



---

# The use of iron salts to control dissolved sulfide in Districts' trunk sewers

Navnit Padival

# Table of Contents

	Page
LIST OF FIGURES .....	4
LIST OF TABLES .....	8
ABSTRACT .....	9
<b>1 INTRODUCTION .....</b>	<b>10</b>
1.1 Sewer Crown Corrosion .....	10
1.1.1 General .....	10
1.1.2 Sulfide Corrosion: The Problem .....	10
1.2 The Bugs .....	10
1.2.1 Sulfate-Reducing Bacteria .....	10
1.2.2 Sulfur-Oxidizing Bacteria .....	12
1.3 Aqueous Chemistry of Sulfur Compounds .....	12
1.3.1 General .....	12
1.3.2 Speciation of H <sub>2</sub> S .....	12
1.4 Predicting Sulfide Generation .....	14
1.5 The Los Angeles County Sanitation Districts' Case .....	14
1.5.1 General .....	14
1.5.2 Intensification of Corrosion Problem .....	14
1.5.3 Treatment Efforts to Mitigate Corrosion .....	16
1.6 Theoretical Considerations .....	16
1.7 Previous Investigations .....	18
1.7.1 General .....	18
1.7.2 City of San Jose, CA .....	18
1.7.3 City of Mesa, AZ .....	18
1.7.4 City of Elgin, IL .....	20
1.7.5 Cities of Clearwater, Naples, and Boynton Beach, FL .....	20
1.7.6 Los Angeles County Sanitation Districts, CA .....	20
1.7.7 Greater Vancouver Regional District, Canada .....	22
1.8 Objectives of the Study .....	22
<b>2 MATERIALS AND METHODS .....</b>	<b>24</b>
2.1 Chemicals .....	24
2.2 Equipment Description .....	24
2.2.1 General .....	24
2.2.2 Chemical Storage Tanks .....	26
2.2.3 Control Valves .....	26
2.2.4 Magnetic Inductive Flowmeter (MIF) .....	26
2.2.5 Air Compressor .....	26

2.2.6	Spill Containment . . . . .	26
2.3	Analytical and Chemical Techniques . . . . .	31
2.4	<b>Monitoring and Testing Procedures . . . . .</b>	<b>31</b>
2.4.1	General . . . . .	31
2.4.2	Monitoring Locations . . . . .	31
2.4.3	Testing . . . . .	33
<b>3</b>	<b>RESULTS AND DISCUSSION . . . . .</b>	<b>34</b>
3.1	General . . . . .	34
3.2	Dissolved Sulfide . . . . .	34
3.3	Total Sulfide . . . . .	41
3.4	Hydrogen Sulfide . . . . .	45
3.5	Sewer Odors . . . . .	50
3.6	Crown pH and Sewer Corrosion . . . . .	50
3.7	Total and Soluble Iron . . . . .	54
3.8	Affect of Iron Addition at SJCWRP on Chemical Use and Sulfide Control in J.O. "B" . . . . .	54
<b>4</b>	<b>CONCLUSIONS . . . . .</b>	<b>57</b>
<b>5</b>	<b>ECONOMICS . . . . .</b>	<b>58</b>
<b>6</b>	<b>REFERENCES . . . . .</b>	<b>62</b>

# List of Figures

---

Figure 1	Process occurring in sewers under sulfide buildup conditions .....	11
Figure 2	Proportions of H <sub>2</sub> S and HS in dissolved sulfide .....	13
Figure 3	A general map of the Los Angeles County Sanitation Districts Joint Outfall Trunk Sewers .....	15
Figure 4	A general map of J.O. "B" and a portion of J.O. "H" Trunk Sewer Systems showing the test locations .....	23
Figure 5	Schematic layout of the Sulfide Control Facility at the SJCWRP .....	27
Figure 6	Ferric and Ferrous Chloride Dosing Facility at the San Jose Creek Water Reclamation Plant .....	28
Figure 7	A view of the flow control valve and bypass line, looking west .....	28
Figure 8	Primary element of the Altoflux Compact Magnetic Inductive Flowmeter located just downstream of the storage tank discharge valve and upstream of the control valves .....	29
Figure 9	A view of the LCD totalizer on the secondary element of the flowmeter, located on the outside of the containment wall to the north .....	29
Figure 10	A view of the compressor and the line connections .....	30
Figure 11	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows average dissolved sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 10 mg/L and four different blend ratios .....	36
Figure 12	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows average dissolved sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 12 mg/L and four different blend ratios .....	36

Figure 13	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows average dissolved sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 14 mg/L and four different blend ratios .....	37
Figure 14	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows average dissolved sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 16 mg/L and four different blend ratios .....	37
Figure 15	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows average dissolved sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 18 mg/L and four different blend ratios .....	38
Figure 16	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows dissolved sulfide levels at monitoring locations along the 25 mile test reach, using a total Fe concentration of 16 mg/L and a blend ratio of 1.9:1, and without treatment .....	38
Figure 17	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows average total sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 10 mg/L and four different blend ratios .....	42
Figure 18	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows average total sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 12 mg/L and four different blend ratios .....	42
Figure 19	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows average total sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 14 mg/L and four different blend ratios .....	43

<b>Figure 20</b>	<b>Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows average total sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 16 mg/L and four different blend ratios .....</b>	<b>43</b>
<b>Figure 21</b>	<b>Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows average total sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 18 mg/L and four different blend ratios .....</b>	<b>44</b>
<b>Figure 22</b>	<b>Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows total sulfide levels at monitoring locations along the 25 mile test reach, using a total Fe concentration of 16 mg/L and a blend ratio of 1.9:1, and without treatment .....</b>	<b>44</b>
<b>Figure 23</b>	<b>Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows average hydrogen sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 10 mg/L and four different blend ratios .....</b>	<b>47</b>
<b>Figure 24</b>	<b>Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows average hydrogen sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 12 mg/L and four different blend ratios .....</b>	<b>47</b>
<b>Figure 25</b>	<b>Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows average hydrogen sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 14 mg/L and four different blend ratios .....</b>	<b>48</b>
<b>Figure 26</b>	<b>Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows average hydrogen sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 16 mg/L and four different blend ratios .....</b>	<b>48</b>

<b>Figure 27</b>	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows average hydrogen sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 18 mg/L and four different blend ratios . . . . .	49
<b>Figure 28</b>	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows hydrogen sulfide levels at monitoring locations along the 25 mile test reach, using a total Fe concentration of 16 mg/L and a blend ratio of 1.9:1, and without treatment . . . . .	49
<b>Figure 29</b>	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer odor levels. Graph shows average odor levels at three monitoring sites along the test reach, using a total Fe concentration of 10 mg/L and four different blend ratios . . . . .	51
<b>Figure 30</b>	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer odor levels. Graph shows average odor levels at three monitoring sites along the test reach, using a total Fe concentration of 12 mg/L and four different blend ratios . . . . .	51
<b>Figure 31</b>	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer odor levels. Graph shows average odor levels at three monitoring sites along the test reach, using a total Fe concentration of 14 mg/L and four different blend ratios . . . . .	52
<b>Figure 32</b>	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer odor levels. Graph shows average odor levels at three monitoring sites along the test reach, using a total Fe concentration of 16 mg/L and four different blend ratios . . . . .	52
<b>Figure 33</b>	Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer odor levels. Graph shows average odor levels at three monitoring sites along the test reach, using a total Fe concentration of 18 mg/L and four different blend ratios . . . . .	53

## List of Tables

---

<b>Table 1</b>	<b>Solubility of Various Iron Complexes in Wastewater Streams .....</b>	<b>19</b>
<b>Table 2</b>	<b>Performance of Ferrous Sulfate for Sulfide Control in Florida .....</b>	<b>21</b>
<b>Table 3</b>	<b>Ferric Chloride and Ferrous Chloride Safety Data .....</b>	<b>25</b>
<b>Table 4</b>	<b>Distribution of Background Parameters in the Sewage Prior to Treatment with Iron Chloride .....</b>	<b>35</b>
<b>Table 5</b>	<b>Percentage Reductions in Sulfide Parameters During the Full Scale Optimization and Treatment .....</b>	<b>40</b>
<b>Table 6</b>	<b>Distribution of Average Total Iron and Soluble Iron in the Joint Outfall "B" .....</b>	<b>55</b>
<b>Table 7</b>	<b>Effectiveness and Costs Associated with Various Sulfide Control Methods .....</b>	<b>59</b>
<b>Table 8</b>	<b>Calculated Chemical Requirements and Associated Total Chemical Costs .....</b>	<b>60</b>
<b>Table 9</b>	<b>Annual Chemical and Operation &amp; Maintenance Costs to treat Districts' Major Joint Outfalls with Iron Chloride .....</b>	<b>61</b>

# Abstract

---

Biogenic corrosion of sewage collection system concrete sewers and structures and treatment plant concrete structures is a concern for the wastewater agencies in the United States, Germany, Japan, the Soviet Union, and many other places in the world. Within the Los Angeles County Sanitation Districts (the Districts) sewer system alone, repair and replacement activities, attributable to crown corrosion, will cost about \$150 million prior to the turn of the century.

The corrosion of sewers is a two-step, biological process. The first step occurs below the sewer hydraulic gradeline, where anaerobic conditions can exist. There, sulfate-reducing bacteria reduce  $\text{SO}_4^{2-}$  ions in the wastewater to  $\text{S}^{2-}$  in the anaerobic slime layer on continuously wetted pipe walls. Sulfide diffuses into the bulk fluid. At neutral pHs, the aqueous sulfide partitions between  $\text{HS}^-$  ion and dissolved  $\text{H}_2\text{S}$  gas. The dissolved  $\text{H}_2\text{S}$  gas can volatilize into the sewer headspace. The second step occurs above the sewer hydraulic gradeline, typically at the pipe crown, where the available  $\text{H}_2\text{S}$  gas is biologically oxidized to  $\text{H}_2\text{SO}_4$  by sulfur-oxidizing bacteria. This acid attacks the cement binder in the concrete leading to corrosion, sewer deterioration, and eventual loss of the pipe load carrying capacity.

Sulfide generation and crown corrosion rates increased markedly in the Districts concrete trunk sewers during the years following the institution of industrial waste pretreatment requirements. Measured rates of crown deterioration may be directly correlated with gas and liquid phase sulfide and metals concentrations in the same sewers. Sulfide control became a major concern for the Districts after pretreatment programs reduced the overall metals concentration by at least 65%.

Salts of many metals, including those of iron, zinc, and copper, react with dissolved sulfide to form insoluble metallic sulfide precipitates, thus significantly reducing release of  $\text{H}_2\text{S}$  to the sewer headspace. For this to be fully effective, the metal sulfide formed must be highly insoluble. Addition of iron salts to control sulfide and odor in sewers has been practiced since the 1920s. Zinc is no longer recommended because of its potential negative effects on downstream treatment processes. Copper is costly and environmentally controlled.

The removal of headspace  $\text{H}_2\text{S}$  via the precipitation of dissolved sulfide was investigated using iron chloride. Full-scale experiments were conducted in a 25-mile sewer with an average flow of 200 MGD. Results were sensitive to the chemical dosages and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  blend ratios used. A concentration of 16 mg/L Fe and a blend ratio of 1.9:1 ( $\text{Fe}^{3+}:\text{Fe}^{2+}$ ) reduced dissolved sulfide levels by 97%. Total sulfide and headspace  $\text{H}_2\text{S}$  were also reduced by 63 and 79%, respectively. Liquid and gas phase sulfide reductions were largely owed to the effective precipitation of sulfide and the limited volatilization of  $\text{H}_2\text{S}$  gas, respectively. The catalytic oxidation of  $\text{S}^{2-}$  in the presence of  $\text{Fe}^{2+}$  and minute amounts of  $\text{O}_2$  may have occurred. The combined use of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  proved more effective than either salt alone. No specific relation between the concentration of Fe or  $\text{Fe}^{3+}/\text{Fe}^{2+}$  blend ratio and crown pH was inferred. Iron salts may retard crown corrosion rates by precipitating free sulfide, thus reducing its release to the sewer headspace as  $\text{H}_2\text{S}$  and/or by inhibiting responsible bacteria.

## 1.1 Sewer Crown Corrosion

1.1.1 General. Concrete corrosion due to the biological reduction and oxidation of sulfur compounds is a concern for the design and operation of sewage collection systems and treatment plants (ASCE, 1989; Parker, 1947; and Thistletonwayte, 1972). Corrosion of concrete sewers is encountered throughout the world. Severe problems are not confined to warm climates. Rapid corrosion rates have been reported in northern Germany, Sweden, and cold-weather portions of the Soviet Union (Holmstrom and Wilander, 1977; Rozhanskaya *et al.*, 1977; and Sand *et al.*, 1983). A recently completed multicity survey conducted for the Environmental Protection Agency suggests that evidence of biogenic sewer corrosion is present in many municipal sewerage systems within the U.S. (Witsgall *et al.*, 1989). Corrosion is especially severe in the Los Angeles County Sanitation Districts (the Districts) Trunk Sewer System. At the Districts, repair or replacement of excessively corroded sewerage facilities has already cost about \$50 million (Redner, 1992).

1.1.2 Sulfide Corrosion: The Problem. The generation of acid in sewer crowns and the related pipe corrosion is a two-step process. The kinetics of both steps are microbially controlled. Local chemical and physical conditions are determinants of specific rates of microbial activity. Sulfate ( $\text{SO}_4^{2-}$ ) ions in wastewater are reduced to sulfide ( $\text{S}^2-$ ) by the sulfate-reducing bacteria (SRB) in the anaerobic slime layer on continuously wetted pipe walls. At pHs most common to wastewater, an appreciable fraction of the  $\text{S}^2-$  so generated is present as hydrogen sulfide ( $\text{H}_2\text{S}$ ). Volatilization enables  $\text{H}_2\text{S}$  gas to reach the sewer crown, where, in the presence of molecular oxygen ( $\text{O}_2$ ) and moisture,  $\text{S}^2-$  is reoxidized to  $\text{SO}_4^{2-}$  with the attendant production of sulfuric acid ( $\text{H}_2\text{SO}_4$ ). The latter process is catalyzed by the sulfur-oxidizing bacteria (SOB) (Figure 1). This reaction is illustrated below:



The acid attacks the cement binder in the concrete pipe causing progressive disintegration and eventual loss of the pipe load carrying capacity.

## 1.2 The Bugs

1.2.1 Sulfate-Reducing Bacteria. In the sewer environment, two genera of SRB, *Desulfovibrio* and *Desulfotomaculum*, are responsible for  $\text{S}^2-$  production via dissimilative reduction of  $\text{SO}_4^{2-}$  (Postgate, 1959; Pfennig *et al.*, 1971; Stanier *et al.*, 1976; and Sand, 1987). They are strict anaerobes and are unique due to their massive  $\text{S}^2-$  producing ability.

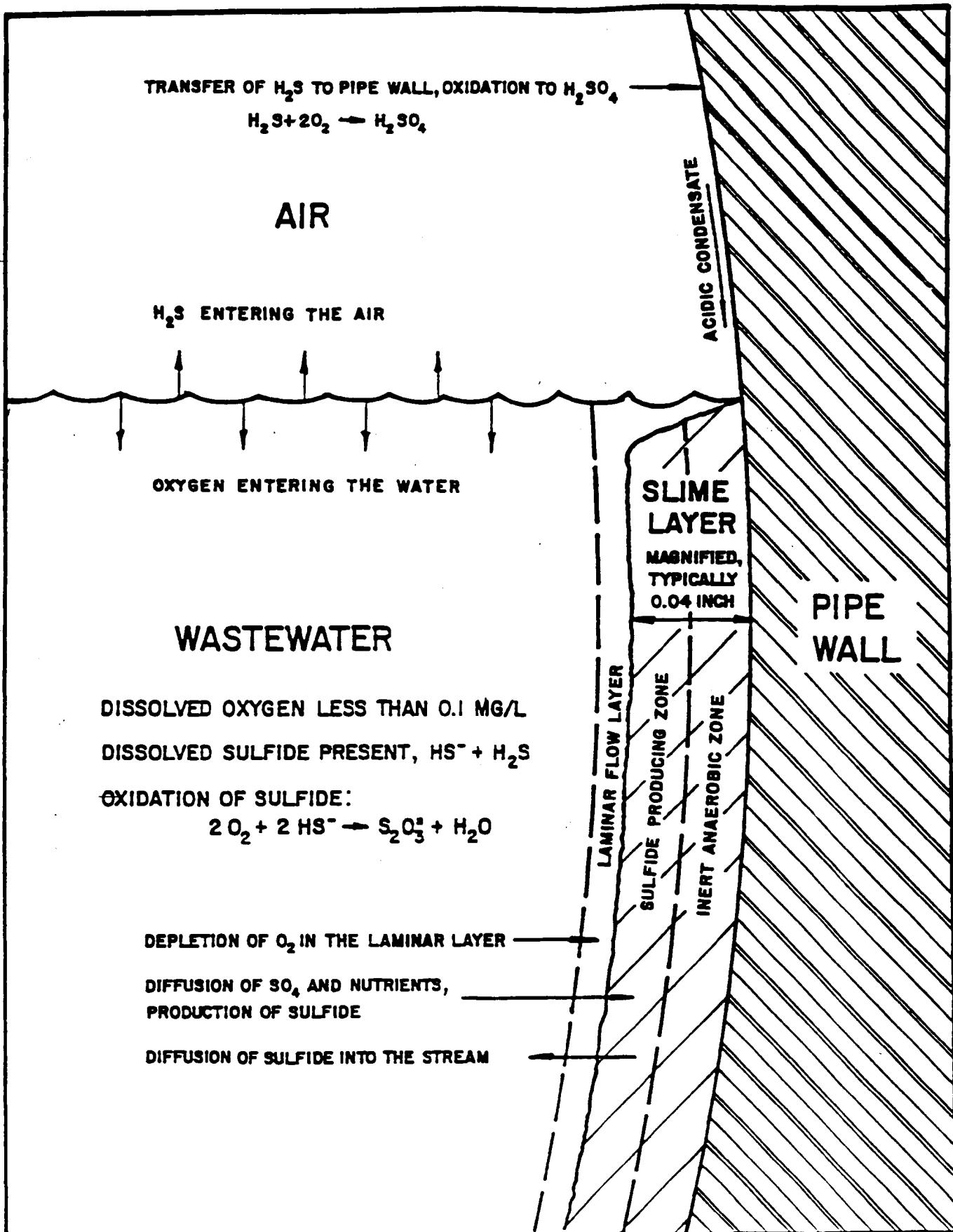


FIGURE 1. Process Occurring in Sewers Under Sulfide Buildup Conditions (U.S. EPA, 1974).

**1.2.2 Sulfur-Oxidizing Bacteria.** The obligately aerobic, chemolithoautotrophic acidophile *Thiobacillus thiooxidans* is primarily responsible for the  $S^{2-}$  oxidation and  $SO_4^{2-}$  production. These bacteria oxidize inorganic sulfur compounds (such as  $H_2S$ ) for energy generation (Vishniac, 1974 and Kelly, 1981).

*T. thiooxidans* are present in large numbers in the Districts' sewage collection system (Price, 1989). Populations of  $10^7$  to  $10^9$  organisms/gram of corrosion product have been detected in samples collected from severely corroded Districts' sewers (Unpublished data, 1991). Similar findings have been reported by Milde *et al.* (1983) in the Hamburg Municipal sewer system, Germany.

### 1.3 Aqueous Chemistry of Sulfur Compounds

**1.3.1 General.** Domestic and industrial wastewaters contain one or several species of sulfur compounds. Of the thirty-plus inorganic and ionic sulfur species that exist, only six are thermodynamically stable in aqueous solution at 25°C and 1 ATM: bisulfate ( $HSO_4^-$ ), sulfur ( $S^0$ ), sulfate ( $SO_4^{2-}$ ), hydrogen sulfide ( $H_2S$ ), hydrosulfide ( $HS^-$ ), and sulfide ( $S^{2-}$ ). Other forms of inorganic sulfur such as polysulfides, polythionates, and thiosulfate also occur in the natural environment, but are considered to be thermodynamically unstable and generally not found in significant concentrations. Sulfite ( $SO_3^{2-}$ ) and thiosulfate ( $S_2O_3^{2-}$ ) are found in some industrial wastewaters (Garrles and Naeser, 1958).

**1.3.2 Speciation of  $H_2S$ .** Most odor and corrosion problems in sewerage systems are caused by  $H_2S$  gas. It has a pronounced rotten egg odor discernible in amounts as low as a few hundredths of a ppmv.

