultative and obligate anaerobic bacteria, thereby preventing the formation of sulfide. Okabe et al. (2003) reported on work on sewer system biofilms. In their study, adding nitrate forced the sulfate reduction zone deeper into the biofilm and significantly reduced the volumetric sulfate reduction rate. This is considered direct evidence of the impact of nitrate on the activity in the sewer systems biofilm.

In the removal reaction, the nitrate supplies oxygen, which allows biochemical oxidation of sulfide by bacteria such as *Thiobacillus denitrificans*.

Nitrate addition can reportedly control dissolved sulfide concentrations exceeding 0.5 mg/L or less. The required dose ranges from 4 to 15 lb of calcium nitrate per pound of sulfide prevented (Moody and Riek, 1999; Hamilton et al., 1992; George Butler Associates, Inc., 1999).

A minimum requirement is 7.2 kg of nitrate per kilogram of sulfide prevented (Davis Process, 1988; WEF, 2004). This does not include any demand for reacting with existing sulfides. This requires an additional 2.4 kg of nitrate per pound of sulfide reacted. Total requirement is 7.2 plus 2.4, or 9.6 kg nitrate per 1 kg sulfide controlled.

Perry et al. (1997) reported on work in four different force mains. These force mains required nitrate dosing of 16, 12, 9.6, and 10.4 kg of nitrate per kilogram of sulfide. Data reported generally appear to indicate that nitrate dosing upstream needs to be sufficient to keep residual downstream at the discharge point in the range of 0.4 to 0.8 mg/L in order to be effective at keeping headspace H₂S below 10 ppm. This appeared to equate to approximately 12 mg of nitrate per milligram of sulfide reacted or prevented.

It is sometimes noted that the true dose is dependent on the layout of the collection system, which affects the amount of slime layer that must be impacted, and as a result, dosing requirements based solely on pounds of sulfide prevented or reacted may not be accurate. Thus, trying to determine accurate nitrate-dosing requirements by means of jar testing would likely prove ineffective because the natural slime layer is not present in a jar test. Melbourne Water (1989) reported ratios as high as 20 or 30 lb of nitrate per 1 lb of sulfide. This may be indicative of the impacts of the slime layer on the collection system walls and in sediment in the bottom of slow-moving collection systems. Hamilton et al. (1992) indicated that calcium nitrate dosing requirements were 2.7 gallons per pound of sulfide for large trunk sewers and 1.5 gallons per pound for small lines for typical off-the-shelf Bioxide solutions. This may reflect the impact of different levels of slime layer coatings in terms of both surface area and thickness. Nitrate dosing must be continuous. Batch dosing reportedly does not work (Hobson and Yang, 2000). This is likely because the nitrate is consumed, and sulfate-reducing bacteria quickly reestablish themselves.

Pope (1996) reported that calcium nitrate dosing requires field testing and cannot be done effectively with a jar test. Pope also indicated that calcium nitrate worked better for the force main application than the gravity lines. Vollersten et al. (2005a) estimated during batch jar testing 4.6 g of nitrate required per gram of sulfide. This dose is well below the 10.4:1 ratio highlighted above for both prevention and reaction. This relatively low dose may be a result of jar testing that does not include all the effects that would be seen in the field.

Although a dose rate must be selected in order to design the delivery system, the rate should be varied during operation to avoid waste and excess nitrate loading in the downstream process. One approach, if the necessary monitoring equipment can be installed, is to vary the nitrate dose on the basis of the nitrate concentration entering the treatment plant or at the discharge point of the force main. During startup, the nitrate dose is varied until a minimum nitrate concentration entering the plant headworks or reaching the downstream end of the force main is found that maintains the sulfide concentration below the target. Thereafter, the feed rate is slaved to the sulfide concentration and to the nitrate concentration entering the plant so that the previously determined residual concentration is maintained.

7.6.2 Handling and Equipment

Nitrate salt solutions are neither corrosive nor hazardous and do not require special equipment. Nitrate feed systems include a storage tank with metering pumps and associated valves and piping. Figure 7-8 shows a feed system for US Filter's nitrate brand Bioxide.



Figure 7-8. Bioxide Storage and Delivery System

7.6.3 Treatment Effectiveness

Hobson and Yang (2000) noted that dissolved sulfide was suppressed in rising mains down to 0.1 mg/L with a corresponding suppression in overall odor. In the same system where sulfide was controlled by iron dosing, non-H₂S odor residual was reported.