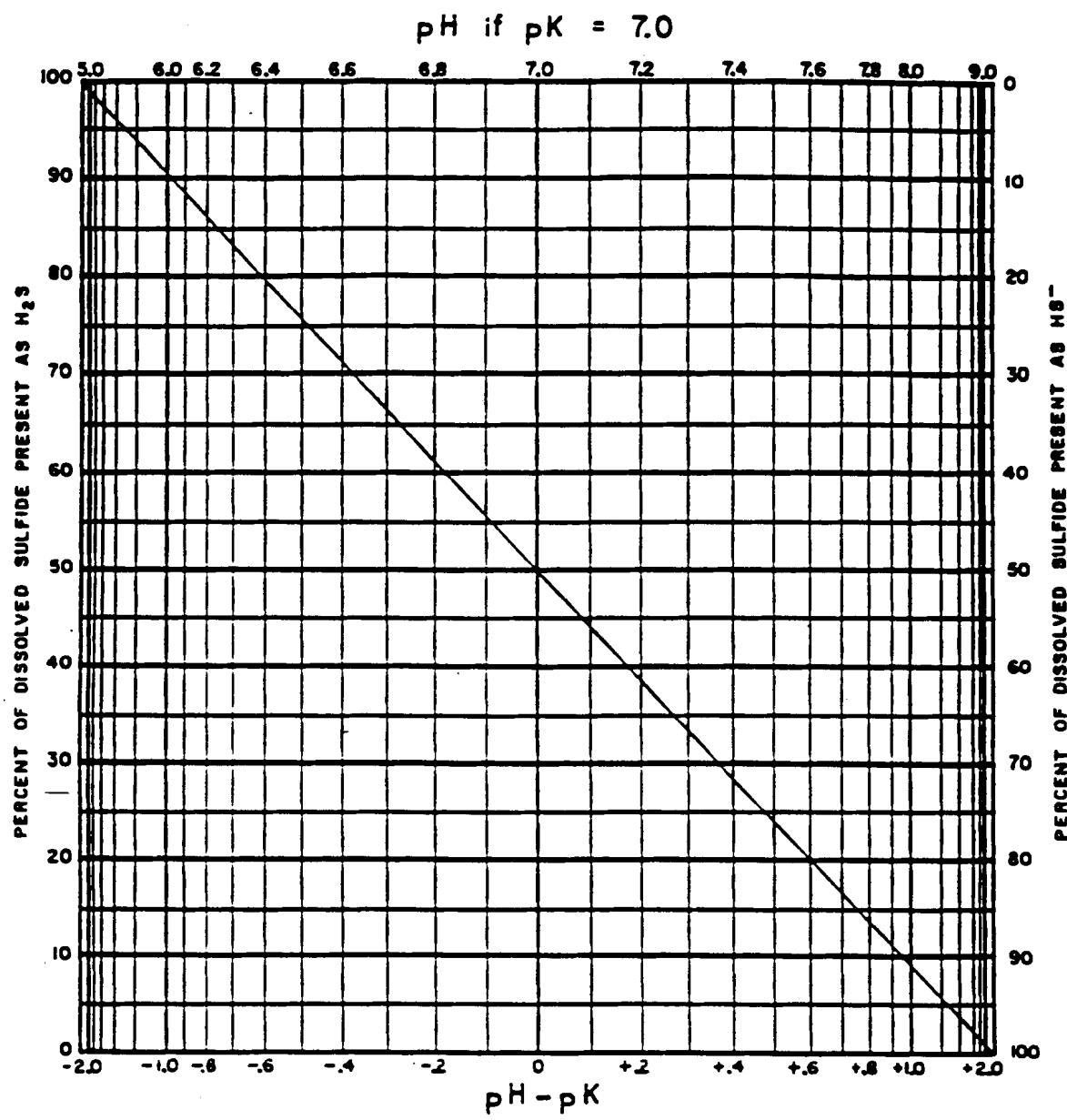
$H_2S$  is a weak acid that dissociates as follows:



Because this dissociation involves the hydrogen ion ( $H^+$ ), the existence of dissolved sulfide in wastewater is pH sensitive. At high pHs, free  $H^+$  ions combine with  $O_2$  from water and the reaction is forced to the right. At low pHs, with an abundance of  $H^+$  ions, the reaction is forced to the left.  $H_2S$  is the principal  $S^{2-}$  at pH 7 and below (typical of a sewer environment), but is virtually absent at pH 9 and above. Figure 2 shows this pH dependent relationship graphically.

The volatilization of  $H_2S$  gas under any condition is concentration dependent. Thus, at pH 7,  $H_2S$  will volatilize about half as fast as from a strong acid solution having the same dissolved sulfide content. At pH 9, it will escape only 1% as fast as from an equally acidic solution. If part of the  $H_2S$  gas escapes, the remaining dissolved sulfide will be divided between  $HS^-$  and  $H_2S$  in the same ratio as before, because the equilibrium re-establishes itself almost instantly.

When  $S^{2-}$  formation is occurring throughout a collection system, it will not accumulate if  $O_2$  or other oxidizing agents are available to oxidize it. Because wastewater typically contains large quantities of aerobic bacteria,  $O_2$  in the wastewater is rapidly depleted. This depletion is accelerated in sewers with little or no vertical grade, in partially impeded lines where velocities are not adequate to promote reaeration of the wastewater, and in surcharged sewers or force



**FIGURE 2.** Proportions of  $\text{H}_2\text{S}$  and  $\text{HS}^-$  in Dissolved Sulfide (U.S. EPA, 1974).

mains. Low velocities also promote settling of wastewater solids, further restricting flow and promoting S<sup>2</sup> formation (Pomeroy and Bailey, 1981).

#### 1.4 Predicting Sulfide Generation

Unlike current design procedures, traditional sewer design methods did not provide sufficient pipe wall thickness to withstand corrosion rates over its design life. Pomeroy and Parkhurst (1977) devised an empirical formula to predict sulfide generation in sewers flowing partially-full. Independent variables were derived from specific wastewater characteristics, flows, and physical parameters. Holder *et al.* (1983) used this model to calculate sulfide generation rates and steady, liquid-phase sulfide levels. The average annual concentration of total dissolved sulfide is used to predict corrosion rates (U.S. EPA, 1974). These equations are used in designing sewers to suppress SRB activity and control dissolved sulfide concentrations. Wall thickness is then relied upon to absorb tolerable corrosion rates. Alternative design methods are available for controlling corrosion, including the use of corrosion resisting pipe materials, but the utility of billions of dollars worth of unprotected sewerage facilities already in place depends on maintenance of low predictable corrosion rates.

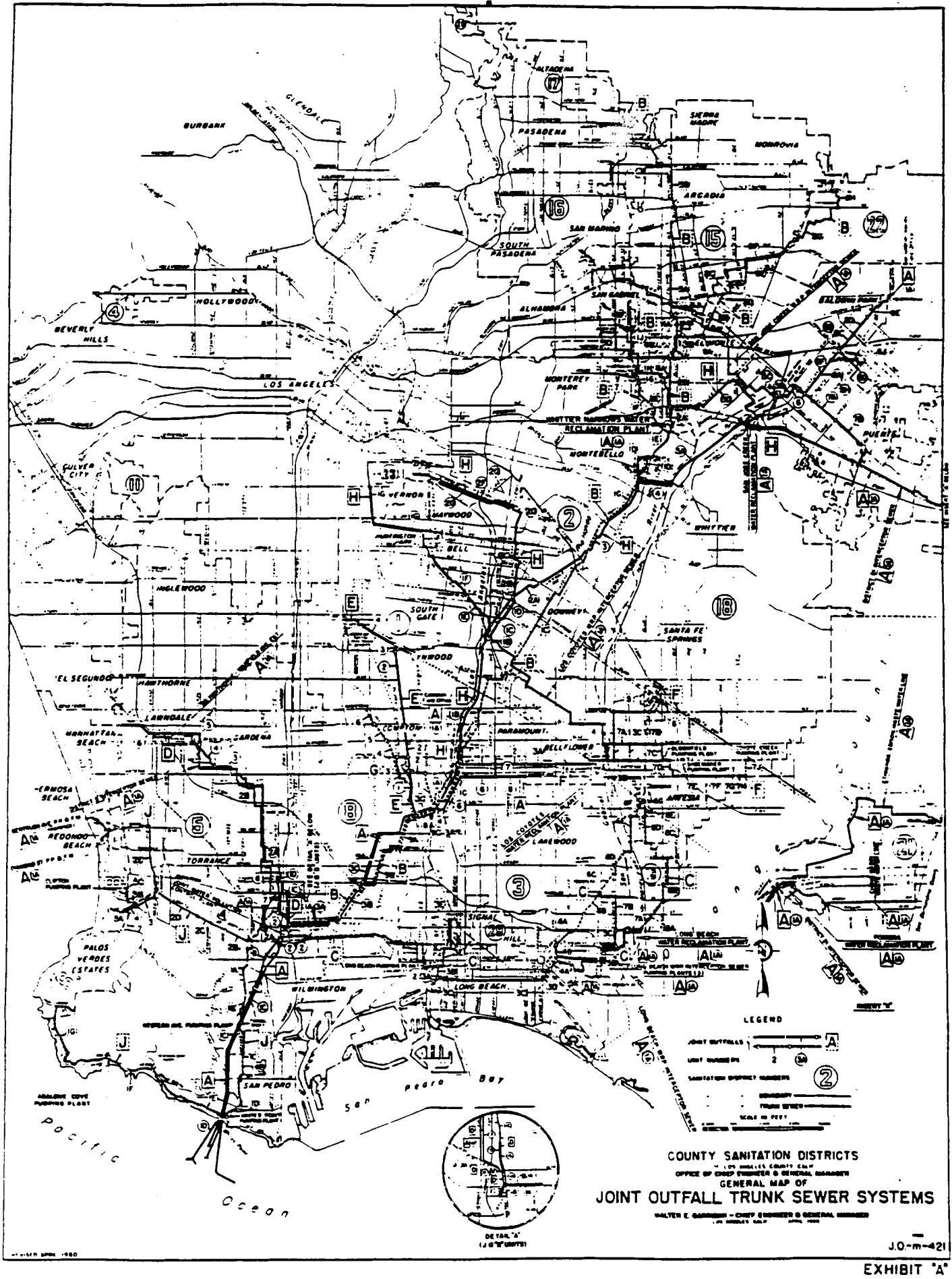
The Pomeroy-Parkhurst (1977) model was based on research conducted in the Districts' wastewater collection system. Therefore, it was not surprising that actual corrosion measured in the Districts' sewers closely matched the model predictions (Pomeroy *et al.*, 1985). The 1970's sewer inspections projected lives ranging from several decades to hundreds of years (Jin and Won, 1989). Subsequent monitoring in the 1980s, indicated that (i) dissolved sulfide concentrations were considerably higher than anticipated from the model and (ii) corrosion rates were far in excess of those predicted on the basis of the dissolved sulfide measurements.

#### 1.5 The Los Angeles County Sanitation Districts' Case

1.5.1 General. The Districts own and operate approximately 1,200 miles of trunk sewers ranging from 6 to 144 inches in diameter. These sewers are primarily constructed of reinforced concrete (RC) and vitrified clay, but include some non-reinforced concrete, and clay-tile lined RC. Rehabilitated sewers have been relined with reinforced thermosetting resin pipe (Hobas) and thermoplastic pipe (NuPipe, U-Liner, and Spirolite); inversion lined with thermosetting resin pipe (Instituform); and top encased with RC over PVC T-lock used as a corrosion barrier. New relief or replacement/relocation sewers have been constructed with PVC T-lock lined RC pipe. The main collection RC sewers range from 60 to 144 inches in diameter and carry peak flows from 45 to 280 MGD. Figure 3 is a general map of the Districts' Joint Outfall Trunk Sewer System.

Since its inception, the Districts have attempted to control sulfide-induced corrosion, from the initial use of clay-tile liners, through the design of adequate velocities along with sulfide control treatment in its tributaries. The philosophy was to control sulfide into the Joint Outfall System and to provide sufficient reaeration in the system to maintain aerobic conditions.

1.5.2 Intensification of Corrosion Problem. The wastewater quality significantly improved because (i) in the mid to late 1970s, ocean discharge regulations limited toxic metals concentrations to sewers, (ii) U.S. EPA implemented its categorical pretreatment regulation for industrial discharge to municipal sewers in the early 1980's, and (iii) the Districts implemented EPA's pretreatment requirements in conjunction with its own industrial waste pretreatment program (Martyn and Kremer, 1987). These regulations produced large reductions in



**FIGURE 3.** A general map of the Los Angeles County Sanitation Districts Joint Outfall Trunk Sewer Systems.

concentrations of potentially toxic metals contributed by metal finishing and electroplating industries. Sulfide control became a major concern after pretreatment programs reduced the overall metals concentration by at least 65%.

**1.5.3 Treatment Efforts to Mitigate Corrosion.** Full-scale attempts to impede corrosion include (i) caustic shock dosing, (ii) continuous treatment with iron salts, (iii) air injection in force mains to oxidize  $S^2$  in the wastewater, and (iv) caustic and sodium carbonate spraying of the sewer crowns. Experimental evaluations of  $S^2$  oxidation prior to its transport to the sewer headspace using hydrogen peroxide addition and oxygen were performed. Control of  $S^2$  transport to the sewer headspace by raising the sewage pH with the continuous addition of caustic was successfully tested, but is prohibitively expensive. The costs associated with the Districts' ongoing treatment programs are very high and have not been fully justified based on the effectiveness of treatment demonstrated, except for high-pH spraying of the crowns. Among the above mentioned treatment alternatives, control of sulfide by continuous addition of iron salts has been used since 1986.

## 1.6 Theoretical Considerations

This section sets forth principles on reactions between iron and sulfide in liquid phase. The most common basis is a consideration of equilibrium relations. A lack of specific data concerning iron-sulfide, solid-solution reactions makes the assessment of kinetic factors tedious. The literature mostly reports work done in ideal conditions, including wastewater characteristics (synthetic sewage). Wastewater quality could change significantly affecting the dissolution and precipitation reactions and related heterogenous equilibria.

The salts of many metals, including those of iron, zinc, and copper, react with dissolved sulfide to form metallic sulfide precipitates, thus reducing  $H_2S$  release to the sewer headspace. For this to be fully effective, the metal sulfide formed must be highly insoluble. Addition of iron salts to sewage to precipitate insoluble iron sulfide and to control dissolved sulfide levels has been practiced in a number of places since the 1920s (Pomeroy and Bowlius, 1946). Zinc was once used for sulfide control by both the City of Los Angeles (U.S. EPA, 1974) and the Districts (Won, 1988). The use of zinc is no longer recommended because of the potential negative effects on activated sludge treatment processes and on effluent quality. Copper is relatively costly and environmentally controlled.

Iron salts of chloride and sulfate have been added to wastewater collection systems either in the ferric or ferrous forms. Iron has generally been thought to become tightly bound to sulfide and other radicals in wastewater, thereby reducing its availability to form iron sulfide any distance downstream from the point of application. There have been applications, however, where the addition of iron held dissolved sulfide levels to a few tenths of a mg/L for distances up to 20 miles (Won, 1988).  $FeCl_3$  and  $FeCl_2$  have also been used in wastewater treatment to control the  $H_2S$  content of anaerobic digester gas (Dezham *et al.*, 1988).

Both  $Fe^{3+}$  and  $Fe^{2+}$  iron are effective in removing dissolved sulfide by precipitation. Several distinct iron sulfide complexes may form after iron addition, including pyrrhotite (varies from  $FeS$  to  $Fe_4S_5$ ), ferric sulfide ( $Fe_2S_3$ ), smythite ( $Fe_3S_4$ ), pyrite ( $FeS_2$ ), and marcasite (also  $FeS_2$ ) (U.S. EPA, 1974).  $Fe^{3+}$  iron can also remove  $S^2$  by directly oxidizing it to  $S^0$  (Pomeroy and Bowlius, 1946). In the course of this reaction,  $Fe^{3+}$  iron is reduced to  $Fe^{2+}$  (Dohnalek and

FitzPatrick, 1983). The  $\text{Fe}^{3+}$  formed is then precipitated as ferrous sulfide ( $\text{FeS}$ ). It is generally supposed that this reaction proceeds as follows:



In accordance with this equation, 7 parts of iron should precipitate 4 parts of sulfide. In this reaction, the  $\text{H}^+$  ion concentration has no significant effect within the pH range normally encountered in domestic sewage. However, the reaction is greatly influenced by the presence of traces of dissolved  $\text{O}_2$  (Pomeroy and Bowlius, 1946).

Further, the authors hypothesize that the presence of  $\text{O}_2$  or even any weak oxidizing agents assist the formation of iron disulfide ( $\text{FeS}_2$ ). This is suggested by the following reaction:



Not only does  $\text{O}_2$  accelerate the precipitation of iron sulfide complexes, but iron also catalyses the oxidation of  $\text{S}^{2-}$  even beyond the formation of  $\text{FeS}_2$ . In many instances, the decrease in total sulfide can be more than one-half the decrease in dissolved sulfide, thus more than would be accounted for merely by the formation of  $\text{FeS}_2$  (Pomeroy and Bowlius, 1946).

If a mixture of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  salts is added to sulfide-bearing water, better results may be obtained than with either salt alone. Presumably, such a reaction proceeds as follows:



Pomeroy and Bowlius (1946) report that a mixture of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  salts were more effective than either alone. By using only a few mg/L of excess  $\text{Fe}^{3+}$  iron,  $\text{S}^{2-}$  can be reduced to levels of 0.2-0.3 mg/L in the absence of aeration or to 0.1 mg/L with slight aeration. The most effective results were obtained with solutions containing about two-thirds of the iron in the  $\text{Fe}^{3+}$  form. This suggested the precipitation of  $\text{Fe}_3\text{S}_4$ , but no evidence is available to indicate that such a compound could be produced in this way. It may exist as an intermediate step in the transition pathway to  $\text{FeS}_2$ .

From the above equations and hypotheses on precipitation of iron sulfides, it would be expected that  $\text{Fe}^{3+}$  salts would be more effective than the  $\text{Fe}^{2+}$  compounds. However, Jameel (1989) reports that in practice, there is no such difference. In the complete absence of  $\text{O}_2$ , the  $\text{Fe}^{3+}$  salt is better than  $\text{Fe}^{2+}$ . But a little  $\text{O}_2$  greatly improves the effectiveness of  $\text{Fe}^{2+}$  salts and is without effect on the  $\text{Fe}^{3+}$ , so that under these conditions the relationship is reversed. Thus, the  $\text{Fe}^{2+}$  salts are better when added to a free-flowing sewer, where some  $\text{O}_2$  is always present. The principal effect of the  $\text{Fe}^{3+}$  salt, when added to sewage of low  $\text{S}^{2-}$  content, seems to be oxidation of the  $\text{S}^{2-}$  at the time of mixing; very little precipitation occurs unless the initial  $\text{S}^{2-}$  concentration exceeds 10 mg/L (Jameel, 1989). Similar findings have also been reported by Pomeroy and Bowlius (1946) and Dohnalek and FitzPatrick (1983).

The efficiency of sulfide removal using iron salts is normally less than that predicted by the solubility products for iron-sulfide systems. Iron can be consumed in precipitation reactions with one of a variety of anions to form sparingly soluble precipitates, including phosphate, carbonate, and hydroxide ions present in the wastewater. Iron can also hydrolyze water upon dissolution, resulting in the formation of charged, iron-hydroxide complexes.  $\text{Fe}^{2+}$  iron resulting from the dissolution of an iron salt, such as  $\text{FeCl}_2$ , actually can exist in equilibrium with several forms of hydroxylated iron ions. This equilibrium is pH dependent. Therefore,  $\text{Fe}^{2+}$  iron can also combine with the hydroxide ion to form soluble, charged complexes (Stumm and Morgan, 1970).

Table 1 presents a list of the possible iron-containing solids that might form when either  $\text{FeCl}_2$  or  $\text{FeCl}_3$  is added to raw wastewater. This indicates that raw wastewater is highly supersaturated with respect to ferric hydroxide  $[\text{Fe}(\text{OH})_{3(4)}]$  and ferric phosphate  $[\text{FePO}_{4(4)}]$ ; moderately supersaturated with respect to ferrous sulfide  $[\text{FeS}_{(e)}]$ ; slightly supersaturated with respect to ferrous phosphate  $[\text{Fe}_3(\text{PO}_4)_{2(4)}]$ ; and undersaturated with respect to ferrous hydroxide  $[\text{Fe}(\text{OH})_{2(4)}]$  and ferrous carbonate  $[\text{FeCO}_{3(4)}]$  with minimum concentrations of  $\text{Fe}^{3+}$ . These conditions suggest that the sparingly soluble iron solids:  $\text{Fe}(\text{OH})_{3(4)}$ ,  $\text{FePO}_{4(4)}$ ,  $\text{FeS}_{(e)}$ , and possibly  $\text{Fe}_3(\text{PO}_4)_{2(4)}$  form when  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  iron is added to raw wastewater (Stumm and Morgan, 1970).

## 1.7 Previous Investigations

1.7.1 General. The chemistry of both iron and sulfur have been studied in great detail due to their prevalence and economic importance. A comprehensive discussion of the individual and combined chemistries of iron and sulfur would require far more space than is available here. The material summarized here is selected to provide the necessary background for discussion leading to the control of sulfide in sewers.

1.7.2 City of San Jose, CA. In a study conducted by the City of San Jose Department of Water Pollution Control, it was reported that when  $\text{FeCl}_2$  is added to raw wastewater, some of  $\text{Fe}^{2+}$  is rapidly oxidized to  $\text{Fe}^{3+}$  in oxygenated environments, at a favorable pH (7.1-7.6). Thus, adding  $\text{FeCl}_2$  to the system is equivalent to adding a mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Likewise, in a reducing environment of raw wastewater,  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$ , and addition of  $\text{FeCl}_3$  amounts to adding a similar mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions (Dezham *et al.*, 1988).

In the same study, the authors report that when iron encounters highly reducing environments, where sulfide concentrations are relatively higher than the other anions (especially hydroxides), iron can more effectively precipitate sulfide. However, both these factors: the reducing environment and the relative predominance of sulfide; tend to make iron available for precipitation as  $\text{FeS}_{(e)}$ . The reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  can cause dissolution of iron, because both  $\text{Fe}(\text{OH})_{2(4)}$  and  $\text{Fe}_3(\text{PO}_4)_{2(4)}$  are more soluble with respect to iron concentration than their ferric counter parts,  $\text{Fe}(\text{OH})_{3(4)}$  and  $\text{FePO}_{4(4)}$  (Table 1). The reductions achieved in the dissolved sulfide concentration support the contention that mechanisms such as these were in effect when  $\text{FeCl}_2$  and  $\text{FeCl}_3$  were added to raw wastewater.

1.7.3 City of Mesa, AZ. In 1987, the City of Mesa, AZ and Brown and Caldwell Consulting Engineers, Pasadena, CA, conducted a sulfide and odor research control study in the City's interceptor sewer using a variety of chemicals, including  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ , and a blend of both the salts. The City of Mesa is at the eastern upstream end of the regional wastewater system that serves the Phoenix metropolitan area. Long interceptors and high temperatures have made the Mesa collection system vulnerable to sulfide generation. The City of Mesa has to control the

**Table 1. Solubility of Various Iron Complexes In Wastewater Streams<sup>†</sup>**

Compound	Formula	- pK <sub>sp</sub>	- log concentration product	Supersaturated; precipitate expected
Ferrous Phosphate	Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	32	31.2	Slightly
Ferrous Sulfide	FeS	18.1	12.9	Yes
Ferrous Hydroxide	Fe(OH) <sub>2</sub>	14.5	18.4	No
Ferrous Carbonate	FeCO <sub>3</sub>	10.4	11.8	No
Ferric Phosphate	FePO <sub>4</sub> ·2H <sub>2</sub> O	26	13.6	Yes
Ferric Hydroxide	Fe(OH) <sub>3</sub>	38.7	25.6	Yes

<sup>†</sup>CRC Handbook of Chemistry and Physics (1972).

dissolved sulfide concentrations to 0.5 mg/L as a part of the regional operating agreement. The Southern Avenue and the Baseline Road Interceptors are part of this regional system. Total sulfide levels as high as 5 mg/L have been reported in both these interceptors. The City placed the Horne Road Sulfide Control Station in operation in December, 1985. The station feeds  $\text{FeCl}_2$  into both interceptors (Jameel, 1989).

Jameel (1989) reports that since January 1986, 95% control of dissolved sulfide has been provided in these interceptors. For the Baseline Road Interceptor, a dose of 12 mg/L of  $\text{FeCl}_2$  has controlled the dissolved sulfide concentration at the monitoring point to 0.2 mg/L. For the Southern Avenue Interceptor, a  $\text{FeCl}_2$  dose of only 2.4 mg/L, has controlled these concentrations to 0.4 mg/L. Following these studies, two additional stations were constructed in March, 1987 at a cost of \$200,000: the Alma School Road and the Noche De Paz Stations. These two new stations are located on the Baseline Road Interceptor. Operation of the three stations has been trouble-free and is controlling dissolved sulfide in the above mentioned sewers to 0.5 mg/L.

**1.7.4 City of Elgin, IL** Dohnalek and FitzPatrick (1983) investigated  $\text{H}_2\text{S}$  removal using various chemicals and oxidants in bench-scale jar tests that simulated actual conditions in the City of Elgin treatment plant. Variations in aeration rate, chemical dosage, aqueous pH, and detention time were also examined. A ferrous sulfate ( $\text{FeSO}_4$ ) dosage of 9 mg/L reduced sulfide concentrations to 0.05 mg/L, largely owing to catalytic effect of  $\text{Fe}^{2+}$ . Peroxide, permanganate, and ferrate also lowered the sulfide concentrations, with more rapid kinetics than  $\text{Fe}^{2+}$ . An economic analysis showed that  $\text{Fe}^{2+}$  is a cost-effective alternative for sulfide removal. They also concluded that other oxidants may prove economical under certain conditions.

**1.7.5 Cities of Clearwater, Naples, and Boynton Beach, FL** Performance of  $\text{FeSO}_4$  for sulfide control revealed that only partial control was achieved and that the residual sulfide levels were still sufficient to cause significant odor and corrosion problems. The dose ratio of  $\text{FeSO}_4$  to dissolved sulfide was calculated to be in the range from 2.5:1 to 5:1. Results of the  $\text{FeSO}_4$  study in Florida are summarized in Table 2. They speculated that  $\text{FeSO}_4$  addition to the wastewater may allow more downstream sulfide generation in lieu of sulfide depletion (Bowker R.P.G. et al., 1985).

**1.7.6 Los Angeles County Sanitation Districts, CA** In 1988, the County Sanitation Districts completed a full-scale evaluation of  $\text{FeCl}_2$  to control sulfide levels in a large diameter gravity sewer. The study indicated that: (i) complete control of dissolved sulfide was difficult, although effective control was achieved for at least 25 miles downstream of the chemical injection point; (ii) the dosage required for 90% sulfide control is 7:1 ratio of  $\text{FeCl}_2$  to dissolved sulfide if the dissolved sulfide is 4 mg/L or greater, 15:1 if the dissolved sulfide is between 1 to 4 mg/L, and 100:1 if the dissolved sulfide is less than 1 mg/L; (iii) sewer odor and headspace  $\text{H}_2\text{S}$  levels were reduced by 40 to 70%; (iv) the sewer crown pH increased from 1 to 2. The study concluded that the cost to control dissolved sulfide concentrations to a level of 0.5 mg/L in this 25 mile gravity sewer carrying 200 MGD was \$1,500/day (Won, 1988).

A long-term monitoring of  $\text{FeCl}_2/\text{FeCl}_3$  blend treatment was conducted by the Districts between August, 1990 and April, 1991. Effects of the blend varying from 1:1 to 2:1 (ferric to ferrous) were examined along a 25 mile reach in a portion of the Districts' Joint Outfalls B and H. The study justified the following conclusions: (i) iron addition provides good control of dissolved sulfide with concentrations averaging 0.1 mg/L at each monitoring location and remained undetectable 65% of the time, (ii) better than 90% control of dissolved sulfide, relative

**Table 2. Performance of Ferrous Sulfate for Sulfide Control in Florida (Bowker R.P.G. *et al.*, 1985)**

Location	Average wastewater flow (MGD)	Average ferrous sulfate dosage (mg/L)	Dissolved sulfide (mg/L)
Clearwater	5	0	6 to 8
		30	< 1
Naples	5.5	0	5 to 20
		25	1 to 2
Boynton Beach	12	0	10
		25	0.5 to 2

to background levels, was achieved at several sites, (iii) H<sub>2</sub>S in the headspace was reduced by at least 60% at all the monitoring stations, and (iv) a slight to moderate depression in crown pH was observed at all the sites monitored (Weiss, 1991).

**1.7.7 Greater Vancouver Regional District, Canada.** The Greater Vancouver Regional District (GVRD) needs to control sulfide in their wastewater to combat concrete corrosion and odors in sewers and treatment plants. Beginning in 1991, GVRD studied the effectiveness of FeCl<sub>2</sub> to control odor and corrosion in the sewers of their Annacis Island wastewater collection system. To meet the objectives of the odor and corrosion control program, dissolved sulfide needs to be limited to a low enough level to eliminate H<sub>2</sub>S gas release to the sewer headspace. The dosing strategy is based on the premise that, although iron treatment has some impact on the environment, dosage rates will be maintained to provide acceptable effluent soluble iron concentrations. They report the following conclusions: (i) sulfide is present and produced all year round in the sewers inspite of -10°F winters, without iron treatment, (ii) uncontrolled dissolved sulfide levels up to 2.5 mg/L are encountered during warm periods, (iii) immobilization of dissolved sulfide reduced H<sub>2</sub>S in the sewer atmosphere significantly and controlled sewer odors with approximated theoretical iron concentrations exceeding 10 mg/L Fe in the wastewater, (iv) addition of iron to the forcemains effectively controlled H<sub>2</sub>S gas release at force main/gravity sewer intersections, and (v) since the wastewater characteristics are highly variable and unpredictable, it would be impossible for GVRD to control iron dosages to exactly meet sulfide demands which necessitates the use of excess iron to ensure continuous control of sulfide (So and Merry, 1993).

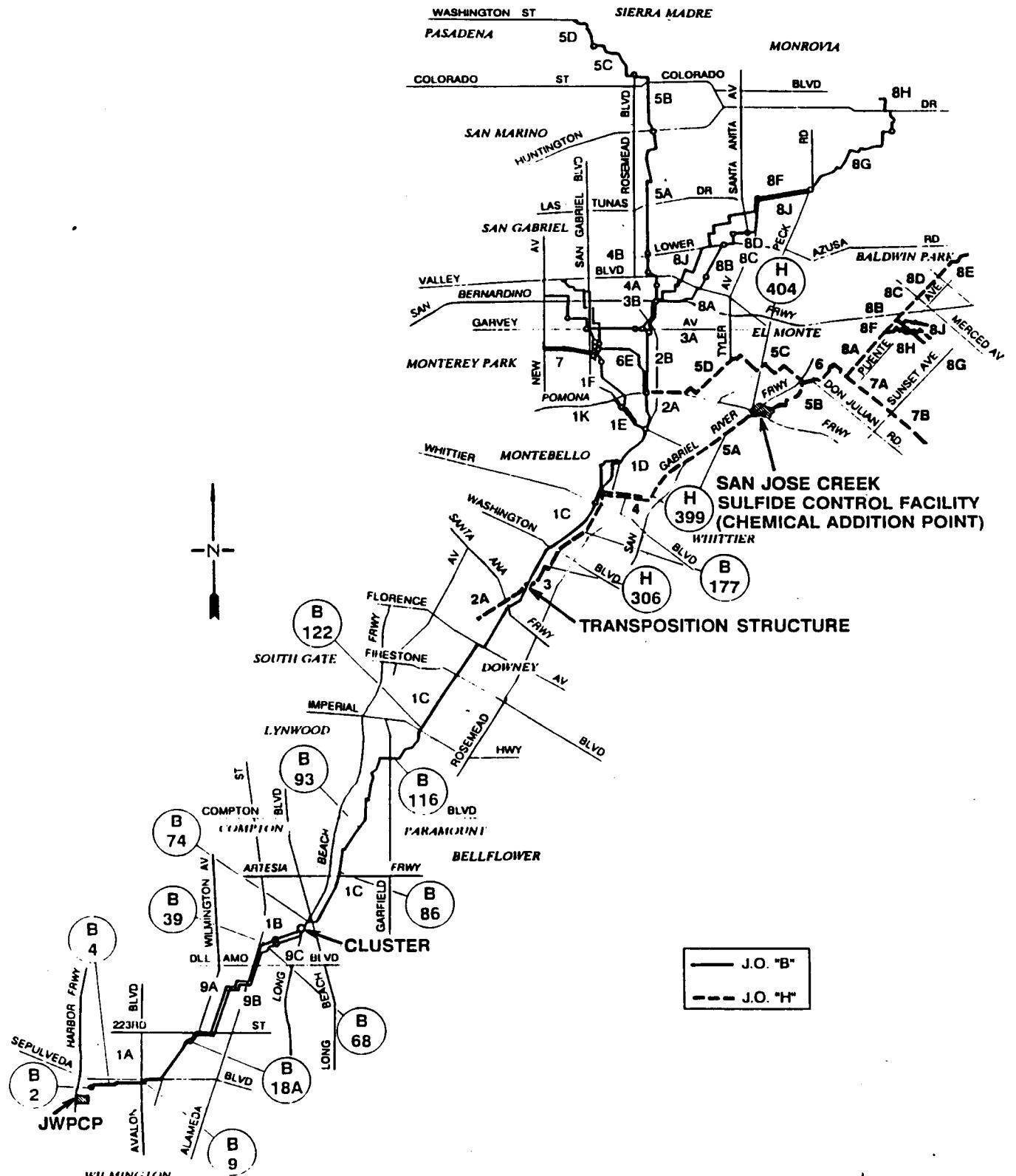
## 1.8 Objectives of the Study

The use of iron salts to control dissolved sulfide, thus reducing release of H<sub>2</sub>S to the sewer headspace is very common. Iron combines with sulfide to form insoluble precipitates. The use of a combination of FeCl<sub>3</sub>/FeCl<sub>2</sub> has been thought to be more effective than either salt alone. This full-scale investigation was undertaken to evaluate the effectiveness of the chemical and to establish an optimum dose of Fe and Fe<sup>3+</sup>/Fe<sup>2+</sup> blend ratio to achieve maximum control of dissolved sulfide and sewer odors.

The addition of FeCl<sub>3</sub> at the Districts' San Jose Creek Water Reclamation Plant (SJCWRP) primary sedimentation tanks is thought to be influencing the chemical use and sulfide control in the test reach. To assess such effects, a short-term study was conducted by temporarily interrupting iron addition at the primary tanks. Both studies were conducted in a portion of the Districts' Joint Outfall "B" (J.O. "B") and Joint Outfall "H" (J.O. "H") Trunk Sewers.

Figure 4 is a general map of J.O. "B" and a portion of J.O. "H" Trunk Sewer System, which includes the entire test reach. In Figure 4, the circled designations are test locations (manholes) along the test reach. Each of the two Joint Outfalls is broken down into shorter sections referred to as Units, which are shown on Figure 4 by designations such as 1A, 3, 9A, 9B, etc.

**ALTADENA**



**FIGURE 4. A GENERAL MAP OF J.O."B" AND A PORTION OF J.O."H"  
TRUNK SEWER SYSTEMS SHOWING THE TEST LOCATIONS.**

## 2.1 Chemicals

Liquid  $\text{FeCl}_3$  and  $\text{FeCl}_2$  is produced from the action of hydrochloric acid (HCl) on iron in the absence of  $\text{O}_2$ . It is a common byproduct of the steel industry. The steel manufacturers use a HCl bath, called "pickle liquor", to clean and descale the formed steel prior to surface coating. The used pickle liquor, high in iron, is further concentrated with scrap carbon steel to yield  $\text{FeCl}_3$  and  $\text{FeCl}_2$ . The final product is filtered to remove residue. The Districts' source for these chemicals is Imperial West Chemical Company, Antioch, CA. Vacuum trucks deliver about 4,000 gallons of  $\text{FeCl}_3$  and  $\text{FeCl}_2$  at concentrations of 39 to 45% and 27 to 33%, respectively.

$\text{FeCl}_3$  and  $\text{FeCl}_2$  are non-flammable, strong acids. Both are corrosive to concrete, fabric, and most metals. Storage temperatures should be maintained above 30°F. The physical and chemical properties of both chemicals are listed in Table 3.

$\text{FeCl}_3$  and  $\text{FeCl}_2$  are irritating to the skin and eyes. Proper procedures, safety equipment, and clothing should be used to prevent exposure hazards. Safety goggles, plastic or rubber gloves, and hard hats are mandatory. Rubber suits, rubber shoes, face shields, and dust-type respirators are also recommended by the manufacturer. Fiberglass, glass, plastic materials, and rubber-lined equipment are recommended for the handling and storage of these chemicals. The Districts' require their personnel to wear plastic or rubber gloves, safety goggles, and hard hats when exposure to these chemicals is a possibility.

## 2.2 Equipment Description

**2.2.1 General.** The San Jose Creek Sulfide Control Facility was constructed in November 1988 at a total construction cost of about \$175,000. The objective of the station was to institute sulfide treatment for corrosion control in a portion of J.O. "B" and J.O. "H". The system was designed to feed chemicals using progressive cavity, Moyno pumps. In October of 1990, the Moyno pumps were replaced with dual head, BIF, diaphragm pumps. The BIF pumps could provide more accurate feed rates, but particulate matter in the chemicals damaged the viton diaphragms of the pumps. In addition to this, serious vibration (due to hydraulic hammer) problems were encountered, albeit pulsation dampeners were provided. The BIF pump representative replaced the dual head, diaphragm pumps with another type of diaphragm pump, furnished by BIF. Even though pulsation dampeners were provided with these pumps, serious vibration problems continued. The pump problems reflected directly on the chemical feed rates and effectiveness of treatment, and resulted in numerous shutdowns and damaged piping. This lead to the use of a gravity-feed system with control valves as suggested by Won in 1988.

The  $\text{FeCl}_3$  and  $\text{FeCl}_2$  are delivered to the storage tanks located in the southwest corner of SJCWRP. The chemicals are blended at a predetermined ratio in a common discharge line downstream of the control valves and fed to the sewer through a 6-inch PVC line. The control

**Table 3. Ferric Chloride and Ferrous Chloride Safety Data<sup>†</sup>**

Characteristics	Parameters	Ferrous chloride	Ferric chloride
Physical and chemical	Boiling point	217°F	240°F
	Specific gravity ( $H_2O = 1.0$ )	That of $H_2O$	That of $H_2O$
	Vapor pressure (mm of Hg)	That of $H_2O$	That of $H_2O$
	Vapor density (air = 1)	That of $H_2O$	That of $H_2O$
	Solubility in $H_2O$	36%	46%
	Reactivity in $H_2O$	None	None
	Appearance and odor	Pale green; very slight odor	Red/brown; pungent
Fire and explosion	Melting point	None	None
	Unusual fire and explosion hazard	None	oxidizer; reacts with organics and ferrous metals
	Special fire fighting procedures	None	Non-flammable
Reactivity	Auto-ignition temperature	None	Stable
	Reactivity	Stable; avoid contact	Stable; avoid contact
	Incompatibility	Organics and ferrous metals	Ferrous metals, copper, aluminum
Hazardous polymerization		Will not occur	Will not occur

<sup>†</sup>Based on information provided by Manufacturer

valves and in-line magnetic flowmeters are electrically connected to a Programmable Logic Controller (PLC) from which the chemical dosage rates are programmed. The dosage rates are controlled by automatic opening or throttling of the control valves. Figure 5 is a schematic drawing showing the layout of the Sulfide Control Facility and the path of the control signal wiring. The Facility (Figure 6) consists of two tanks, two flow control feed valves, two magnetic flowmeters with separate signal converters, and associated piping and valves.

**2.2.2 Chemical Storage Tanks.** The two chemical tanks are fiberglass reinforced plastic tanks designed for the storage of  $\text{FeCl}_3$  and  $\text{FeCl}_2$ . Each tank is 12-foot in diameter and 14-foot high with a nominal storage capacity of 12,000 gallons. Individual vent, overflow connection, drain valve, sight glass gauge level indicator, and manway access are standard. The tank sight glasses are graduated to determine tank levels. Each division on the tank sight glasses represents about 500 gallons of the chemical. The tanks' 4-inch PVC fill piping is arranged such that the tanks cannot be filled at the same time. However, the discharge piping is set up to allow chemical feed from both tanks simultaneously.

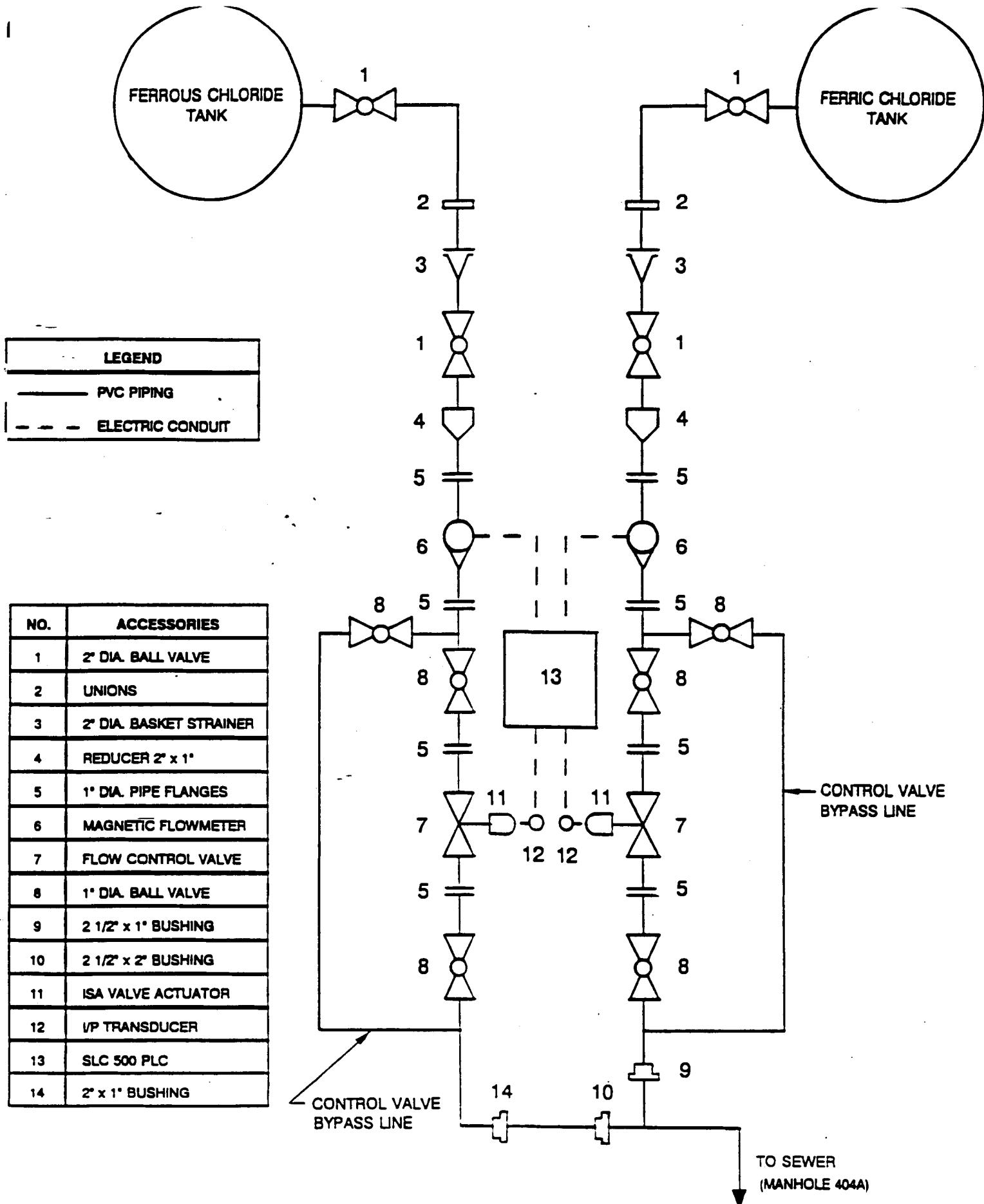
**2.2.3 Control Valves.** The  $\text{FeCl}_3/\text{FeCl}_2$  flow control valves directly regulate the flow from the storage tank outlets. Each valve is rated (adjustable) at 1.0 to 12 gpm. It is controlled by a direct positioner which receives the controller signal to open or close to achieve the desired pre-programmed rates. The valves are automatically operated by the PLC which is programmed to follow a 24-hour flow variation at the most downstream point.