Bentzen et al. (1995) reported on a proprietary approach in the United Kingdom to dosing sodium nitrate (Nutriox). Nitrate was dosed upstream of a wastewater plant at a pump station in an attempt to keep excess nitrate from entering the treatment plant downstream. The intent was to keep wastewater treatment plant sulfide loading below 0.5 mg/L and nitrates below 2 mg/L. Dosing reportedly controlled liquid and gas phase H₂S being formed in the force main coming into the plant and downstream in the plant's primary clarifiers. Typical dosing was 319 L per day to the 1,200-m³/day plant flow (equal to 266 gallons of Nutriox per million gallons of wastewater). This reduced dissolved sulfides from around 4 mg/L to an average of 0.24 mg/L (a 95 percent reduction). Primary clarifier effluent sulfide levels were also reduced from around 5.4 mg/L to 2 mg/L. This means there was a 63 percent reduction in the primary clarifier H₂S levels as a side effect of dosing Nutriox in the collection system. Nitrate levels entering the plant were around 2 to 3 mg/L.

Sercome (1994) reported on work in the United Kingdom in a system with many pump stations and force mains. Over a 4- to 5-day period, sodium nitrate dropped headspace H₂S from 50 to 1 ppm at the discharge of the rising main.

Yang (1999) presented work that suggested that in a side-by-side study on a rising main, both H₂S and overall odor units are reduced by Nutriox (nitrate), but that iron salts affected only H₂S and had high residual non-H₂S odors as measured by odor panel odor units.

Churchill and Elmer (1999) reported on the use of commercial-grade CaNO₃ (not Nutriox or Bioxide) at a 1.5 percent solution to control force H₂S emissions that were coming from a hydraulic drop in a collection system section just downstream of a 21-in. gravity sewer's slow-moving flow that was partially fed by an 8-in. force main with 90 minutes of detention time. Nitrate dosing dropped the gas phase H₂S from an average of 68 ppm to near zero in approximately 3 days.

Nowak et al. (2004) reported on work in Vienna, Austria, where calcium nitrate was dosed at 10 to 20 mg/L, reducing odor levels peaking as high as 33,000 odor units/m³ and H₂S levels of only 5 to 10 ppm. The paper suggests that odors were being caused by more than H₂S, although other specific compounds were not defined. At this nitrate dosing, H₂S formation was “prevented,” and odor concentrations “declined significantly.” A review of data plots suggests that nitrates dropped the background odor units by approximately 85 percent.

Hagekhalil et al. (1994) reported on the use of a 54 percent calcium nitrate solution in gravity collection systems in southern California. Nitrate residuals in the range of 0.58 mg/L at the downstream end dropped liquid and gas phase H₂S down from 1.9 mg/L of dissolved liquid sulfide and 91 ppm gas phase to 0.02 mg/L liquid and 2 ppmv gas (an over 98 percent reduction). This required a calcium nitrate dose of 2.31 to 4.4 gallons nitrate per pound of sulfide removed, depending on the system. This equated to 10.4 to 20 lb nitrate per pound of sulfide.

7.6.4 Downstream Treatment Plant Effects

Bentzen et al. (1995) reported that nitrate dosing in the collection system reduced the soluble BOD reaching the plant by 35 percent. Also noted at the plant was improved nitrification during the nitrate-dosing period, which was associated with the lower BOD and soluble sulfide load.

Moody and Riek (1999) reported that nitrate dosing several hours upstream of a treatment plant was successful at keeping dissolved sulfide to below 0.5 mg/L. When this occurred, residual nitrate levels at the plant reportedly caused “denitrification in the primary clarifier solids and floatation of the solids.” Adjusting the target sulfide concentration upward to 1 mg/L and reducing the residual nitrate hitting the plant diminished the impacts on solids floatation in the primaries.

7.7 pH Adjustment

pH can be an important parameter for most of the liquid phase odor control methods described above, but it can also be used directly to mitigate hydrogen sulfide release. There are two methods of reducing H₂S-related odors using pH adjustment. One is to shift the wastewater pH so that chemical equilibrium favors nonvolatile sulfide species. The other uses a temporary but more drastic pH increase to deactivate the sulfur-reducing bacteria.