The control valves are plastic globe-type, designed to provide highly responsive low flow control for corrosive chemicals (Figure 7). The actuator is made of polypropylene except for the aluminum integral positioner. The control air signal is directly piped to the positioner diaphragm. An increase or decrease in control signal pressure causes the diaphragm to move up or down, respectively. This change in pressure and diaphragm movement actuates the piston position forcing closure or opening of the valve.

**2.2.4 Magnetic Inductive Flowmeter (MIF).** Each chemical feed system has a flowmeter which measures the  $\text{FeCl}_3$  or  $\text{FeCl}_2$  flowrate at a range from 0 to 25 gpm. Each flowmeter has a primary element mounted in the discharge line of the tanks (Figure 8) and a remote signal converter (Figure 9). The signal converter receives a low level DC voltage signal from the primary element and converts it to a 4 to 20 mA output signal. The signal converter's liquid crystal display shows flowrate and totalized flow.

**2.2.5 Air Compressor.** The air compressor provides pressure to regulate the position of the control valves (Figure 10). Changes in air pressure are accomplished by the 4 to 20 mA output signal (from the PLC) relayed to the control valve through an I/P transducer. The compressor is equipped with a 7.5 HP motor and is capable of delivering 32 scfm of air at 140 psig. It is an automatically controlled, two-stage, belt driven, air-cooled compressor. This air compressor was originally designed to air pad the chemical delivery trucks. Currently, the air compressor is used solely for instrument air for the control valves. It is recommended that separate compressors be provided for instrument air and air padding delivery trucks to avoid control valve fluctuations during off-loading of chemicals.

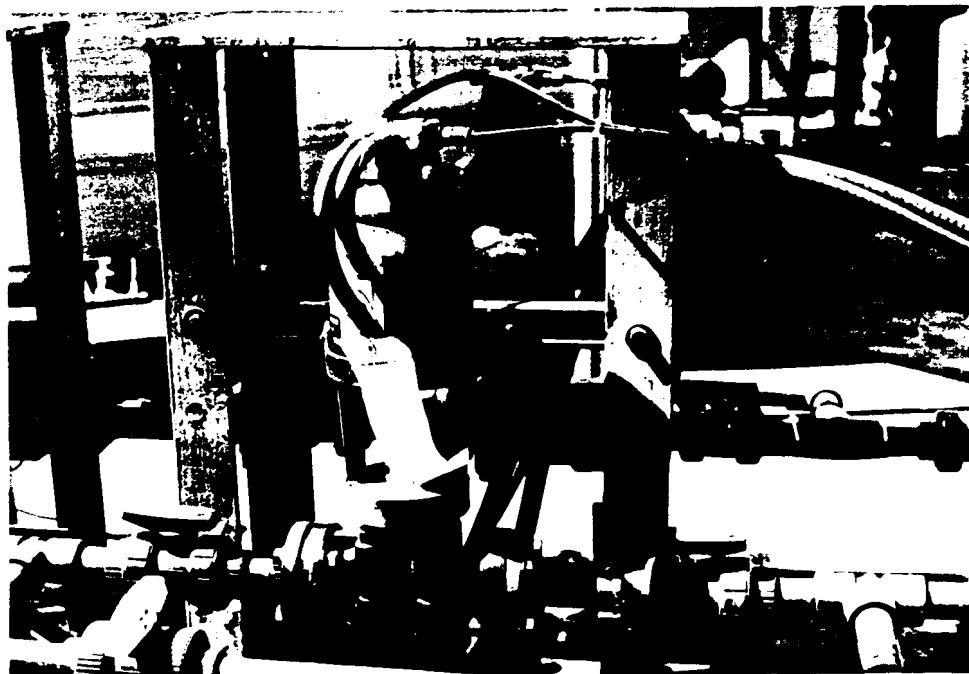
**2.2.6 Spill Containment.** Complete spill containment is provided by the masonry wall surrounding the facility. Provisions for removing spilled chemical from within the containment area consists of a sump and an eductor at the station which conveys the chemical to the sewer.



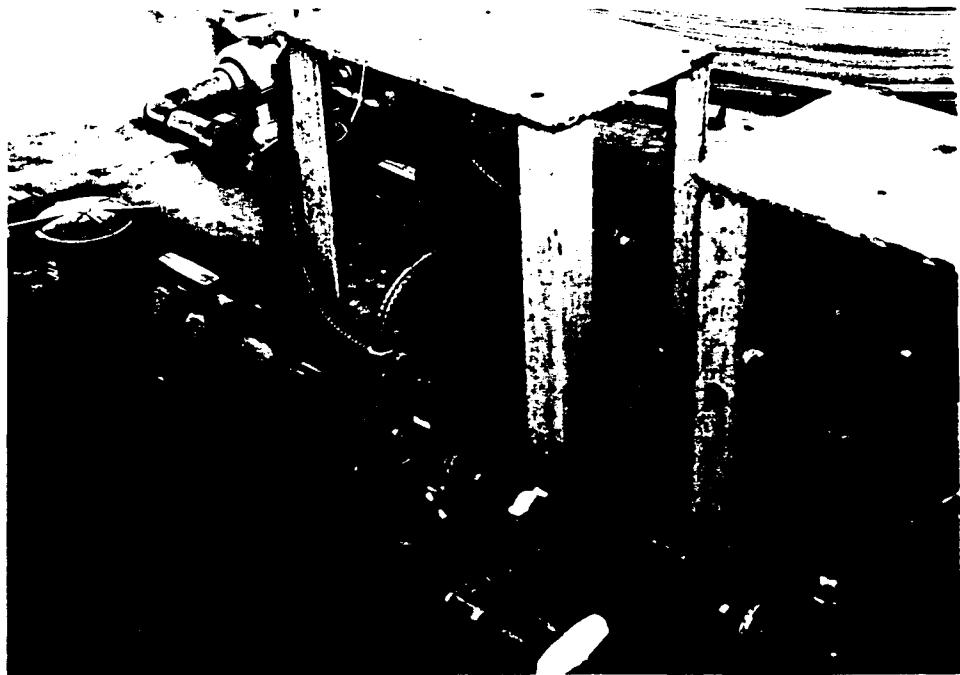
**FIGURE 5.** Schematic layout of the Sulfide Control Facility at the SJCWRP.



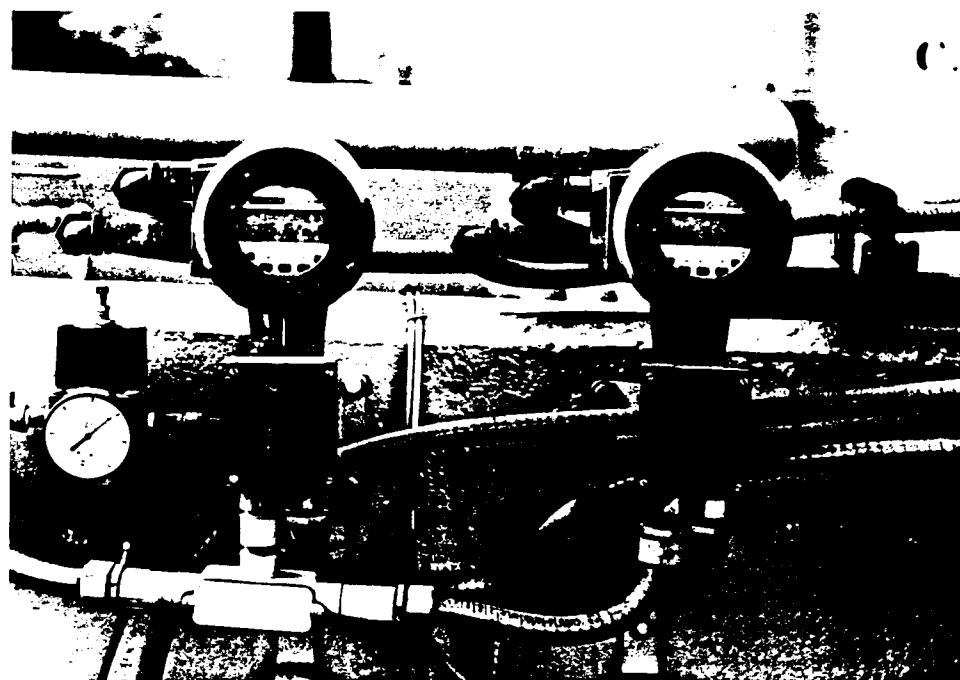
**FIGURE 6.** Ferric and Ferrous Chloride Dosing Facility at the San Jose Creek Water Reclamation Plant.



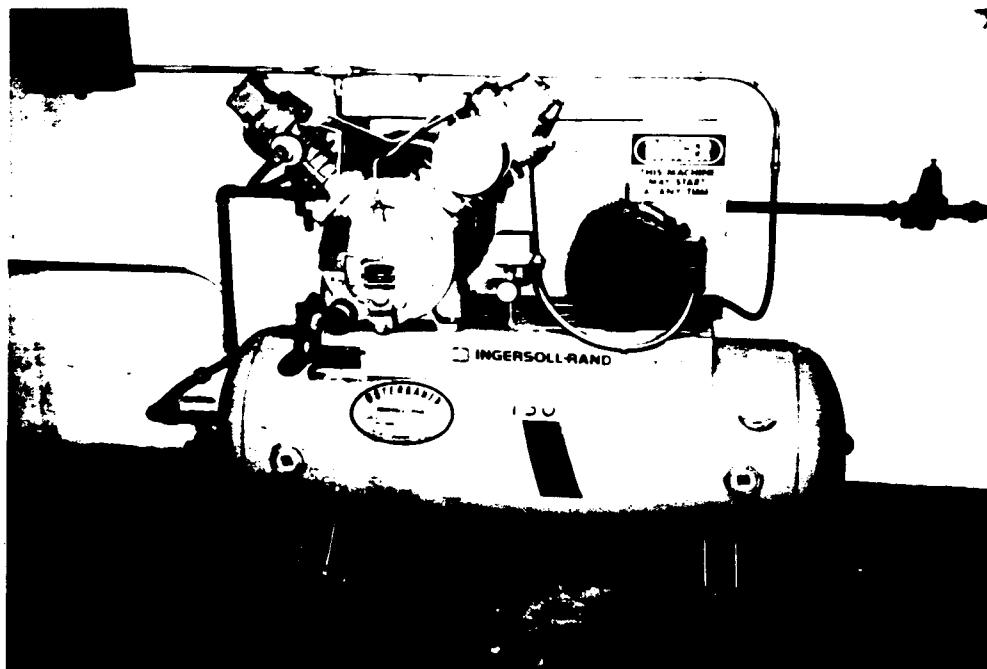
**FIGURE 7.** A view of the flow control valve and bypass line, looking west.



**FIGURE 8.** Primary element of the Altoflux Compact Magnetic Inductive Flowmeter located just downstream of the storage tank discharge valve and upstream of the control valves.



**FIGURE 9.** A view of the LCD totalizer on the secondary element of the flowmeter, located on the outside of the containment wall to the north.



**FIGURE 10.** A view of the compressor and the line connections.

## **2.3 Analytical and Chemical Techniques**

To evaluate the sulfide dynamics of iron treatment, routine sulfide circuits were conducted by the Compton Field Office Engineering Technicians. Post and pretreatment samples were collected at selected sites along the study reach. The sewage was monitored for total sulfide, dissolved sulfide, pH, temperature, total iron, and soluble iron. The sewer headspace was tested for atmospheric H<sub>2</sub>S and sewer odors. The pipe crown was tested for condensate pH.

Total and dissolved sulfide were determined in the field using the Methylene Blue Method in accordance with *Standard Methods for Examination of Water and Wastewater* (AWWA; APHA; and WPCF, 1990). Sewage and crown pHs were measured using pH indicator sticks (American Scientific Products Inc.). Sewage temperature was measured using thermometers.

H<sub>2</sub>S and odors in the sewer atmosphere were sampled before the manholes were opened. H<sub>2</sub>S was measured using MSA tubes (Mine Safety Appliances Co., Pittsburgh, PA). All odor samples were collectively transported to and analyzed at the Districts' Compton Odor Laboratories. The analyses were performed in accordance with the American Society for Testing and Materials (ASTM) D1391-78 standards entitled *Standard Test Method for Measurement of Odor in Atmospheres*.

Soluble and total iron were determined by atomic absorption spectrophotometry (AA). This technique utilizes a light beam which is directed through a flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized metal. Soluble iron samples were filtered through a 0.45  $\mu$  filter prior to analysis.

Diurnal flow recordings were made using depth measurements prior to this study. A Leopold Stevens Stage Recorder Type F was used over 7 days. The flow measurements were used to establish chemical feed setpoints.

## **2.4 Monitoring and Testing Procedures**

**2.4.1 General.** Portions of the large diameter sewers have experienced serious sulfide corrosion damage, some to the point that the reinforcing steel is exposed. Sulfide corrosion is ongoing, which makes it necessary to take steps to protect the sewers from further damage. Measured rates of pipe corrosion may be dependent on gas and liquid phase sulfide concentrations. It is a well known fact that iron treatment effectively controls dissolved sulfide and reduces sewer odors. However, iron chloride addition may control corrosion by precipitating free sulfide, thus significantly reducing its release to the sewer headspace as H<sub>2</sub>S. Reduction in headspace H<sub>2</sub>S could limit SOB activity.

The full-scale optimization of iron addition was conducted from June 1 through December 4 of 1992. Background data were collected from June 1 through June 13 of 1992. The background data were gathered five days a week (Monday through Friday) from the monitoring sites over a two week period. During treatment, samples were also collected (Monday through Friday) from the same locations.

**2.4.2 Monitoring Locations.** To determine the effectiveness of iron treatment, testing was conducted at selected locations along the entire sewer reach. During the daily sulfide circuits, a total of 16 locations were monitored, including the inlet works at JWPCP. Total and dissolved

sulfide, sewage and crown pH, and headspace H<sub>2</sub>S were monitored at all the locations. Total and soluble iron and odor samples were collected at only three locations (Manholes H399, B74, and B2).

The 25-mile test reach consists of sections of two separate trunk sewers. The upper end of the test reach consists of 5 miles of J.O. "H", from the point of chemical injection, downstream to the transposition structure. The lower section of the test reach, from the transposition structure, downstream to the Joint Water Pollution Control Plant (JWPCP), consists of 20 miles of J.O. "B". At the transposition structure, J.O. "H" and J.O. "B" switch flows (Figure 4).

The J.O. "H" system has a total of 76 miles of trunk sewer. The 5-mile section under study carries flows through the Cities of Montebello, Santa Fe Springs, and Whittier to the City of Pico Rivera. The SJCWRP treats all of the flow from the SJCWRP Interceptor and most of the flow from J.O. "H" Unit 5A. During the early morning hours, the entire J.O. "H" flow is diverted into the plant. The only flow remaining at the chemical injection point consists of the skimmings, primary and secondary sludge, and the plant sewer flow. During high flows, part of the flow in J.O. "H" bypasses the treatment plant. The major flow input (27 to 35 MGD) to the study reach comes from the District 21 Interceptor. The District 21 Interceptor includes sludge from the Pomona Water Reclamation Plant and industrial waste from the Chino Basin area.

The most upstream manhole in the entire test reach is Manhole H404A (chemical application point). Manhole H399 is located approximately 1/2 mile downstream of Manhole H404A. The District 21 Interceptor discharges into the study reach upstream of Manhole H402. However, access to the sewer reach between Manholes H402 and H400 is difficult. Therefore, Manhole H399 was chosen as the most upstream location for analysis because the sewage includes the District 21 Interceptor discharge and the chemical is more evenly mixed.

J.O. "B" consists of a total of 69 miles of trunk sewers (Figure 4). The lower 20 miles of this sewer make up the remaining part of the test reach. This section extends from the transposition structure (where flow from J.O. "B" is replaced by flow from J.O. "H") to a point downstream, designated the cluster (confluence of several Districts' Joint Outfalls), and further downstream where it terminates at the inlet works of Joint Water Pollution Control Plant (JWPCP) in the City of Carson. In the 12-mile sewer from the transposition structure downstream to the cluster, the flow varies between 35 to 65 MGD during the course of the day, with the average being 50 MGD. Around the cluster, the test reach receives flows from J.O. "E" (20 to 45 MGD), J.O. "F" (20 to 50 MGD), and J.O. "H" (85 to 120 MGD, which includes flow diverted from J.O. "B" at the transposition structure plus the flow from other J.O. "H" units) trunk sewers. At this location, J.O. "F" Unit 1 and J.O. "B" Unit 1C merge and enter J.O. "B" Unit 1B. At the same site, J.O. "H" Unit 1A enters J.O. "B" Unit 9C. J.O. "B" Units 1B and 9C run parallel downstream of the cluster for a distance of 4 miles after which the flow is in a single 144 inch diameter sewer (J.O. "B" Unit 1A) to the JWPCP.

In this study, the sulfide dynamics at the cluster were considered very important due to the various flow inputs. However, the main thrust of this evaluation was to examine conditions in the test reach above and below the cluster. At the cluster, the sewer configuration made sewage sampling very difficult. Therefore, Manhole B74 was selected as the downstream sampling location to report conditions above the cluster.

At the cluster and downstream to the inlet works at JWPCP, flow varies from 160 to 280 MGD. At a site approximately 1/3 mile upstream of JWPCP, at Manhole B2, the flow averages

about 200 MGD. Manhole B2 was considered a substitute location for sampling near the inlet works because of the difficult access for sampling at the inlet works and the influence of gas samples by the wet/carbon odor scrubbers installation at the inlet works.

**2.4.3 Testing.** The literature indicates that the use of  $\text{FeCl}_3$  and  $\text{FeCl}_2$  alone are effective in controlling sulfide in wastewaters. But there is a lot of speculation about their performance, when used in combination to control sulfide in sewers. To assess this performance, a full-scale study was conducted to determine the optimum concentration of Fe and blend ratio ( $\text{Fe}^{3+}:\text{Fe}^{2+}$ ) to control dissolved sulfide in the sewer.

Varying the concentration of Fe and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  blend ratio was necessary to evaluate the effects on sulfide control. During the full-scale testing and optimization of iron addition, the total concentration of iron and blend ratio was varied for each experimental run. A total of five concentrations of iron were tested - 10, 12, 14, 16, and 18 mg/L (as Fe). For each concentration of iron, four blend ratios ( $\text{Fe}^{3+}:\text{Fe}^{2+}$ ) were tested - 1:1, 1.3:1, 1.6:1, and 1.9:1 (mg/L:mg/L). Each dose and blend ratio were tested for one week.

The hypothesis proposed by Pomeroy and Bowlius (1946) indicated that 7 parts of iron should precipitate 4 parts of sulfide. Historical records showed that in J.O. "B", the dissolved sulfide levels can range from 3 to 8 mg/L at the most downstream point. With these factors in mind, the dosage levels were carefully selected to bracket the total concentration of Fe and blend ratio that was believed to achieve maximum control of sulfide in our sewers.

# **3**

# **Results & Discussion**

## **3.1 General**

The full-scale testing with iron chloride lasted for five months. The combined effort put forth by the Compton Field Office Engineering Technician staff, JWPCP Laboratory Personnel, and the SJCWRP Instrumentation Personnel, yielded an extensive database of all required parameters. It included total and dissolved sulfide,  $H_2S$ , sewage and crown pH, total and soluble iron, and odor units.

For analytical simplicity and effective presentation of the data, the 25-mile study reach is divided into two parts; the point of application to the cluster and from the cluster to the inlet works at JWPCP (Figure 4). The sulfide dynamics were assessed at three locations, although 16 other sites were sampled. The sampling sites corresponding to three locations are: Manholes H399, B74, and B2. Presentation of all data would have been very difficult and repetitious. However, I have presented more data (histogram plots of dissolved sulfide, total sulfide, and headspace  $H_2S$ ) for the apparent "best" iron level and  $Fe^{3+}/Fe^{2+}$  blend ratio. In doing so, two of the 16 monitored locations (Manhole B18A and Manhole B39) were eliminated. The two locations received only partial treatment because of the existing sewer system configuration.

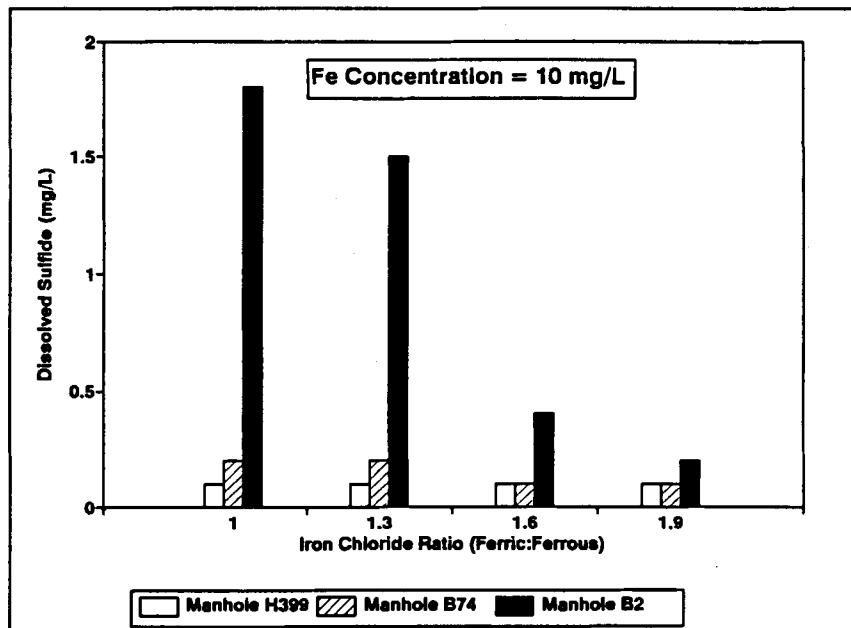
## **3.2 Dissolved Sulfide**

Table 4 summarizes uncontrolled sulfide levels measured at different sites along the test reach during the first two weeks of the study. The background dissolved sulfide, at Manhole H399, varied from 0.1 to 0.4 mg/L, with an average of 0.2 mg/L. Measured levels were less than 0.2 mg/L at least 75% of the monitoring time. At Manhole B74 and Manhole B2, background dissolved sulfide ranged from 0.2 to 5.8 mg/L and 2.3 to 8.6 mg/L, respectively. The measurements were consistent with observations made from 1988 through 1991. The four-fold dilution of sewage at the cluster could influence this variability. Just downstream of this point, the flow passes through a double-barrel section (4 miles) which surcharges 85% of the time. Certain reaches of this double barrel section are always surcharged. Also, of particular concern, are several significant industrial waste point discharges to the sewer from oil refineries. The data collected during the day-to-day sulfide circuits indicated that these two conditions can contribute to sulfide buildup that is rapid, significant, and very unpredictable.

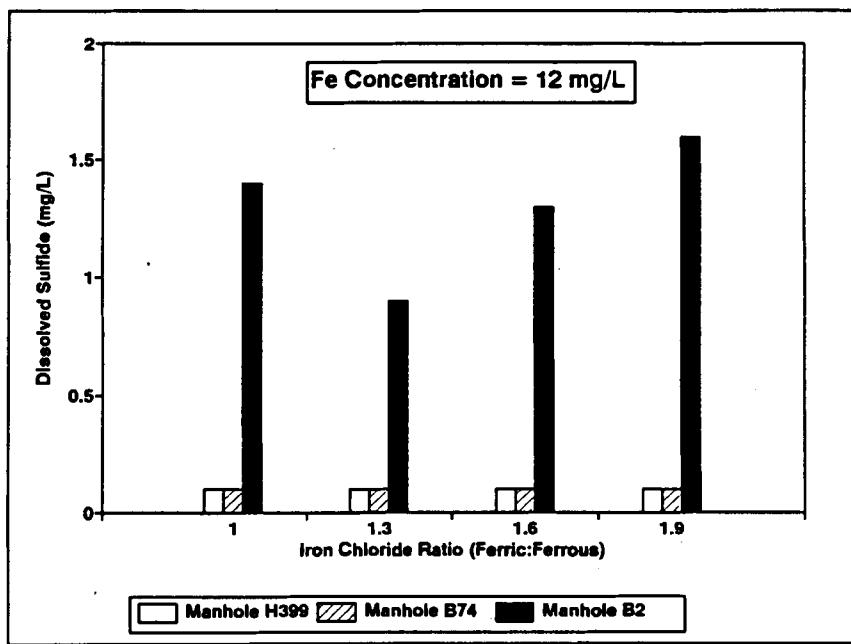
Figures 11 through 15 show dissolved sulfide concentrations measured at Manholes H399, B74, and B2 at different concentrations of Fe and at various combinations of  $Fe^{3+}/Fe^{2+}$  blends. Dissolved sulfide levels at Manhole H399, remained below detectable limits almost 100% of the time for all concentrations of Fe and blend ratios tested. In the study reach from Manhole H399 down to Manhole B74, excellent control was achieved for the following reasons: (i) sewage is fairly aerobic (Won, 1988); (ii) excess iron is present at all times; and (iii) catalytic oxidation of sulfide in the presence of ferric iron and small amounts of oxygen (Pomeroy and Bowlus, 1946; Jameel, 1989; and Dohnalek and FitzPatrick, 1983).

**Table 4. Distribution of Background Parameters in the Sewage Prior to Treatment with Iron Chloride**

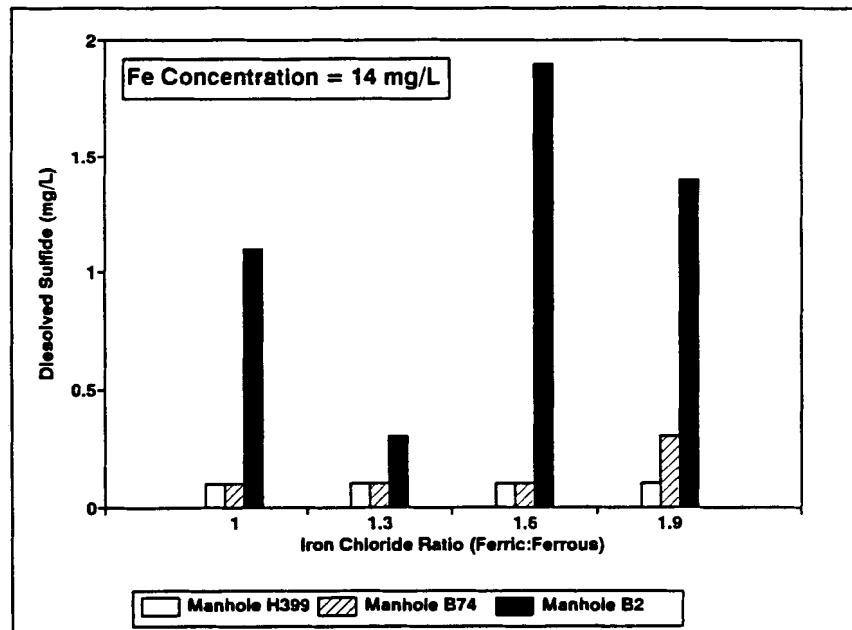
Location	Uncontrolled concentrations measured in the J.O. "B" sewage					
	Dissolved sulfide (mg/L)		Total sulfide (mg/L)		Hydrogen sulfide (ppmv)	
	Range	Avg.	Range	Avg.	Range	Avg.
Manhole H399	0.1 - 0.4	0.2	0 - 2.8	0.6	0 - 6	< 2
Manhole B74	0.2 - 5.8	4.7	6.3 - 14.6	9.8	2 - 25	11
Manhole B2	2.3 - 8.6	6.4	8.5 - 15	12.5	8 - 40	17



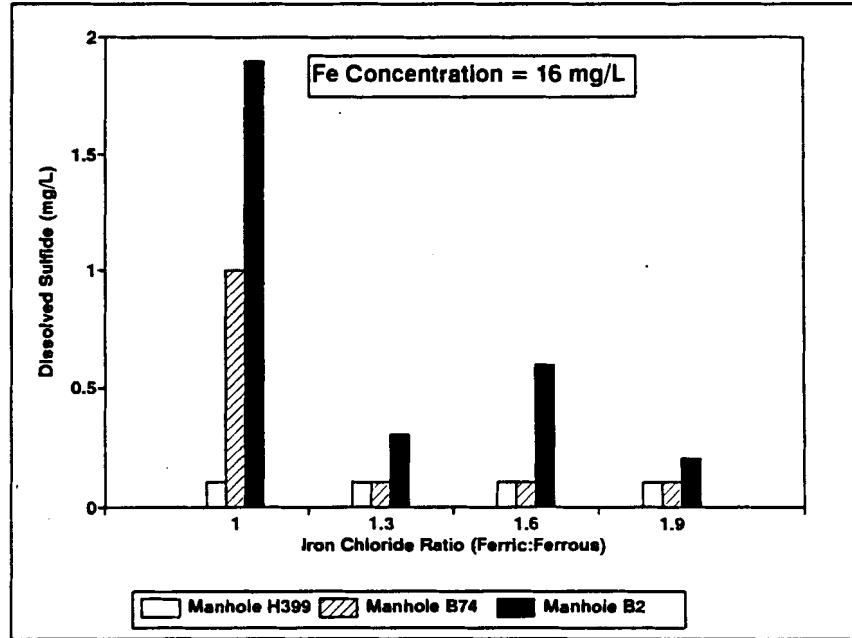
**Figure 11.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows average dissolved sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 10 mg/L and four different blend ratios.



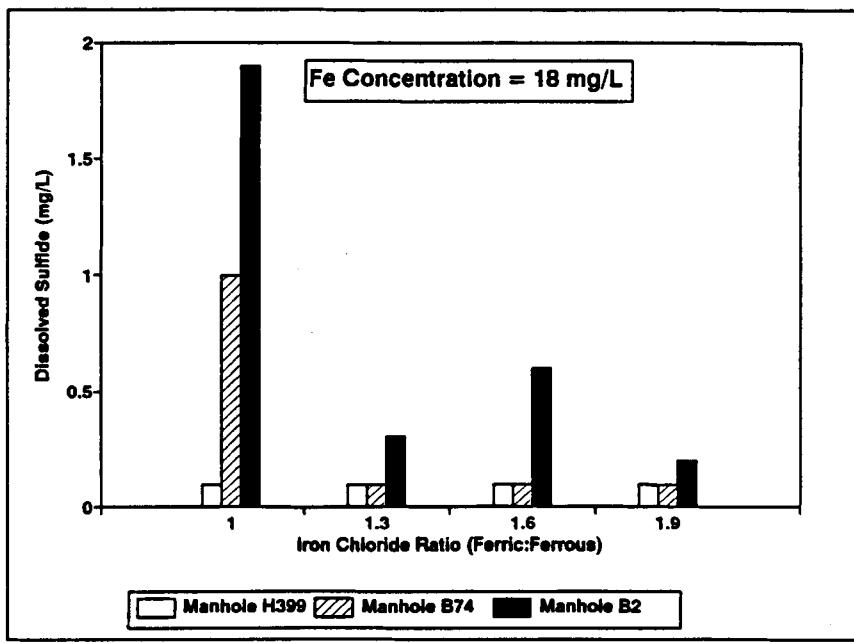
**Figure 12.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows average dissolved sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 12 mg/L and four different blend ratios.



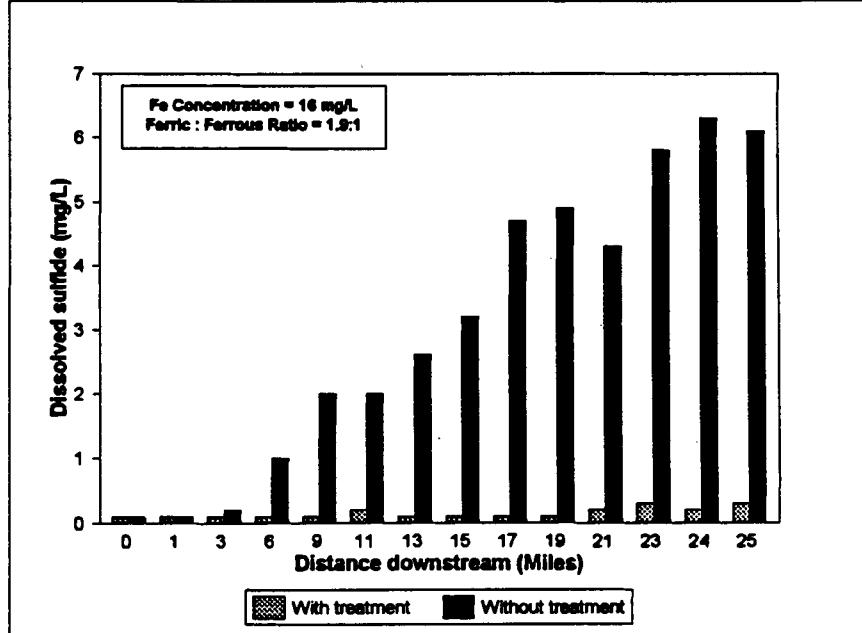
**Figure 13.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows average dissolved sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 14 mg/L and four different blend ratios.



**Figure 14.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows average dissolved sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 16 mg/L and four different blend ratios.



**Figure 15.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows average dissolved sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 18 mg/L and four different blend ratios.



**Figure 16.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on dissolved sulfide concentrations. Graph shows dissolved sulfide levels at monitoring locations along the 25 mile test reach, using a total Fe concentration of 16 mg/L and a blend ratio of 1.9:1, and without treatment.

Table 5 illustrates percentage reductions in sulfide parameters during iron treatment. At Manhole B74, reductions in dissolved sulfide stayed above 94% at almost all the concentrations of Fe and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  blend ratios. At Manhole B2, these reductions ranged from 48 to 97%, with an average of 84%. At a concentration of 16 mg/L Fe, reductions observed at Manhole B2 were generally higher than the other four concentrations of Fe tested. A  $\text{Fe}^{3+}/\text{Fe}^{2+}$  blend of 1.9:1 (at an Fe concentration of 16 mg/L) delivered a maximum reduction of 97% along the test reach from Manhole B74 to Manhole B2. In contrast to this, a blend ratio of 1:1 delivered only a 70% reduction at the same concentration of Fe along the same sewer reach. At Manhole B2, 16 mg/L Fe and a blend ratio of 1.9:1 provided the best control of dissolved sulfide.

The data, in general, indicated that iron reacted with sulfide very well. The maximum control of dissolved sulfide at 16 mg/L Fe was not a surprise. The reaction was stoichiometric, as predicted in the literature: 7 parts of iron should precipitate 4 parts of sulfide. In fact, 16 mg/L Fe precipitated more sulfide than predicted by the equation. This may be attributable to the presence of  $\text{Fe}^{3+}$  iron. The reduction of  $\text{Fe}^{3+}$  iron to  $\text{Fe}^{2+}$  iron (in the presence  $\text{O}_2$ ) via the formation of  $\text{S}^\circ$  and further on the precipitation of  $\text{FeS}$  as predicted by the equations is possible (Dohnalek and FitzPatrick, 1983 and Pomeroy and Bowlius, 1946). Similar stoichiometric relations have been reported in the literature: 4 parts of anhydrous  $\text{FeCl}_3$ , or  $\text{FeCl}_2$  (1.8 parts of Fe) alone reacted with 1 part of  $\text{S}^2-$  in the wastewaters of the City of Mesa (Jameel, 1989).

All of the monitoring results (along the 25-mile test reach) indicated that dissolved sulfide increased steadily with distance downstream in the presence and absence of treatment (Figure 16). After addition of iron salts was initiated, good control was achieved in the study reach from Manhole B74 to Manhole H399, with concentrations averaging below 0.1 mg/L at each of the monitoring stations, at least 75% of the time. These results fell well within the range of reductions observed during a long-term monitoring of  $\text{FeCl}_3/\text{FeCl}_2$  blend treatment conducted by the Districts between August, 1990 and April, 1991 (Weiss, 1991). During that period, in the reach Manhole B74 to Manhole H399, levels averaged below 0.1 mg/L, 65% of the time. Again, the reductions observed are of no surprise since this section of the study reach was loaded with excess iron at all times during treatment (30 to 45 mg/L as Fe).

One might believe that iron concentrations are directly proportional to the amount of sulfide precipitated. In reality, this is not true, since  $\text{S}^2-$  is in competition with other complexing species such as carbonates, phosphates, and hydroxides. That is, a limitation is exerted by  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$  towards any sulfide species encountered in the wastewaters. Dohnalek and FitzPatrick (1983) also report certain limitations of iron-sulfide systems. Therefore, addition of iron in amounts higher than what is actually required (stoichiometrically), will not provide a higher level of sulfide treatment.

In a study conducted by Won (1988) in the same trunk sewer, it was concluded that complete and consistent control of dissolved sulfide was difficult to maintain using  $\text{FeCl}_2$  alone. In comparing Won's study and the study reported here, the latter indicates better control using a blend of  $\text{FeCl}_3$  and  $\text{FeCl}_2$  in lieu of the  $\text{FeCl}_2$  alone. Pomeroy and Bowlius (1946) also report that by using only a few mg/L of excess  $\text{Fe}^{3+}$  iron, sulfide levels can be reduced more than with  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$  iron alone. They report that effective results were obtained with solutions containing about 66% of the iron in the  $\text{Fe}^{3+}$  form via the possible formation of  $\text{Fe}_3\text{S}_4$  (precipitation pathway is not defined). In our study, effective dissolved sulfide control was also observed when the excess  $\text{Fe}^{3+}$  iron used was almost twice as much as the  $\text{Fe}^{2+}$  iron.

**Table 5. Percentage Reductions in Sulfide Parameters During the Full Scale Optimization and Treatment**

Iron concentration (mg/L)	Blend ratio ( $\text{Fe}^{3+}:\text{Fe}^{2+}$ )	Percentage reductions in sulfide after treatment								
		Manhole H399			Manhole B74			Manhole B2		
TS	DS	$\text{H}_2\text{S}$	TS	DS	$\text{H}_2\text{S}$	TS	DS	$\text{H}_2\text{S}$		
10	1:1	67	99	25	55	96	50	38	72	48
	1.3:1	50	99	0	67	96	70	77	48	48
	1.6:1	67	99	23	62	99	88	48	94	36
	1.9:1	83	99	23	70	99	79	78	97	54
12	1:1	50	99	0	71	98	56	30	78	22
	1.3:1	67	99	23	63	98	38	38	86	50
	1.6:1	67	99	0	58	98	26	24	80	15
	1.9:1	83	99	23	72	99	49	40	75	48
14	1:1	67	99	0	65	98	75	33	83	70
	1.3:1	67	99	38	63	99	53	42	95	36
	1.6:1	67	99	0	69	99	64	44	70	52
	1.9:1	83	99	38	67	94	62	47	78	64
16	1:1	67	99	0	68	79	56	28	70	38
	1.3:1	83	99	38	78	98	88	57	95	75
	1.6:1	83	99	0	72	98	64	53	91	73
	1.9:1	83	99	46	84	98	47	63	97	79
18	1:1	83	99	0	75	98	83	48	84	56
	1.3:1	83	99	31	64	99	68	33	91	61
	1.6:1	67	99	0	63	97	26	40	88	81
	1.9:1	83	99	0	75	99	73	47	94	78

TS = Total sulfide

DS = Dissolved sulfide

Iron concentrations listed is at Manhole B2 for a flow of 200 MGD

### 3.3 Total Sulfide

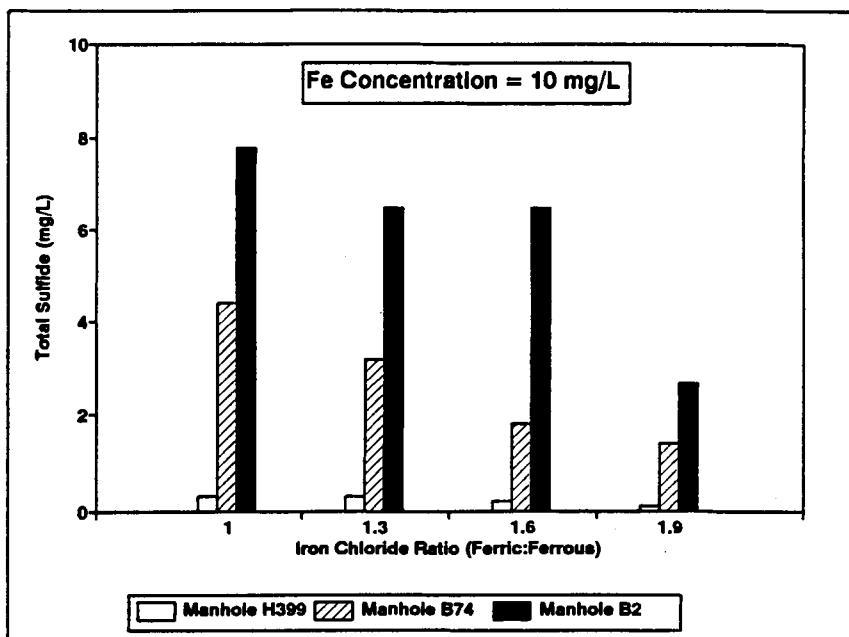
The background total sulfide levels ranged from 0 mg/L, at Manhole H399 to as high as 15 mg/L, at Manhole B2. Sulfide buildup appeared to be very fast in the sewer section from Manhole B74 downstream to Manhole B2. As mentioned above (Section 3.2), the 4-mile, double-barrel, surcharged section of J.O. "B", probably plays a critical role in altering the sulfide dynamics of the system. Table 4 shows a summary of the background total sulfide levels at Manhole H399, Manhole B74, and at Manhole B2.

Figures 17 through 21 show total sulfide concentrations measured at the three locations mentioned above at various concentrations of Fe and at different  $\text{Fe}^{3+}/\text{Fe}^{2+}$  blend ratios. From the injection point, concentrations steadily increased with distance downstream, whether or not iron was present. Throughout the study, a general drop in levels was observed downstream of the cluster, probably because of dilution, whether or not iron was present. In the study reach above the cluster, iron seems to retard the rate at which  $\text{S}^2$  accumulates in the wastewater. Below Manhole B74 downstream to Manhole B2, accumulation, in the presence and absence of treatment appeared to be similar. However, these rates in the entire study reach, in the absence of treatment, when normalized on a surface area basis, appeared to be similar (data not presented).