7.7.1 pH Stabilization

pH affects the distribution of the three sulfide species—H₂S, HS⁻, and S⁻²—in the solution. An increase in pH drives sulfide to ionic forms (HS⁻ and S⁻²) that are nonvolatile. For example, at a pH of 7, roughly 50 percent of sulfides are present as H₂S, whereas at a pH of 8.5, only 3 percent are present as H₂S. If wastewater pH drops, the sulfide species ratios shift rapidly toward H₂S, which is volatile. Therefore, increasing wastewater pH can reduce odor problems as long as the higher pH is maintained. Figure 7-9 shows the relative fraction of each sulfide species as function of pH.

Figure 7-9, which was generated on the basis of *p*k_a values for hydrogen sulfide, shows that at a pH of 9 or above, almost no dissolved sulfide is in the volatile form. Some literature also suggests that slight shifts in pH can begin to inhibit growths of anaerobic organisms that produce sulfides (Melbourne Water, 1989).

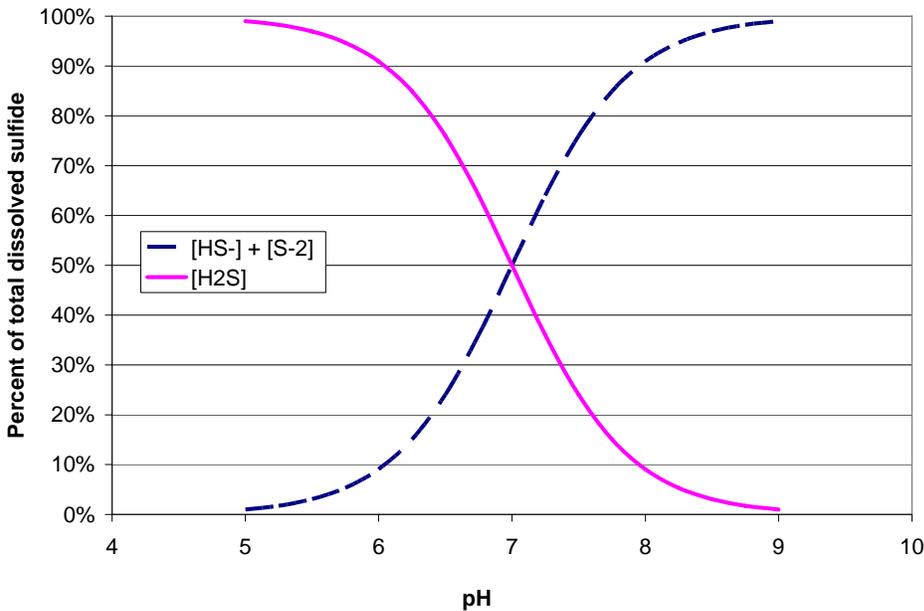


Figure 7-9. Fraction Dissolved Sulfide (Volatile and Nonvolatile)

7.7.1.1 Dose

Magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and sodium hydroxide (NaOH) are the two chemicals most commonly used to raise pH. Magnesium hydroxide can raise pH to a maximum of 9 and sodium hydroxide to a pH of 14. Even with overdosing, magnesium hydroxide reportedly does not raise the pH over 9 (Moore, 2003a), reportedly because it is not as soluble and acts as a buffer, whereas caustic is readily soluble and can have a quick effect on pH, driving it up much higher.

Jefferson et al. (2002) reported on work just upstream of a treatment plant. In this instance, magnesium hydroxide worked well to adjust pH up to about 9. Owing to the relatively insolubility of MgOH , overdosing only caused the pH to remain stable at up to 9.5.

The chemical dose will depend on the buffering capacity of the wastewater. To estimate the amount of chemical needed to achieve the target pH, a sample of the wastewater should be jar tested with a concentrated solution of the desired control chemical until the target pH is reached. Lime has also reportedly been used (EPA, 1985). Dosing experiences for each chemical are outlined below.

Magnesium hydroxide is most commonly known as an acid-stomach remedy and is essentially industrial-grade milk of magnesia. Typically, magnesium hydroxide comes in a 58- to 60-percent slurry with a paintlike consistency. It freezes near 32°F and should be stored in stirred or agitated tanks. It reportedly works by pH shifting to keep already-formed sulfides in solution, sulfide binding with magnesium cations, and pH inhibition of the slime layer. It is also reported to have beneficial downstream impacts by providing alkalinity to the treatment plant processes. Dosing can be either direct to the wastewater or as an intermittent spray coating on the crown of gravity collection systems.