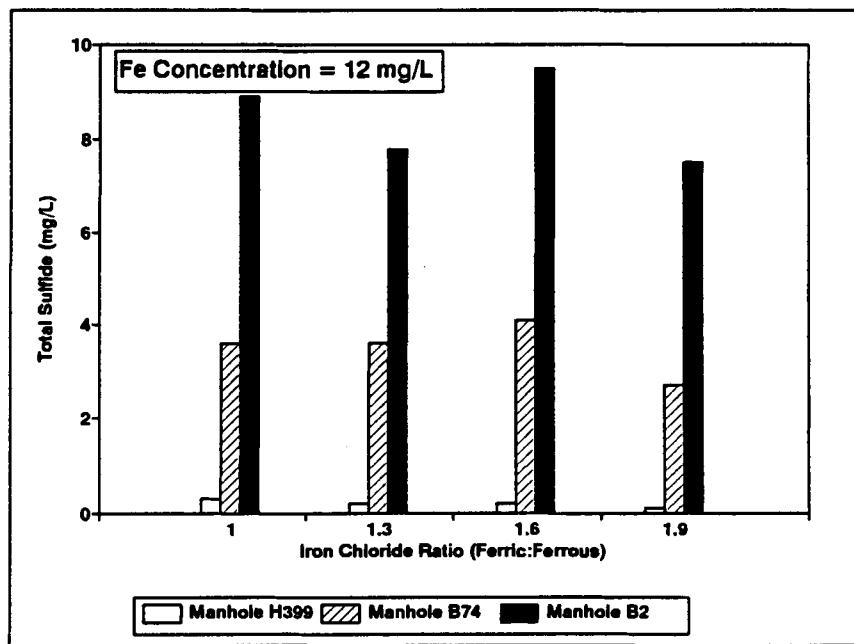
Table 5 provides a summary of percentage reductions of sulfide parameters, with iron treatment. A general drop in total sulfide was observed during treatment. At Manhole H399, the reductions for various dosages and blend ratios ranged from 50 to 83%, with 73% being average. At Manhole B74, these reductions were generally lower, ranging from 55 to 84%, with an average of 68%. At Manhole B2, these reductions further lowered to an average of 45%, with a range from 24 to 78%. At a concentration of 16 mg/L Fe and blend ratio of 1.9:1, a maximum reduction of 63% was observed at Manhole B2. However, the greatest drop (78%) in total sulfide level at Manhole B2, was delivered by 10 mg/L Fe at a blend ratio of 1.9:1. Figure 22 compares total sulfide concentration, in the presence and absence of 16 mg/L, 1.9:1 blend treatment.

Reductions of total sulfide observed along the study reach can be attributable to two factors. Firstly, the possibility of catalytic oxidation of  $\text{S}^2$  ions, in the presence of  $\text{Fe}^{2+}$  and minute amounts of dissolved  $\text{O}_2$  is good. If catalytic oxidation occurred, most of the  $\text{S}^2$  would be oxidized to  $\text{S}^\circ$  (Section 1.6). However, the kinetics associated with this oxidation reaction suggest the formation of several other unknown intermediates of sulfur (Pomeroy and Bowlus, 1946). Such reactions could occur in the upstream sections of the study reach because the sewage is relatively aerobic and dissolved  $\text{O}_2$  content is at least 0.1 mg/L (Won, 1988). The kinetics and mechanisms associated with this reaction are very complex.

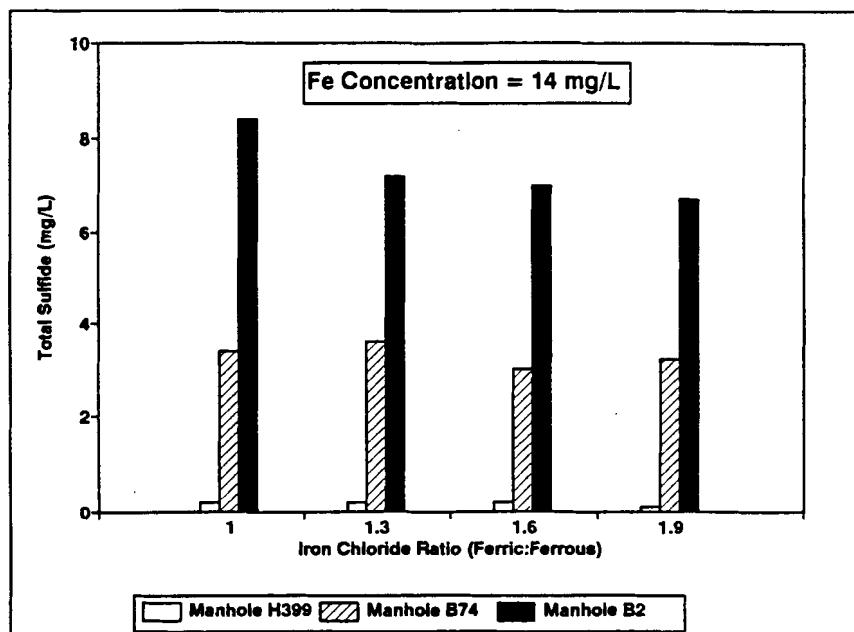
The rates associated with catalytic oxidation could be directly proportional to the amount of dissolved  $\text{O}_2$ , thereby delivering better reductions of total sulfide in the upstream section (Manhole H399 to B74) of the study reach (which might have occurred). The literature indicates that such complexity is evidenced and/or influenced by; sewage pH, sewage  $\text{S}^2$  concentrations,  $\text{O}_2$  levels, transition metals, and organic content of the liquid phase (Chen, 1974). At micromolar levels, transition metals and organics, have more of a catalytic effect than an inhibitory effect on the oxidation of  $\text{S}^2$  (Chen *et al.*, 1972). The potential of domestic sewage being supplemented with several transition metals and trace organics is good.



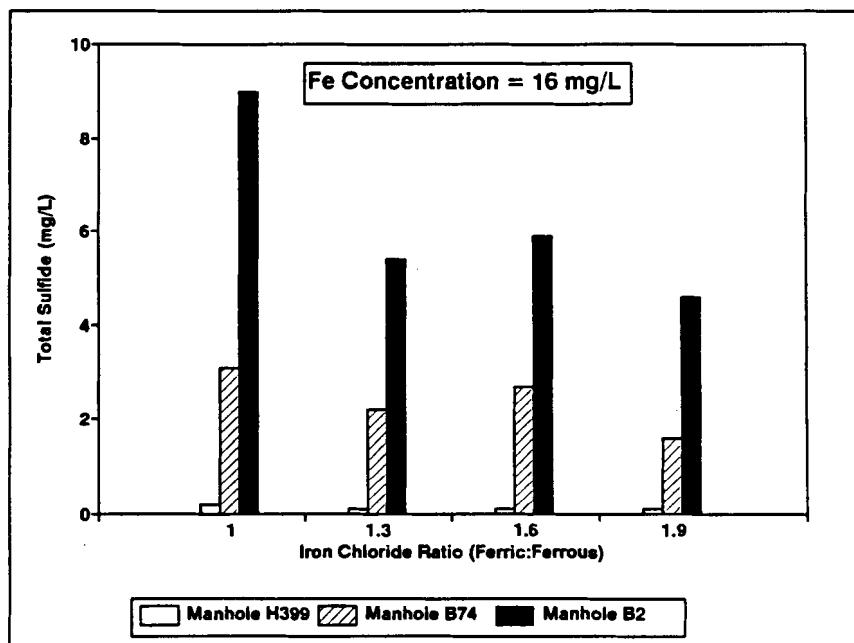
**Figure 17.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows average total sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 10 mg/L and four different blend ratios.



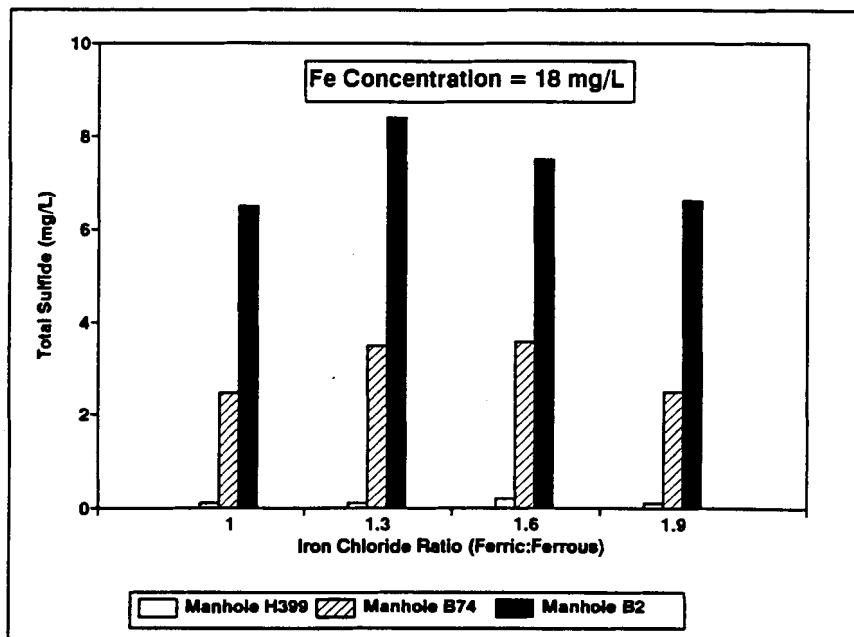
**Figure 18.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows average total sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 12 mg/L and four different blend ratios.



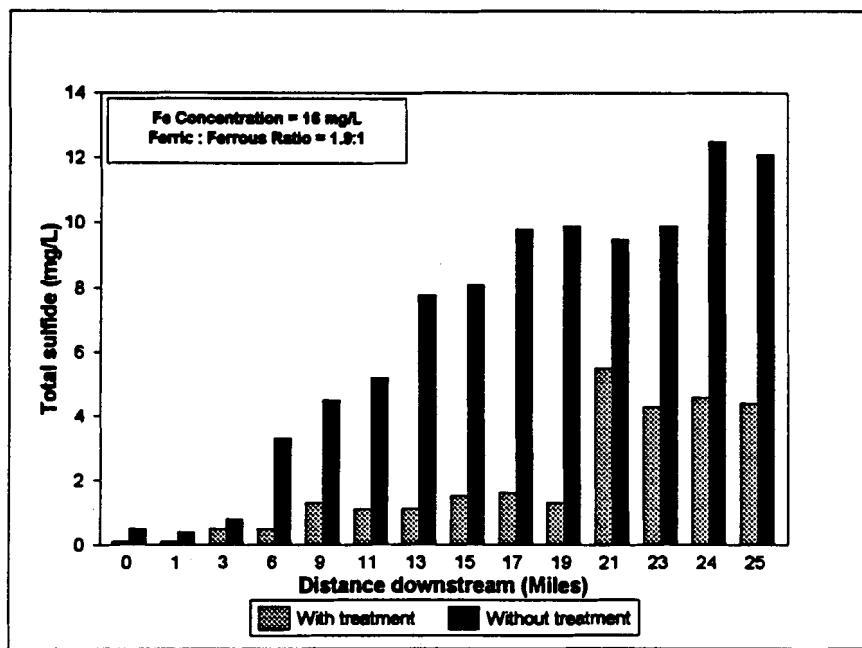
**Figure 19.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows average total sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 14 mg/L and four different blend ratios.



**Figure 20.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows average total sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 16 mg/L and four different blend ratios.



**Figure 21.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows average total sulfide levels at three monitoring sites along the test reach, using a total Fe concentration of 18 mg/L and four different blend ratios.



**Figure 22.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on total sulfide concentrations. Graph shows total sulfide levels at monitoring locations along the 25 mile test reach, using a total Fe concentration of 16 mg/L and a blend ratio of 1.9:1, and without treatment.

Secondly, SRB may be experiencing inhibitory or catalytic effects. The data suggests, however, that some toxic effect may in fact be exerted by iron in the study reach above the cluster and up to the application point. This toxicity may be relieved in the sewer reach from Manhole B74 down to Manhole B2 due to the dilution provided by the flow inputs around the cluster (J.O. "E", "F", and "H"). Saleh *et al.* (1964) and Jack and Thompson (1983) have provided lists of substances and metals that could inhibit SRB activity. Iron is one of them.

If iron induced a catalytic effect on SRB, it would be expected that SRB from systems treated with iron, would produce more sulfide at higher rates, than SRB in untreated systems. This theory needs further investigation and can be determined by generation rates of the same SRB, but reacting to two different conditions; treated vs. untreated. Also, it could be that SRB are in competition with other bacteria in the sewage. Iron could exert a selective pressure against the competitors of SRB allowing SRB to expand their niche. This could result in higher sulfide output. Iron addition could have permitted the establishment of a unique type of SRB in the pipe slime layers. This uniqueness might have shutoff its sulfate-reduction pathway (in the presence of Fe) and somehow triggered its energy derivation from the metabolism of Fe (Weiss, 1992). While this is mere speculation, it needs to be looked into from a microbiological standpoint. The chemically catalyzed oxidation of  $S^{2-}$  (discussed above) is relatively faster than the its biological counterpart.

At certain monitoring locations (data not included), better percent reductions of total sulfide were observed at lower concentrations of iron than at higher levels. This could generally be attributable to higher background sulfide levels that could have provided a more effective sulfide precipitation on a weight to weight basis. It was also observed that effective sulfide control was achieved in the upper 17 miles of the study reach. This partially contradicts the Pomeroy and Bowlius study (1946) which concludes that the effects of iron is limited to short sewer reaches, beyond which the sulfide levels would rise again. Won (1988) also reports effective sulfide control in the upper 20 miles of the study reach.

### 3.4 Hydrogen Sulfide

It is believed that measured rates of pipe corrosion may be directly dependent on headspace  $H_2S$  levels. These levels can be significantly reduced by precipitating free sulfide with the use of iron chloride. Reducing headspace  $H_2S$  could limit the activity of SOB at the crown.

Previous investigators at the Districts have concluded that median values of  $H_2S$  are more representative than mean values when a large range of erratic data needs to be interpreted. However, due to limited samples obtained for every experimental run, results reported here are based on mean values. Won (1988) reports that  $H_2S$  gas monitoring, by grab sampling, is fairly representative of what is actually occurring in the sewer and supports the consideration of mean values. In an in-house study conducted by the Districts in its large diameter sewers, Won (1988) compared the results of continuous and grab sample monitoring in the absence and presence of iron salts treatment. In comparing results, the coefficients of variance were well within an acceptable range.

The background sewer headspace  $H_2S$  ranged from 0 ppmv at Manhole H399 to 40 ppmv at Manhole B2 (Table 4). In certain instances, these values were as high as 100 ppmv irrespective of the location and pipe configuration at the manhole structures along the study reach. Also, high values were more frequently reported in the trunk sewer section between

Manhole B74 and Manhole B2 when compared to the upstream reaches in the absence of iron. It is speculated that H<sub>2</sub>S levels measured at 100 ppmv could have been a lot higher, but were limited by the capability of the instrument. Previous sulfide records have shown similar variability. These higher levels were erratic and not specific to any location. Therefore, they were eliminated from the data analysis.

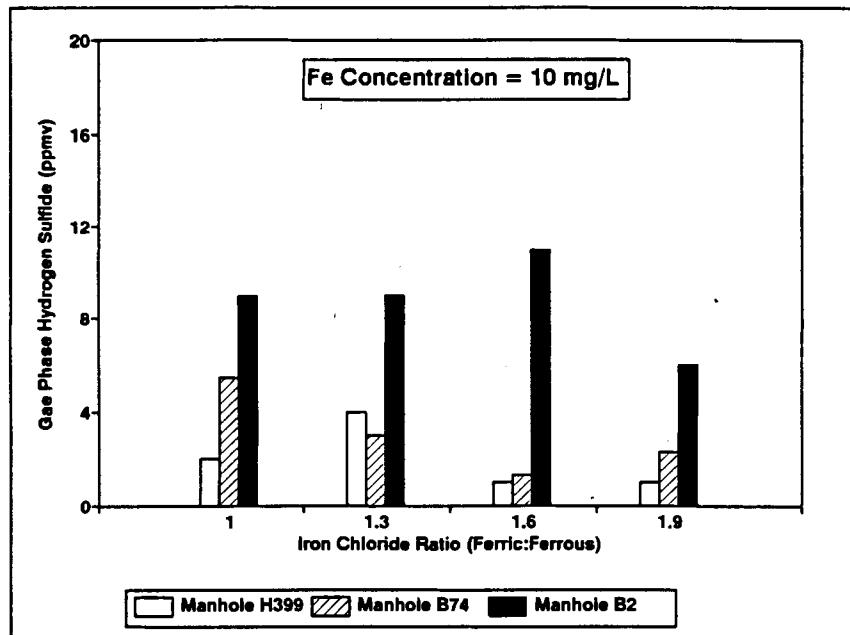
Figures 23 through 27 show mean concentrations of headspace H<sub>2</sub>S monitored along the study reach (at three monitoring locations) for each combination of Fe concentration and blend ratio tested. These results indicate that concentrations of Fe and observed reductions were directly proportional. However, no apparent relationship between the various combinations of blend ratio and the H<sub>2</sub>S reductions at a constant concentration of Fe was seen.

During Iron addition, the reductions in headspace H<sub>2</sub>S ranged from 0 to 46%, at Manhole H399 suggesting partial reaction with iron (Table 5). At Manhole B74, up to 88% reduction was seen, with an average of 61%. At Manhole B2, reductions were moderate and averaged 54%. Throughout the optimization study, reductions generally were maximum at Manhole B74, when compared to the other two locations. Treatment with an iron blend reduced headspace H<sub>2</sub>S gas at all the monitoring locations along the sewer test reach. The degree of reduction, however, was less than the control provided over dissolved sulfide.

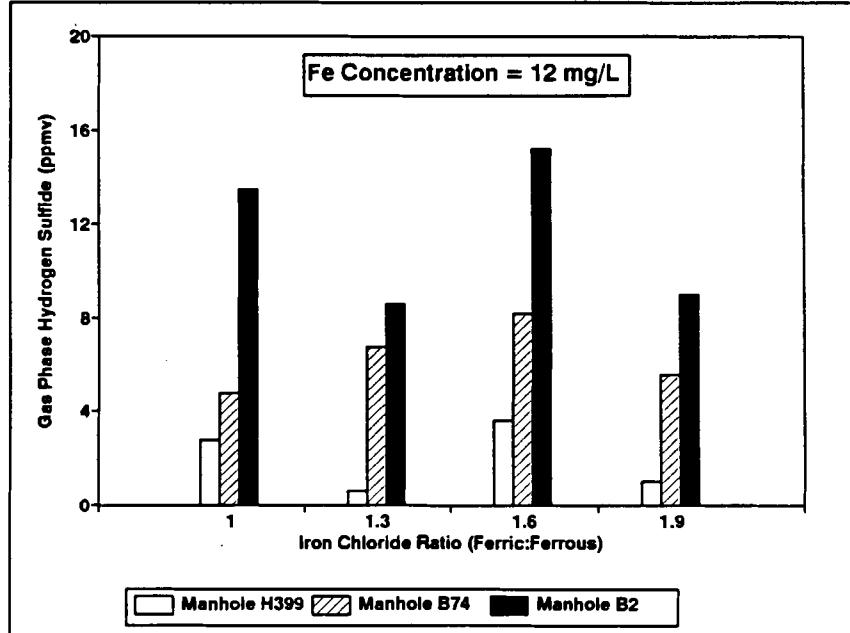
The average reductions in headspace H<sub>2</sub>S, at all three monitoring sites was the greatest at 16 mg/L Fe. At Manhole B2, reductions were similar with those at 18 mg/L Fe. At Manhole B74, reductions ranged from 47 to 88%, with 16 mg/L Fe. The greatest reduction was achieved with a blend ratio of 1.3:1. At Manhole B2, a 79% reduction was observed at 16 mg/L Fe and blend ratio of 1.9:1. In contrast to this, at the same concentration of Fe, a blend ratio of 1:1 offered a reduction that was half as good. A clear distinction between percentage reductions in H<sub>2</sub>S gas and blend ratios (1.3:1, 1.6:1, and 1.9:1) at a concentration of 16 mg/L Fe was difficult. The data suggests that H<sub>2</sub>S gas reduction is greater when Fe<sup>3+</sup> iron used exceeded the Fe<sup>2+</sup> iron. These reductions almost fall within the range that has been predicted in the literature. Won (1988) and Weiss (1991), respectively, reported maximum reductions of 70% and 80% in the same trunk sewer. In a sulfide control study, DeZham *et al.* (1988) reports satisfactory control (30 to 60%) of H<sub>2</sub>S gas using a 30% FeCl<sub>2</sub> solution. Also, hydrogen sulfide reduction seemed to be consistently greater along the 34-mile sewer reach using an iron concentration of 16 mg/L and a blend ratio of 1.9:1.

During treatment, at some of the monitored locations, unusually high levels of H<sub>2</sub>S were reported although the dissolved sulfide levels were reduced to below detectable levels with treatment. The H<sub>2</sub>S levels recorded on such occasions were way above the background values. Such disparity in headspace H<sub>2</sub>S data has led to a lot of speculation (from a corrosion standpoint).