Reported rates of liquid phase dosing directly to the wastewater vary greatly. Moore (2003b) reported typical dosing requirements ranging from 25 to 100 gallons per million gallons of wastewater treated. It can either be applied directly to the wastewater flow or sprayed on the crown of a gravity sewer line.

Magnesium hydroxide was tested as a sulfide control chemical in CH2M HILL's (2001) Orange County Sanitation District study. Roughly 700 pounds of magnesium hydroxide per million gallons were dosed as a slurry to a long gravity interceptor. The vapor phase H₂S concentration went from 110 to 21 ppm, a substantial gas phase H₂S reduction. These results are in contrast to manufacturer-recommended doses of between 10 and 100 gallons of 58 percent solution per million gallons. If possible, jar tests should be conducted to determine the appropriate dose for the wastewater in question. When this method is used, care should be exercised that dilution from side sewers does not lead to a pH drop and downstream odor problem.

7.7.1.2 Equipment and Handling

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

7.7.2 Caustic Shock Loading

Odor also can be controlled by shock-dosing the H₂S-producing bacteria living in the slime layer on the sewer wall. Raising the pH of the wastewater to 13.0 or higher for 30 minutes has been demonstrated to inactivate the sulfate-reducing bacteria for periods of 3 to 14 days. Churchill and Elmer (1999) reported on work where shock dosing was used to control odor release from a force main; pH shocking was reported as effective but "short lived."

7.7.2.1 Dose

A Los Angeles field study found that raising the pH in a gravity sewer to 13.2 for 30 minutes decreased the sulfide concentration from 4.5 mg/L to zero on the first day. By the third day after shock loading, the sulfide concentration was up to 0.25 mg/L, and it continued to increase thereafter. The study also described shock loading up to a pH of 11.4, which did not work (Hamilton et al., 1992). The appropriate dose should be determined by titrating a sample of wastewater with the NaOH solution to be used until a pH of 13 is reached. A study by the Los Angeles Sanitation District found that a dose rate of 3,000 lb of 50 percent NaOH solution (260 gallons) per million gallons of wastewater for 30 minutes was required to obtain odor control by shock loading in their system with their wastewater.

7.7.2.2 Equipment and Handling

Shock dosing is often applied directly from a tanker truck. This method saves the capital cost of storage and feed equipment. Sodium hydroxide is dangerous to handle, and so appropriate equipment and safety measures are required for its use.

7.7.2.3 Treatment Effectiveness

pH Adjustment Using Caustic Khan (1992) reported on sewer corrosion studies done in Southern California using continuous caustic dosing to adjust pH levels. For a jar test on the specific Los Angeles wastewater system, it took 80 mg/L to adjust the pH to 9. In field application, 91 mg/L was actually required. This level of dosing and pH adjustment decreased manhole gas phase H₂S by 71 to 78 percent. Manhole odor levels in terms of D/T reduction decreased from 2,800 D/T to 300 D/T.

pH Adjustment Using Magnesium Hydroxide Orange County Sanitation District (2000) reported on dosing Thioguard (a proprietary magnesium hydroxide solution) into trunk sewers in southern California. The required dosing was 96 gallons MgOH per million gallons of wastewater. This reduced headspace H₂S concentrations by 86 to 98 percent. No discussion of broad-spectrum odor reduction was provided.

Caustic pH Shocking Crowley et al. (2002) reported on pH shocking on a pump station force main in North Carolina. A 3-mile-long, 30-in.-diameter ductile iron force main discharged into a 9.15-ft drop into a manhole where H₂S odors were released. In this instance, pH shocking up to 12 for 20 minutes or more got rid of H₂S odor emissions but only for 4 days. It took 3 mL per 1,000 mL of 25 percent caustic added to wastewater to raise the pH to 12. This reduced the dissolved sulfide by only 43 percent but virtually removed gas phase sulfides that came back in 4 days. This was reinforced in findings provided by Walton et al. (2003), indicating that partial biofilm recovery (33 to 55 percent) occurred within 1 to 2 days, and complete recovery was observed in 3 to 4 days. This was also reported by Hamilton et al. (1992).

Jin (1987) reported results of sodium hydroxide shocking on large-diameter sewers in southern California. This study focused on large-diameter (51 in. to 144 in.) gravity sewers in order to determine the economic impacts of this approach to odor and corrosion control. Projected chemical costs from this 1987 study were estimated to be nearly \$15 million annually to achieve 95 percent control of dissolved sulfide. The paper also describes the history of the pH-shocking program and indicates that initial shocking was attempted with lime slurries but that doing so did not prove effective and was problematic because of the settling of the slurry solids, which caused sewer-cleaning problems. The overall program was changed in favor of using caustic solutions delivered from trucks.

The literature reports that in most instances, caustic shocking would have to be repeated every 1 to 2 weeks. This research recommended three treatments a week at 12.6 pH to achieve 90 percent control of dissolved sulfide. Raising the pH above 13 showed further reduction, but recovery was still complete within 2 weeks. Gas phase reductions were significantly less. For instance, if dissolved sulfides were reduced 74 percent, then gas was reduced 48 percent. It was also noted that caustic treatment did not affect the crown pH on the concrete surface. This paper (Jin 1987) reported a wide range in recovery of 38 to 100 percent slime layer recovery within 7 days and complete recovery in 2 weeks. Dissolved sulfide reduction plots in this study indicate the levels can return within 3 days. Figure 7-10 is a copy of the testing reported for smaller-diameter (approximately 24 in.) sewers. Similar results were reported for larger-diameter ones.

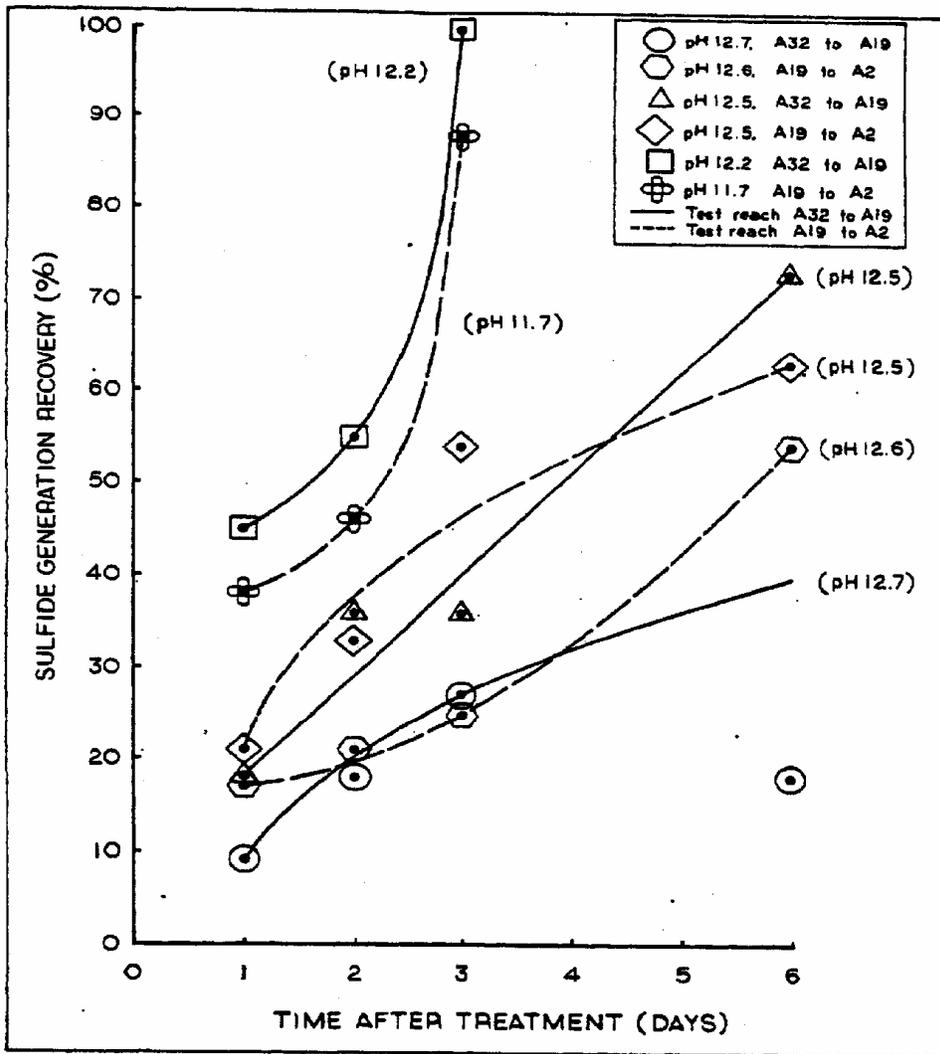


Figure 7-10. Sulfide Generation Recovery in Joint Outfall "A" with Caustic Treatment

7.7.2.4 Downstream Treatment Plant Effects

Melbourne Water (1989) indicates that wastewater with a pH level above 9.0 entering a downstream treatment plant can be harmful to biological processes, such as an activated sludge or fixed film treatment system. Dao (2004) indicated that periodic shock dosing upstream of a treatment plant in California was linked to "frequent episodes of effluent quality deterioration."