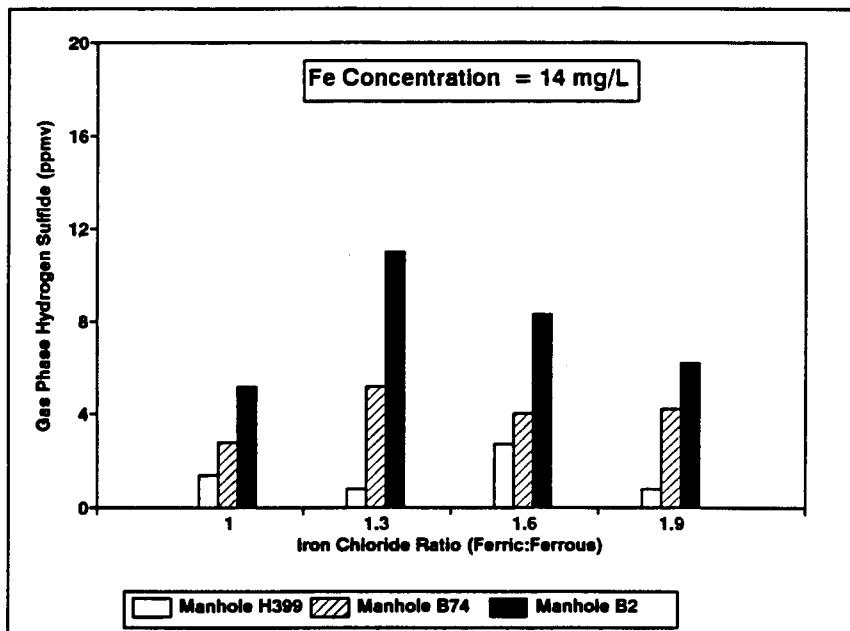
To assess H<sub>2</sub>S gas effects on pipe material and crown deterioration, the Districts conducted a ten week study in two of its large diameter sewers in 1989 (J.O. "H" and J.O. "B"). A total of 34 manholes representing four different classes of pipe condition were monitored for H<sub>2</sub>S gas. The four classes monitored were selected based on the remaining serviceable life of the sewers; 0, 0-10, 10-50, and 100 years. In grab samples taken from locations where the remaining serviceable life of the sewer is estimated to be less than 10 years (mostly from Manhole B74 to Manhole B2), H<sub>2</sub>S was detected 95% of the time. All measurements exceeded 2 ppmv 90% of the time. In the same study, all H<sub>2</sub>S measurements were less than 2 ppmv 90%



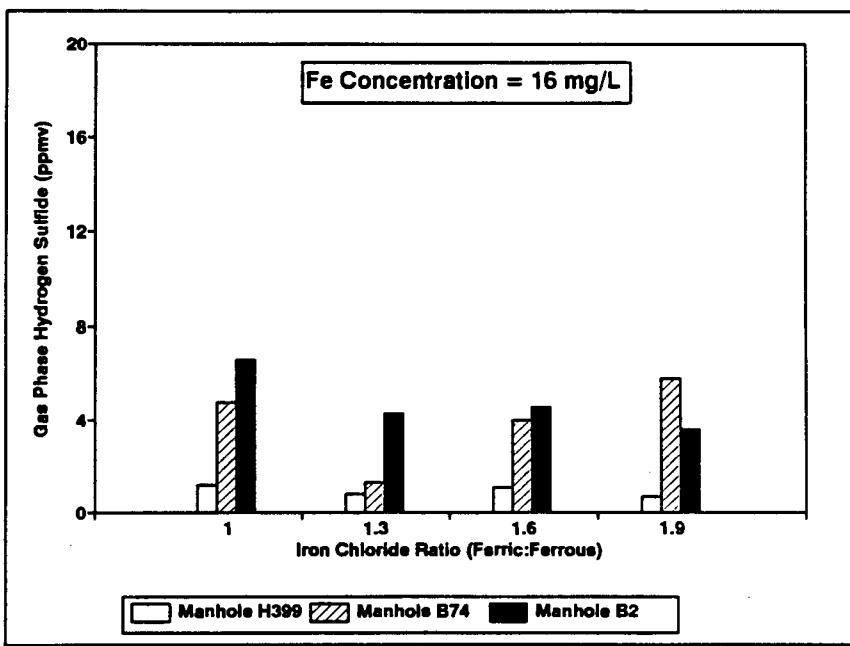
**Figure 23.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows average hydrogen sulfide level at three monitoring sites along the test reach, using a total Fe concentration of 10 mg/L and four different blend ratios.



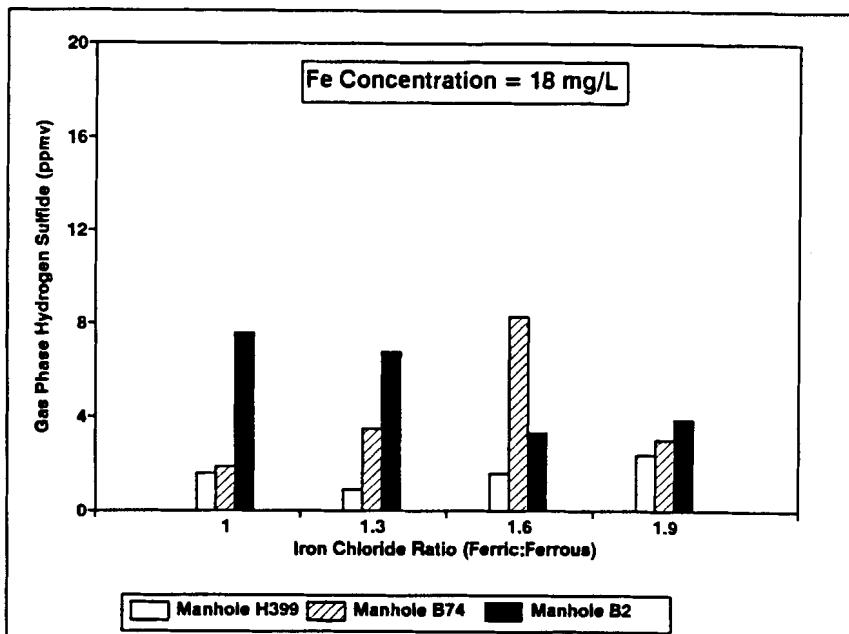
**Figure 24.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows average hydrogen sulfide level at three monitoring sites along the test reach, using a total Fe concentration of 12 mg/L and four different blend ratios.



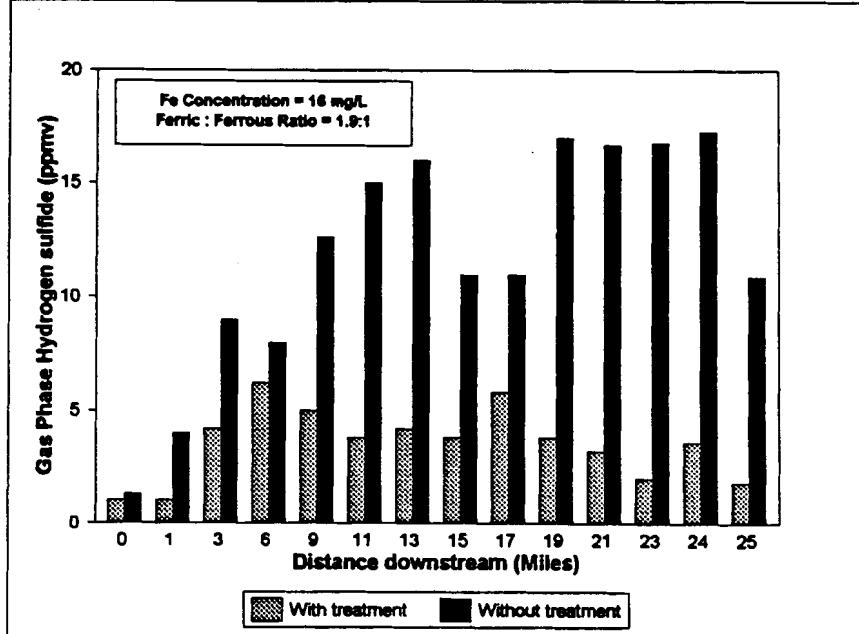
**Figure 25.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows average hydrogen sulfide level at three monitoring sites along the test reach, using a total Fe concentration of 14 mg/L and four different blend ratios.



**Figure 26.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows average hydrogen sulfide level at three monitoring sites along the test reach, using a total Fe concentration of 16 mg/L and four different blend ratios.



**Figure 27.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows average hydrogen sulfide level at three monitoring sites along the test reach, using a total Fe concentration of 18 mg/L and four different blend ratios.



**Figure 28.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer headspace hydrogen sulfide concentrations. Graph shows hydrogen sulfide levels at monitoring locations along the 25 mile test reach, using a total Fe concentration of 16 mg/L and a blend ratio of 1.9:1, and without treatment.

of the time in the sewer reach from Manhole B74 to Manhole H399. Most sections of this sewer have life expectancies of 100 or more years. It was therefore recommended that a treatment which controls H<sub>2</sub>S gas to less than 2 ppmv be relied upon to arrest sulfide-induced corrosion in all Districts' sewers (Weiss, 1992).

### 3.5 Sewer Odors

Hydrogen sulfide gas is thought to be primarily responsible for causing sewer odors. Odors can also result from compounds such as, mercaptans which are commonly found in industrial discharges. One important objective of this treatment is to control sewer odors by minimizing transport of H<sub>2</sub>S gas to the atmosphere. Odor measurements were in accordance with the recommended standards. This test calls for the use of the human nose and a good deal of experience and judgement.

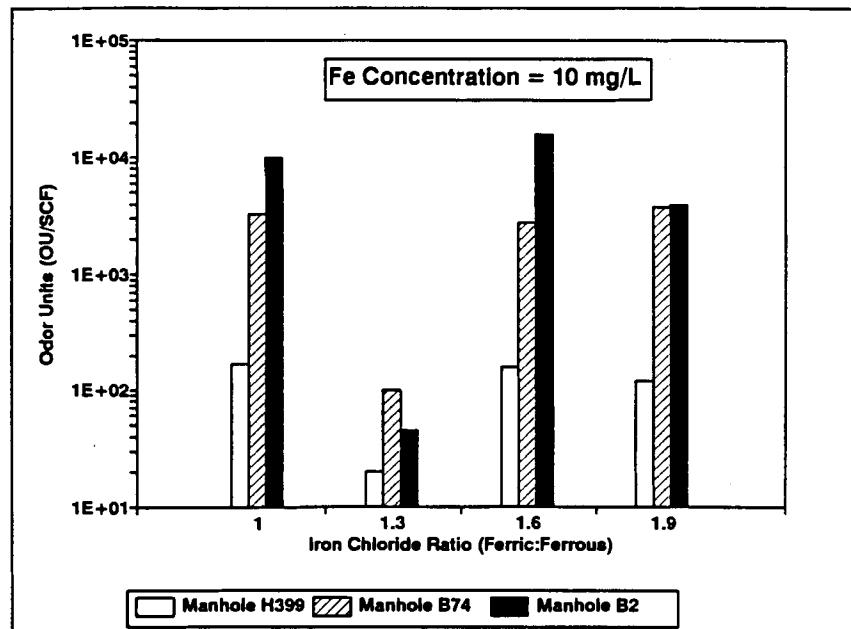
Odor samples were collected only twice during the two week background study. One of the gas sample bags leaked and the other provided no basis for comparison with odor samples collected during iron treatment. Figures 26 through 30 represent average odor levels monitored at the three sample sites located along the test reach. No specific correlation was observed between the amount of iron chloride or the blend ratio added and the odor levels measured.

In this study, uncertainty of the odor data made it very difficult to draw inferences or speculations. For example, at certain locations along the study, odors were reported to range from moderate to strong. The corresponding H<sub>2</sub>S levels were nil. This suggests that compounds other than H<sub>2</sub>S can be responsible for sewer odors. However, frequent reports of results indicating otherwise were also made. That is, when recorded H<sub>2</sub>S ranged from 20 to 40 ppmv, slight odors were reported. Therefore, the sensitivity of the analysis is questionable and was not relied upon. Previous investigators have also reported similar difficulties (Won, 1988 and Weiss, 1992). Hence, the data is merely presented and readers are open to their speculations.

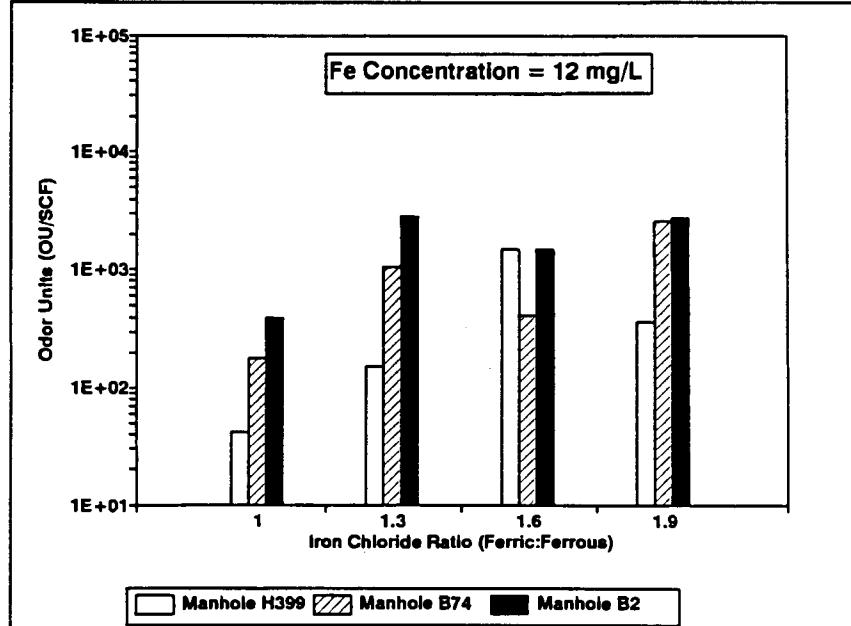
### 3.6 Crown pH and Sewer Corrosion

*Thiobacillus thiooxidans* is primarily responsible for acid production by oxidizing volatilized H<sub>2</sub>S gas in the presence of molecular O<sub>2</sub> and moisture. The H<sub>2</sub>SO<sub>4</sub> formed dissolves the cement binder in the concrete pipe, leading to the loss of structural integrity. Sulfate acidity is directly affected by the carbonate alkalinity of the concrete. The acid concentration is an indication of bacterial activity. Measured rates of pipe deterioration may be dependent on gas and liquid phase sulfide concentrations. Iron salts may control corrosion by precipitating free sulfide, thus significantly reducing its release to the sewer headspace as H<sub>2</sub>S. The reduced headspace H<sub>2</sub>S concentrations may limit SOB activity.

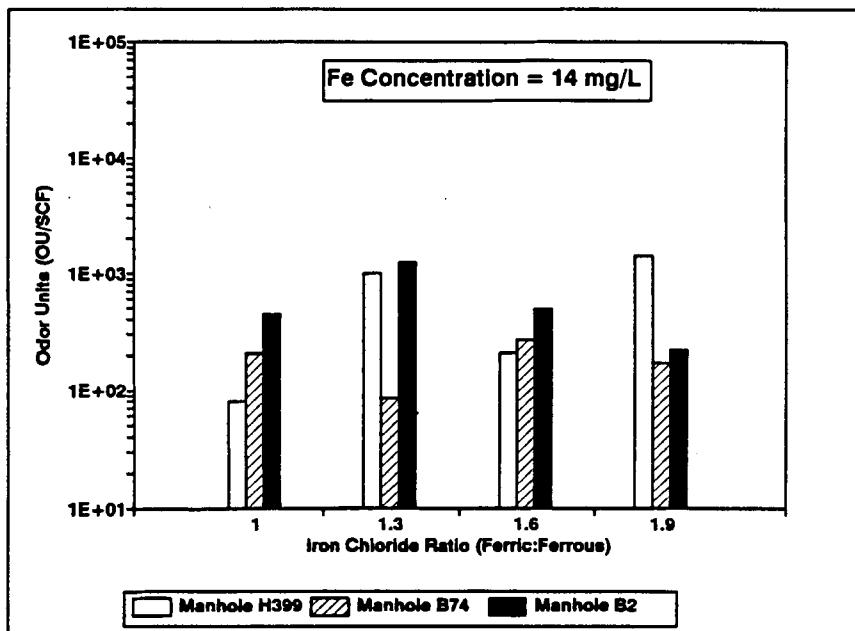
In our study, crown pHs generally ranged between 1 to 5, with or without iron treatment. In the presence of iron, no consistent increase in crown pH was observed at any location. Results showed no specific relation between the concentration of Fe or blend ratios, with that of pipe crown pH. The sewer reach from Manhole B74 to Manhole H399 had higher pHs (in the 3 to 5 range) than the reach from Manhole B74 and downstream to Manhole B2 (mostly below 2). Instances of increases and decreases in crown pH were observed, whether or not iron was present. No inferences could be drawn regarding crown pH control, with iron treatment. In a study conducted in the same trunk sewer, Won (1988) reports an increase of one pH unit at all



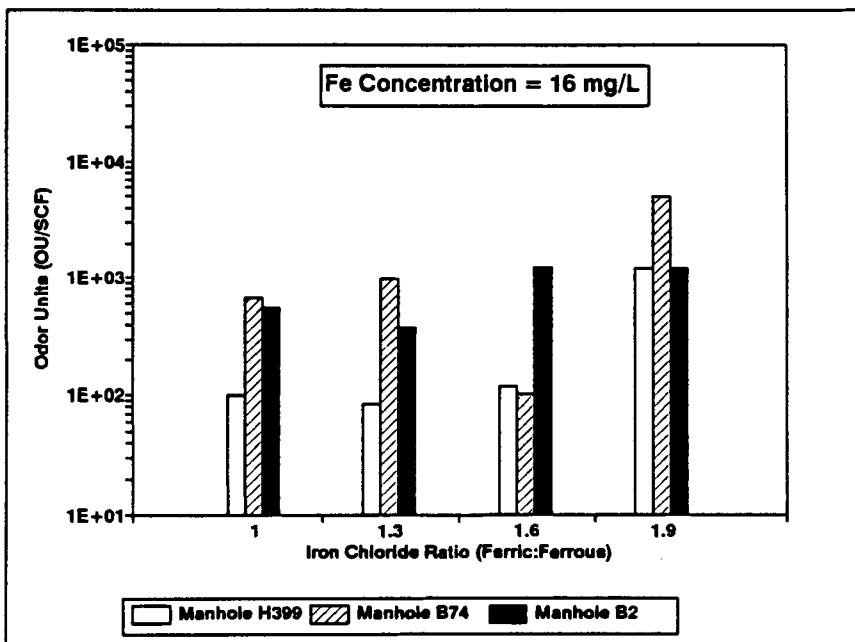
**Figure 29.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer odor levels. Graph shows average odor levels at three monitoring sites along the test reach, using a total Fe concentration of 10 mg/L and four different blend ratios.



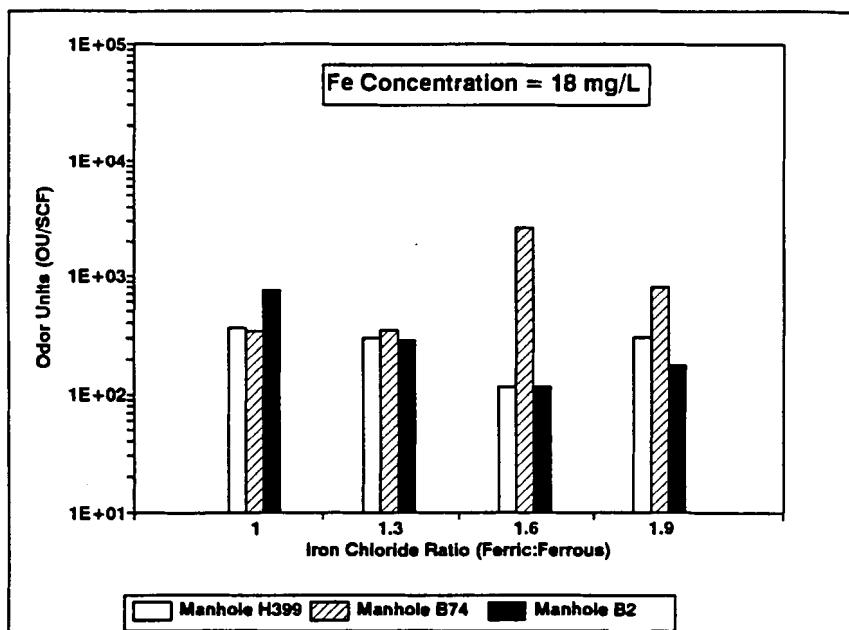
**Figure 30.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer odor levels. Graph shows average odor levels at three monitoring sites along the test reach, using a total Fe concentration of 12 mg/L and four different blend ratios.



**Figure 31.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer odor levels. Graph shows average odor levels at three monitoring sites along the test reach, using a total Fe concentration of 14 mg/L and four different blend ratios.



**Figure 32.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer odor levels. Graph shows average odor levels at three monitoring sites along the test reach, using a total Fe concentration of 16 mg/L and four different blend ratios.



**Figure 33.** Effect of ferric/ferrous chloride blend addition at SJC Sulfide Control Facility on sewer odor levels. Graph shows average odor levels at three monitoring sites along the test reach, using a total Fe concentration of 18 mg/L and four different blend ratios.

the monitoring locations, with treatment. Weiss (1991) also reports a slight increase in pH at most of the manholes in the same study reach.