7.7.3 Liquid Phase Biological Treatment

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

Two main types of biological treatment methods have been marketed and applied with varying degrees of success. One method, bioaugmentation, seeks to deluge a collection system with bacteria specially bred to oxidize sulfide as it is generated, thereby reversing the natural anaerobic conversion of sulfate to sulfide. The second method, enzymatic treatment, uses substances that either interrupt the bacterial metabolic process that converts sulfate to sulfide or enhance enzymatic activity of microbes that oxidize sulfide.

7.7.4 Bioaugmentation

Four papers in the literature search provided information on the effectiveness of bioaugmentation. Sercombe (1995) studied several liquid phase treatment methods for reducing hydrogen sulfide at six locations within a large sewer network in England. A proprietary brand of bacteria called Bio-Act was applied at one of the treatment works over 6 months. An initial large dose used to establish the bacteria was followed by lower maintenance doses. The paper does not detail which processes were dosed or wastewater flow rates. However, sulfide was reduced from 4 mg/L to an average concentration of 1 mg/L. Also, H₂S gas was reduced from 500 ppm to less than 100 ppm in the primary-tank desludging chamber.

In another bioaugmentation study, Richman (1997) described a treatment program used in Tampa, Florida, to reduce odors by using a combination of ozonation and a patented in-pipe technology. The city claims to have saved \$175,000 in odor control costs. However, the paper does not differentiate between savings due to ozonation and savings due to bioaugmentation.

Nowak et al. (2004) reported on work in Vienna, Austria, collection systems where using bacterial preparations was attempted. The specific products were not identified, but the study indicated that none of the products achieved significant H₂S or odor reduction. Van Durme and Berkenpas (1989) reported on trials of bacterial cultures in Arizona collection systems. They reported no reductions in either dissolved or gaseous sulfide and no noticeable downstream impacts (positive or negative) to the treatment plant.

7.7.5 Enzymatic Treatment

One of the best-known enzymatic treatment methods is anthraquinone, an aromatic ketone reported to block metabolic pathways for sulfate-reducing bacteria. Schneller et al. (2001) reported that anthraquinone binds with a protein that is unique to sulfide-reducing bacteria. Harshman (2003) more specifically reports that anthraquinone interrupts sulfate reduction by interacting with the cytochrome c3 location in the cytoplasmic membrane.

Anthraquinone is also added to some of US Filter's nitrate-based products as an enhancement and distributed under the name Bioxide-AQ. Two field studies testing anthraquinone alone report that it had no effect on dissolved sulfide concentration (Hamilton et al., 1992; Van Durme and Berkenpas, 1989). Wolstenholme et al. (2004) reported on a comparison of Bioxide (calcium nitrate) alone to the combination of Bioxide and anthraquinone (Bioxide-AQ). This work was done on a force main discharge from a naval station receiving waste from docked naval ships. Although dosing duration was not discussed, this paper indicated that when anthraquinone was added, there was no significant difference reported in the odor levels at the force main discharge.

Hamilton et al. (1992) reported that anthraquinone dosed at 10 mg/L inhibited sulfide generation in laboratory tests, but follow-up field dosing of up to 480 mg/L provided no reduction in dissolved or gaseous sulfide on collection systems in southern California. In this

field testing the anthraquinone was only dosed for 30 minutes. This may indicate that batch treatment of anthraquinone is not effective.

In one of the few studies in which a biological treatment method was tried alone, Onondaga County Department of Drainage and Sanitation (2001) reported the results of treating a sanitary sewer with an enzyme blocker called Enzybate-E. Enzybate-E was dosed at 20 ppm for approximately 1 month. While some sulfide reduction was observed, an optimal dose could not be determined from the study, and the product was not determined to be cost-effective for controlling sulfide.

OrTec is a product that uses enzymes and nutrients to enhance the ability of bacteria to oxidize odor-causing compounds. In two studies (OrTec, 2002a, 2002b), wastewater was sparged with nitrogen while DO and OrTec concentrations were varied. The studies showed a decrease in ammonia and D/T concentrations due to the OrTec addition. However, these experiments were carried out in small test tubes for over 30 days, and results were not separated from the effect of BOD consumption. Kim (2004) studied the ability of OrTec to inhibit biofilm development on a column of glass beads dosed with wastewater and OrTec. The treated column had a biofilm mass reduction of 50 percent compared with the control.

Based on this review, the effectiveness of these types of compounds is unclear at best and requires further investigation. Pilot testing would be required in all cases.

7.8 Dosing Summary and Supplier Information

Table 7-2 summarizes dosage information for each liquid phase odor control method. Some chemicals have a wide dosage range. This is representative of the varying results of field- and bench-scale studies. Closer estimates of chemical doses needed for certain applications should be obtained by running a bench-scale test on actual wastewater samples. If possible, bench-scale testing is recommended.

Table 7-2. Dosage Information from Liquid Phase Odor Control Methods

Chemical	Concentration (% by weight)	Solution Density (lb/gal.)	Dose (lb/lb of Sulfide Removed)	
			Low	High
Pure O ₂	95	gas	Not directly comparable to other chemicals	
Cl ₂ gas	100	gas	4	15
NaOCl	15	9.7	10	15
H ₂ O ₂	50	10.0	1	4
KMnO ₄	5	8.7	6	7
NaMnO ₄	20	9.8	7	8
FeCl ₂	30	10.0	4	12
FeSO ₄	6	10.0	5	14
FeCl ₃	40	10.8	3	7
Ca(NO ₃) ₂	60	12.1	4	15
NaOH	50	11.4	Doses must be compared to other methods on a case-by-case basis as they are not directly related to sulfide concentration alone	
Mg(OH) ₂	63	13.3		

7.9 Research Agenda Items

Several potential research gaps were identified with relationship to liquid phase treatment. They are highlighted at the end of this chapter. More-detailed research gap ranking and testing protocols are provided in the final chapter of this report.

7.9.1 Life-Cycle Analysis of Collection System Chemical Addition Impacts on Downstream Processes

Liquid phase treatment of wastewater to remove dissolved sulfides usually involves adding significant quantities of chemicals; several classes of chemical are used. Chemical oxidants (for example, hydrogen peroxide and sodium hypochlorite) are used to oxidize sulfide to sulfate or sulfur, iron salts are used to precipitate sulfide to an insoluble solid form, nitrate is added to prevent sulfide from forming, and pH adjustors (for example, magnesium hydroxide) are used to prevent sulfide from entering the gas phase.

Many of the chemicals used in liquid phase treatment may have side-effects on the downstream treatment plant and receiving waters. For example, chlorine used to oxidize sulfide may have a residual disinfectant effect on activated sludge processes, and iron salts can increase sludge production. Nitrate addition may increase the nitrogen load on the plant. Some chemical suppliers claim that their products have beneficial side effects on downstream processes. For example, a supplier of magnesium hydroxide claims that their product improves flocculation in the primary clarifier.

7.9.1.1 Problem Statement

Although effects of chemical addition on downstream processes have been reported anecdotally, little quantitative information on these effects is available. In particular, the life-cycle analysis (LCA) of protecting infrastructure and preventing emissions verses downstream wastewater treatment impacts are unknown. A study is needed to quantify the downstream effects of adding chemicals to the collection system and compare their performance using an LCA framework that calculates technical options based on economic, social, and environmental parameters. LCA is an ISO-standardized framework for the comparison of alternative products or services from an environmental perspective. The fundamental idea behind LCA is much broader than that behind life-cycle costing and consists of assessing all the physical and energetic flows that occur as a consequence of the selection of a particular process (see below).

7.9.1.2 Research Proposal

The objectives of the proposed study are the following: (1) Identify effects on the downstream processes of commonly used chemicals added to collection systems; (2) develop LCA framework; and (3) quantify effects of chemical dosing on wastewater treatment using LCA.

7.9.2 Pure Oxygen Treatment of Gravity Sewers

Pure oxygen injection has been employed to prevent sulfide generation in force mains. Pressurized pipes flowing full allow much higher oxygen concentrations (and fewer injection stations) than can be applied in gravity sewers. Because of the high unit costs for transporting oxygen and high capital costs for onsite generation, oxygen injection into gravity sewers is usually ruled out. However, small-scale pressure swing adsorption (PSA) could enable oxygen injection spaced frequently enough along gravity sewers to prevent anaerobic conditions from developing between injection points.