### 3.7 Total and Soluble Iron

To account for the iron coming into the JWPCP, we monitored for total and soluble iron at Manhole B2, with and without treatment. We anticipated that monitoring for soluble iron should give us an approximate idea of how much of it would be available in an uncomplexed form. If sufficient soluble iron (uncomplexed) was available, we predicted that consumption and cost of iron chloride at the JWPCP anaerobic sludge digesters would be reduced.

Liquid samples for iron analysis were collected daily during the routine sulfide circuit. During the entire study, the SJCWRP primary sedimentation tanks were fed with  $\text{FeCl}_3$  (5 to 7 mg/L Fe) to enhance flocculation. The biosolids from the primary sedimentation tanks is discharged into the J.O. "H" Trunk Sewer, just upstream of Manhole H399.

Table 6 provides the range and an average for both total and soluble iron concentrations at Manhole B2, with and without treatment. Without treatment, total iron ranged from 4.3 to 8.9 mg/L Fe, with an average of 7.2 mg/L Fe. Some of this iron is contained in the SJCWRP sludge (approximately 1 to 2 mg/L as Fe at the most downstream point of the reach). During treatment, total iron at Manhole B2 was within the expected range. That is, it was approximately the sum of the iron added at the Sulfide Control Facility and that discharged from the sedimentation tanks (sludge) into J.O. "H".

Background soluble iron at the inlet works ranged from 0.25 to 1.53 mg/L Fe. During iron addition, soluble iron was seen at all times in the sewage. As the iron dosage at the Sulfide Control Facility increased, so did the average values of soluble iron measured at Manhole B2. Depending on the dosage at the point of application, the average soluble iron at Manhole B2 ranged from 1.86 to 4.52 mg/L. The availability of soluble iron at Manhole B2 might lead one to believe that excess iron is injected. Although some amount of soluble iron is seen, it may not be available to precipitate sulfide in the wastewater because certain charged, complexed species of  $\text{Fe(OH)}_3$  and  $\text{Fe(OH)}_2$  iron are believed to exist in a soluble form (Stumm and Morgan, 1970). Therefore, the soluble, uncomplexed iron present at the downstream end of the treated sewer, may not be available for control of  $\text{H}_2\text{S}$  in the gas space of the anaerobic digesters at JWPCP.

### 3.8 Affect of Iron Addition at SJCWRP on Chemical Use and Sulfide Control in J.O. "B"

To explore the affect of iron addition at SJCWRP on the chemical use and sulfide control in the test sewer, a two week evaluation was conducted from July 31 through August 14 of 1992. The evaluation was accomplished by temporarily interrupting the  $\text{FeCl}_3$  addition at the primary sedimentation basins.

During the evaluation period, dosing at the Sulfide Control Facility was maintained at 16 mg/L Fe, 1.9:1 blend ratio. A concentration of 16 mg/L Fe and blend ratio of 1.9:1 was predicted to be the optimum dose and ratio required to achieve maximum sulfide control. The prediction was made based on the stoichiometries discussed by Pomeroy and Bowles (1946). Throughout the second week of the evaluation, a normal dose of 5 to 7 mg/L Fe was added at the treatment plant. Historical records of SJCWRP indicate that: (i) the sedimentation basins are overdosed; (ii) detention time of the primary tanks is about two hours; (iii) about 75% of the complexed iron is combined with the raw sludge (primary) and the remaining 25% of the iron is carried over to

**Table 6. Distribution of Average Total Iron and Soluble Iron in the Joint Outfall "B"**

Iron concentration at point of application (mg/L)	Variation of total and soluble iron at Manhole B2			
	Total iron (mg/L) <sup>†</sup>		Soluble iron (mg/L) <sup>†</sup>	
	Range	Average	Range	Average
0	4.3 - 8.9	7.2	0.25 - 1.53	1.21
10	15.5 - 17.7	16.3	1.25 - 2.57	1.86
12	19.8 - 23.3	21.7	1.71 - 2.61	2.16
14	21.2 - 24.4	22.8	1.44 - 2.84	2.42
16	23.0 - 26.3	24.7	1.9 - 4.84	2.91
18	27.2 - 30.2	27.8	4.05 - 4.79	4.52

<sup>†</sup>Total and soluble iron were analyzed by atomic absorption spectrophotometry

the aeration tanks, and discharged to a plant sewer along with the skimmings, secondary sludge, and the plant sewer flow.

The results at Manhole B2 indicated that iron addition to the primary tanks may reduce the use of chemical for sulfide control. When iron salts were added both at the SJCWRP and at the Sulfide Control Facility, concentrations of dissolved sulfide and H<sub>2</sub>S in the sewer were reduced by 97 and 85%, respectively. During interruption of iron addition at SJCWRP these levels rose by 11 and 3%, respectively. Also, it appeared that iron added at the sedimentation tanks influenced the total sulfide concentrations in the system, by further reducing its level by 17%.

This short-term study suggested that maximum sulfide control can be achieved, with a dosage of 16 mg/L and 1.9:1 blend ratio at the Sulfide Control Facility, when iron is also used at the SJCWRP primary tanks. The results also indicated that the wastewater solids discharged from SJCWRP contain soluble iron. This soluble iron, albeit minuscule in amount (approximately 1 mg/L Fe), may exert a sulfide demand. Therefore, the soluble iron present in the biosolids discharged from SJCWRP probably helps control dissolved sulfide in the sewer studied. Should iron usage be interrupted at the sedimentation tanks, the use of chemical at the Sulfide Control Facility should be increased by about 6%.

Iron salts precipitate free sulfide, thus significantly reducing its release to the sewer headspace as H<sub>2</sub>S. Complete and consistent sulfide control is difficult to maintain with iron chloride. Iron treatment is very effective in controlling sulfide to at least 17 miles downstream of the application point. Iron addition at the SJCWRP sedimentation tanks affects the chemical use at the Sulfide Control Facility. The soluble iron present in the discharged biosolids exerts a demand for free sulfide and helps sulfide control in the test sewer.

In comparing this study with Won's, a mixture of ferric and ferrous chloride were found to be more effective than either salt alone. By using excess ferric iron (when compared to ferrous iron), sulfide can be reduced to very low levels. This suggests the possible formation of iron-sulfide intermediates, but no evidence is available. A dosage of 16 mg/L Fe and a blend ratio of 1.9:1 (ferric:ferrous) provided the best control of sulfide throughout the study reach. An average dissolved sulfide reduction of 95% provided only a 70% reduction in sewer headspace H<sub>2</sub>S levels. With treatment, reductions in H<sub>2</sub>S were not proportional to the reductions in dissolved sulfide. Odor reductions ranged from 20 to 70% during the entire study. No specific correlation was established between H<sub>2</sub>S level reductions and fall in odor levels. Reductions in odor levels did not correspond to the test concentrations of Fe or blend ratios.

Iron chloride may retard crown corrosion rates by reducing the availability of H<sub>2</sub>S gas to the sulfur-oxidizing bacteria. However, no specific relation between increase in crown pH and concentration of Fe or blend ratio was observed. This does not eliminate the possibility that iron addition provides some corrosion control. Additional studies, which more precisely define the relationship between headspace H<sub>2</sub>S and crown deterioration rate, are needed to determine whether iron treatment retards corrosion.

The catalytic effect of iron on sulfide in the upper reaches may be an important factor for sulfide removal in the system studied. The sensitivities of sulfide removal below the cluster are not clearly established. Oxygen can accelerate precipitation of iron-sulfide, but iron can also catalyze sulfide oxidation. In many instances, decreases in total sulfide were more than one-half the decrease of dissolved sulfide. This could be accounted for by factors other than iron-sulfide precipitation.

A combination of iron and continuous pH adjustment in the study reach below the cluster needs to be considered. Before a combination of continuous caustic and iron addition can be tested in full-scale, research in this area is required to elucidate the nature of the chemistry, formation of sulfide complexes, and the effect of pH on iron-sulfides.

In the test reach above the cluster, up to the chemical injection point, iron toxicity on sulfate-reducing bacteria may have occurred. Below the cluster, this inhibition seemed to be relieved by the 4-fold dilution provided at the cluster. This needs to be looked into from a microbiological standpoint.

Sulfide is recognized as a major contributor to objectionable odors and corrosion at wastewater collection and treatment facilities. The odor, corrosion, and safety problems associated with sulfide in wastewater have been known for decades and in recent years have become more of a concern to the wastewater industry. Long-term exposure to sulfide-laden air has resulted in extensive deterioration of collection systems. One of the major concerns in arresting sulfide-induced corrosion by controlling sulfide in sewers is its astronomical costs. This could be the bulk of the expenditures involved in operating a large collection system such as the Sanitation Districts.

To determine the cost for various treatment methods which could control sulfide crown deterioration in corroding sewers, the Districts' staff performed an economic analysis. Table 7 is an illustration of the total annual costs incurred by different methods of sulfide control. The total annual cost reported, is the sum of the amortized capital investment plus the total annual operating costs. The table also indicates the effectiveness of different sulfide control methods and compares the effectiveness via a rating system. The rating system used consists of a range of scores from 1 to 6, 1 being excellent and 6, no control (Khan, 1992).

Table 8 presents the total daily chemical costs for the continuous addition of various blends of iron salts at five different total concentrations of Fe to control dissolved sulfide. The annual chemical cost for the treatment of the 200 MGD flow in J.O. "B" using a blend of ferric and ferrous chloride (16 mg/L Fe and 1.9:1 blend ratio) to control dissolved sulfide is \$2.41 million.

The total annual cost to treat the entire Joint Outfall System; J.O. "A", J.O. "B", J.O. "C", and J.O. "D", with a composite flow of 350 MGD, to control dissolved sulfide is about \$4.3 million (Table 9). This cost has been calculated based on the stoichiometry of iron-sulfide complexes and the amount of background dissolved sulfide present in the sewage of each Joint Outfall Trunk Sewer, and is the sum of the amortized capital investment plus the annual operation and maintenance costs plus the annual chemical cost.

**Table 7. Effectiveness and Costs Associated with Various Sulfide Control Methods (Khan, 1992)**

Chemical treatment method	Effectiveness rating scores <sup>†</sup>			Total scores	Total annual cost (millions of \$) <sup>††</sup>
	Dissolved sulfide control	Odor control	Corrosion control		
Caustic spray	6	6	2	14	1 - 2
Oxygen injection	3	4	5	12	9 <sup>‡</sup>
Caustic shock dosing	3	4	4 - 5	10 - 11	12 <sup>‡</sup>
Ferrous chloride	3	3	5	12 - 13	12 <sup>‡</sup>
Ferric/ferrous chloride <sup>†††</sup>	2	3	5	10	4.3
Ferric nitrate	3 - 4	4	5	12 - 13	14 <sup>‡</sup>
Continuous caustic addition	3	1	1	5	15 <sup>‡</sup>
Hydrogen peroxide	3	3	5	11	21 <sup>‡</sup>

Rating: Excellent=1, Very good=2, Good=3, Fair=4, Poor=5, and No control=6.

<sup>†</sup>The effectiveness of treatment scores are based on previous Districts full scale evaluations

<sup>††</sup>The costs are based on previous Districts full scale evaluations.

<sup>‡</sup>Costs are based on treating the average Joint Outfall System flow, and include the amortized capital investment and O&M costs. Land and engineering costs are not included.

<sup>†††</sup>Rating and cost presented based on the results of this study (Table 9) and not taken from reference.

**Table 8. Calculated Chemical Requirements and Associated Total Chemical Costs**

Iron concentration	Blend ratio (Fe <sup>3+</sup> :Fe <sup>2+</sup> )	Anhydrous (x1000 Lbs/day)		Total chemical cost (x1000 \$/day) <sup>††</sup>
		Ferric chloride <sup>†</sup>	Ferrous chloride <sup>†</sup>	
10	1:1	20.2	16.2	4
	1.3:1	23	13.7	4.05
	1.6:1	25	12.4	4.1
	1.9:1	26.7	10.9	4.2
12	1:1	24.2	19.2	4.8
	1.3:1	27.4	16.6	4.9
	1.6:1	29.8	15.8	4.95
	1.9:1	31.5	13.4	5
14	1:1	28.3	22.4	5.6
	1.3:1	31.8	19.5	5.65
	1.6:1	34.7	17.2	5.7
	1.9:1	37.1	15.4	5.8
16	1:1	32.3	25.6	6.37
	1.3:1	36.3	22.4	6.46
	1.6:1	39.4	19.9	6.5
	1.9:1	41.5	17.6	6.51
18	1:1	36.3	28.7	7.16
	1.3:1	41.1	24.9	7.26
	1.6:1	44.7	22.1	7.35
	1.9:1	47.6	19.9	7.42

<sup>†</sup>Quantities based on treating an average flow of 200 MGD.<sup>††</sup>Chemical costs reported are based on the Districts' contract price (\$0.11/anhydrous pound) with Imperial West Chemical Company, effective in May 1993.

**Table 9. Annual Chemical and Operation & Maintenance Costs to Treat Districts' Major Joint Outfalls with Iron Chloride**

Joint Outfall	Capital Investment <sup>†</sup> (\$)	O & M Cost of Station (\$)	Average Flow <sup>‡</sup> (MGD)	Background Dissolved Sulfide <sup>  </sup> (mg/L)	Daily Chemical Usage <sup>##</sup> (Anhydrous lbs.)		Total Daily Chemical Costs <sup>   </sup> (\$)	Total Annual Treatment Cost (Millions of \$)	
					FeCl <sub>3</sub>	FeCl <sub>2</sub>			
A	20,000	20,000	45	5.5	9,600	4,500	1,100	500	0.63
B	20,000	20,000	200	6.4	41,500	17,600	4,600	2,000	2.45
C	20,000	20,000	40	1.2	8,900	4,100	1,000	500	0.59
D	20,000	20,000	55	1.3	9,900	4,700	1,100	500	0.63

<sup>†</sup> \$200,000 at 8% interest amortized over 20 years

<sup>‡</sup> Average flow at the most downstream point of each Joint Outfall

<sup>||</sup> Uncontrolled dissolved sulfide data reported were obtained from routine circuits conducted from 1991 to 1993 at the most downstream end of each Joint Outfall

<sup>##</sup> Chemical usage rates entirely based on background dissolved sulfide and flow observed at the most downstream point of each Joint Outfall. Stoichiometric calculations were based on equations presented and discussed in earlier parts of this report

<sup>|||</sup> Chemical costs reported are based on the Districts' contract price (\$0.11/anhydrous pound) with Imperial West Chemical Company, effective in May 1993

1. APHA, AWWA, and WPCF (1990). *Standard Methods for the Examination of Water and Wastewater*.
2. Sulfide in Wastewater Collection and Treatment Systems (1989). Manuals and Reports on Engineering Practice No. 69, American Society of Civil Engineers (ASCE), New York, NY.
3. Bowker R. P. G. et al. (1985). Design Manual, Odor and Corrosion Control in Sanitary Sewerage Systems and Treatment Plants. EPA 625/1-85/018, U. S. EPA, Cincinnati, OH.
4. Chen, K. Y. et al. (1972). Oxidation of Sulfide by O<sub>2</sub>: Catalysis and Inhibition. *Jour. San. Engrg. Div., ASCE*, 98: SA1:215.
5. Chen, K. Y. (1974). Chemistry of Sulfur Species and Their Removal From Water Supply. *Chemistry of Water Supply, Treatment, and Distribution* (A. J. Rubin, editor). Ann Arbor Science, Ann Arbor, MI.
6. CRC Handbook of Chemistry and Physics (1972). CRC Press Inc., Cleveland, OH.
7. Dezham, P. et al. (1988). Digester gas H<sub>2</sub>S Control Using Iron Salts. *Journal of Water Pollution Control Federation*, Washington, D.C., 60:514-517.
8. Dohnalek, D. A. and FitzPatrick, J. A. (1983). The Chemistry of Reduced Sulfur Species and Their Removal from Ground Water Supplies. *Journal of the American Water Works Association*, 75:298-308.
9. Garrels, R. M. and Naeser, C. R. (1958). Equilibrium Distribution of Dissolved Sulphur Species in Water at 25°C and 1 Atm. Total Pressure. *Geochem. Cosmochim. Acta.*, 15:1-2:113.
11. Holder, G. A., et al. (1983). Studies of Sulfate Removal in a Model Sewer. Paper presented at Aust. Water/Wastewater Assoc. Conf., Australia.
12. Holmstrom, H., and Wilander, A. (1977). Control of Hydrogen Sulfide Production in Sewers. *Vatten* (Sweden), 33, 4, 394.
13. Jack, T. R., and Thompson, B. G. (1983). Patents Employing Microorganisms in Oil Production in Microbial Enhanced Oil Recovery. J. E. Zajic et al. (Eds.), Penn Well Books, Tulsa, Oklahoma.

14. Jameel, P. (1989). The Use of Ferrous Chloride to Control Dissolved Sulfides in the Interceptor Sewers at Mesa, Arizona, Brown and Caldwell Report.
15. Jin, C., and Won, D. (1989). Master Plan, County Sanitation Districts of Los Angeles County, Whittier, CA.
16. Kelly, D. P. (1981). Introduction to the Chemolithotrophic Bacteria, Chapter 79: *The Prokaryotes*. Ed., M. P. Starr. Spring-Verlag, pp. 997-1004.
17. Khan, G. A. (1992). Continuous Caustic Addition for Sewer Corrosion Control. County Sanitation Districts of Los Angeles County, Whittier, CA.
18. Martyn, P., and Kremer, J. (1987). Implementation of an Industrial Wastewater Treatment Program. *Proc. 41st Ind. Waste Conf.*, Purdue University, IN.
19. Milde, K., W. Sand, W. Wolff, and E. Bock (1983). *Thiobacilli* of the Corroded Concrete Walls of the Hamburg Sewer System. *J. of Gen. Microbiol.*, 129, pp. 1327-1333.
20. Parker, C. D. (1947). Species of Bacteria Associated with the Corrosion of Concrete. *Nature*, 159, 439.
21. Pfennig, N., F. Widdel, and H. G. Truper (1971). Chapter 74 of *The Prokaryotes*, Ed. M. P. Starr. Spring-Verlag.
22. Pomeroy, R. D. et al. (1985). Sulfide Occurrence and Control in Sewage Collection Systems. EPA 600/X-85-052, U. S. EPA, Cincinnati, OH.
23. Pomeroy, R. D. and Bailey, H.H. (1981). Iron-Bacteria and Sulfide Problems in Wells. *OpFlow*, 7:12:1.
24. Pomeroy, R. D. and Bowlus, F. D. (1946). Progress Report on Sulfide Control Research. *Sew. Works Journal*, 18, 597.
25. Pomeroy, R. D. and Parkhurst, J. D. (1977). The Forecasting of Sulfide Buildup Rates in Sewers. *Prog. Water. Technol.*, 9, 621.
26. Postgate, J. (1959). Sulfate Reduction by Bacteria. *Ann. Rev. Microbiol.*, 13, pp. 505-520.
27. Price, S. D. (1989). Master's Thesis. *Microbial Catalyzed Acid Production in Los Angeles County Sewers*. The University of Arizona.
28. Process Design Manual for Sulfide Control in Sanitary Sewerage Systems (1974). EPA 625/1-74-005, U. S. EPA, Cincinnati, OH.
29. Redner, J. A. (1992). Sewerage System Superintendent, County Sanitation Districts of Los Angeles County, Compton, CA. Personal Communication.
30. Rozhanskaya, A. M., et al. (1977). Bacterial Analysis of Corrosion of Reinforced Concrete Constructions. *Proceedings 10th International Congress on Metallic Corrosion (India)*, 1, 713.

31. Saleh, A., *et al.* (1964). The Effect of Inhibitors on Sulphate Reducing Bacteria. *Jour. Appl. Bacteriol.*, 27, 281.
32. Sand, W. (1987). Importance of Hydrogen Sulfide, Thiosulfate, and Methylmercaptan for Growth of *Thiobacilli* During Simulation of Concrete Corrosion. *Applied Environmental Microbiology*, 53, pp. 1645-1648.
33. Sand, W., *et al.* (1983). Simulation of Concrete Corrosion in a Strictly Controlled H<sub>2</sub>S Breeding Chambers. *Recent Progress Biohydrometallurgy (Italy)*, 1, 667.
34. So, S. S. and Merry, C. (1993). Senior Engineer and Assistant Project Engineer. Greater Vancouver Regional District, Burnaby, Canada. Personal Communication.
35. Stanier, R. Y., E. A. Adelburg, and J. Ingraham (1976). *The Microbial World*. Prentice-Hall, Inc., pp. 190-197 and 707-710.
36. Stumm, W. and Morgan, J. J. (1970). *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, Wiley Interscience.
37. The Control of Sulfides in Sewerage Systems (1972). D.K.B. Thistletonwayte (Ed.), Ann Arbor Science Publishers, MI.
38. Unpublished data (1991). County Sanitation Districts of Los Angeles County.
39. Vishniac (1974). Organisms Metabolizing Sulfur and Sulfur Compounds Genus 1, *Thiobacillus*. *Bergey's Manual of Determinative Bacteriology (8th Edition)*. R. E. Buchanan and N. E. Gibbons. The Williams and Wilkins Company, Baltimore, pp. 458-461.
40. Weiss, J. W. (1991 and 1992). County Sanitation Districts of Los Angeles County. Memorandums Related to In-house Work.
41. Witzgall, R. A., *et al.* (1989). Sulfide Corrosion Case Histories. Prepared for Water Pollution Control Federation Conference, San Francisco, CA.
42. Won, D. (1988). Sulfide Control with Ferrous Chloride in Large Diameter Sewers, County Sanitation Districts of Los Angeles County.