7.9.2.1 Problem Statement

If oxygen-generating equipment could be made small enough, oxygen injection could save money by replacing chemical addition in gravity sewers. A study is needed to determine the feasibility of developing small PSA units for frequent spacing along gravity sewers.

7.9.2.2 Research Proposal

The objectives of the proposed study are the following: (1) Calculate the range of oxygen generation capacity appropriate for controlling sulfide generation in 0.5-mgd and larger gravity sewers; (2) identify technical and market obstacles preventing PSA manufacturers from developing small-scale PSA systems; and (3) determine the feasibility of introducing a small-scale PSA system to the odor control market.

7.9.3 Magnesium Hydroxide Odor Control Mechanisms Other Than pH Adjustment

Magnesium hydroxide $Mg(OH)_2$ is a common chemical used to prevent sulfide release in sewers. It works primarily as a pH adjuster, raising wastewater pH to between 8.5 and 9. In this pH range, sulfide tends to remain in solution, where it does not cause odor and corrosion problems. Magnesium hydroxide is less soluble, however, than other pH adjusters, for example, caustic soda and lime. As such, it buffers the pH rather than quickly reacting, a favorable characteristic.

Whereas the pH adjustment effects of magnesium hydroxide are generally accepted in engineering practice, other, less-well-understood benefits have been observed and attributed to the chemical. Premier Chemical, a supplier of magnesium hydroxide, claims that sulfide complexes with Mg^{2+} ions form a suspension that keeps its form during treatment processes. This action is purportedly similar to sulfur precipitation by iron salts and results in sulfide removal as well as pH adjustment. Premier Chemical also claims that Mg^{2+} catalyzes the oxidation of dissolved sulfides. The rate of sulfide oxidation is believed to increase approximately two to three times in the presence of magnesium ion.

7.9.3.1 Problem Statement

Although sulfide removal by magnesium hydroxide has been observed anecdotally, independent research has not been carried out to verify the claims of chemical suppliers. Therefore, an independent study is needed to establish the mechanisms responsible for sulfide removal by magnesium hydroxide and to quantify dosages that can be used to design chemical treatment systems.

7.9.3.2 Research Proposal

The objectives of the proposed study are the following: (1) Experimentally determine chemical mechanisms responsible for sulfide removal by magnesium hydroxide; (2) verify or debunk existing theories about sulfide removal mechanisms; and (3) quantify dosage rates for sulfide removal by magnesium hydroxide.

7.9.4 Liquid Phase Biological Treatment

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

Three main types of biological treatment methods have been marketed and applied with varying degrees of success. One method, bioaugmentation, seeks to deluge a collection system with bacteria specially bred to oxidize sulfide as it is generated, thereby reversing the natural anaerobic conversion of sulfate to sulfide. Another method, enzyme blocking, uses substances to

interrupt the bacterial metabolic process that converts sulfate to sulfide. The third method, nitrate addition, seeks to supply sulfate-reducing bacteria with an alternate electron acceptor, whereby bacteria convert nitrate to N₂ gas instead of sulfate to sulfide.

7.9.4.1 Problem Statement

Whereas the effectiveness of nitrate addition is well documented both in practice and in the technical literature, the effectiveness of the other two biological treatment methods has not been sufficiently verified or documented. In some reports, the effectiveness of biological methods (other than nitrate) was inconclusive (Onondaga County Department of Drainage and Sanitation, 2001). In others, biological treatment methods were tested concurrently with nitrate or chemical methods, and the contribution of bioaugmentation or enzyme blocking could not be determined (Arthur and Anker, 2000; Kim et al., 2005). In still other studies, anecdotal reports of the effectiveness of biological treatment methods are provided without showing data or system characteristics (Sercombe, 1995).

Owing to the prolific patenting and marketing of bioaugmentation and enzyme-blocking products, there is a need for systematic research verifying the effectiveness, or lack thereof, of these biological methods. Needed is an independent study that tests leading biological methods under realistic conditions, without the influence of other methods. All relevant parameters should be reported and the duration of the study should allow sufficient time to arrive at conclusive results.

7.9.4.2 Research Proposal

Objective The objectives of the proposed study are the following: (1) Identify the leading biological treatment methods (excluding nitrate addition, which has already been sufficiently tested); (2) conclusively determine the level of effectiveness of each leading product, (3) and determine the applications and doses for products determined to be effective.

Program The program of research would consist of the following three phases: study design, pilot-scale testing, and results documentation.