CAUSES AND CONTROL OF CONCRETE PIPE CORROSION

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SUMMARY

Sulfate reducing bacteria that thrive in sewers while reducing sulfur compounds to produce hydrogen sulfide. The hydrogen sulfide eventually escapes from the wastewater into the air space above the liquid, where sulfur oxidizing bacteria oxidize sulfide to sulfuric acid. In order to control the production of sulfuric acid and the corresponding corrosion, we investigated several aspects of the sulfur cycle.

This report consists of three parts. Part I describes the factors that control sulfur reduction in the sewer liquid and slime layers. The bacteriological, chemical, and physical aspects of sulfur reduction is summarized, and laboratory tests performed to measure hydrogen sulfide production rates, and the impact of additives on the hydrogen sulfide production rate. Part II describes an investigation into the microbiology of sulfur reducing bacteria, their growth requirements, and the impact of selected inhibitors on the growth characteristics of these organisms. Part III investigated the mass transfer of volatile compounds (such as hydrogen sulfide or other organic compounds) from the wastewater in a flowing sewer into the gas phase.

PART I. HYDROGEN SULFIDE PRODUCTION IN SEWERS*

Hydrogen sulfide (H_2S) is produced by sulfur reducing bacteria (SRB) in wastewater flowing down a sewer. The evolution of H_2S in the air space above the wastewater depends on a series of reactions starting with bacterial sulfur reduction to produce $H_2S_{(aq)}$ in the liquid and ending with the mass transfer of $H_2S_{(aq)}$ to $H_2S_{(g)}$ in the gas phase. The reaction rates and equilibria that control this process are complex and still poorly understood. Besides factors such as pH, temperature, and sewage organic strength, one needs to incorporate stream velocity and the impact of specific compounds in the liquid on sulfide reactions and bacterial growth.

This section reviews the factors that contribute to or control H_2S formation in sewage. A laboratory test to measure H_2S formation in the sewage (called the H2SPP test) is described and used to measure the impact of some of these variables on H_2S production. Finally, a sewer model is suggested that can be used to transfer the H2SPP test results to actual field conditions and applications. This report concentrates on H_2S production in sewers. Several literature reviews on sewer corrosion are available (for example US EPA 1985; Thistlethwayte, 1972) for a more broader and general reference on sewer corrosion.

OBJECTIVES AND APPROACH

The objective of this study is to determine those factors that contribute significantly to H_2S formation in sewage. Specifically, we attempt to discern the extent to which recent changes in the sewage composition in LA County Sanitation Districts sewers could enhance H_2S formation. The two most significant changes in wastewater composition are a reduction of metals due to recently imposed sewer discharge regulations, and the addition of waste activated sludge from upstream wastewater treatment plants.

A test procedure to measure the potential for H_2S production in sewage is used to evaluate the impact of various sewage constituents on H_2S formation. This laboratory test measures H_2S formation in sewage over an extended period of time. The rate of and potential for H_2S production is measured. Using this test, the impact of metals, inhibitors, toxicants, bacterial densities, etc. can easily be evaluated and the impact of various components assessed. Before the results are transferred to field conditions, other phenomena such as biofilm kinetics and mass transfer rates from the wastewater to the air space must be addressed. The latter aspects can easily be incorporated in a proposed sewer model.

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HYDROGEN SULFIDE PRODUCTION IN SEWERS

Hydrogen Sulfide Production Models

Several models have been proposed to evaluate H_2S production in sewers. These models predict the $H_2S_{(g)}$ concentration in the air space and therefore combine H_2S production and evolution kinetics. The Pomeroy and Parkhurst (1977) model is often used. For partially full flow conditions, this model proposes that the rate of sulfide production in the biofilm can be written as:

$$r_s = M_1 C_{BOD} \Theta^{(T-20)} \quad (1)$$

where

r_s = Rate of sulfide generation in the biofilm, g/m^2-h

M_1 = Effective sulfide flux coefficient for sulfide generated in slime, m/h

C_{BOD} = BOD concentration in wastewater, mg/L

Θ = Temperature coefficient, usually $\Theta = 1.07$

Equation 1 only accounts for sulfide generation in the biofilm, which is considered to be the primary source of H_2S production. The coefficient, M_1, is approximately 3.2×10^{-4} m/h for partially full pipes and 1×10^{-3} m/h for full flowing pipes.

Thistlethwayte's (1972) model is slightly more complex:

$$r_s = M_2 V C_{BOD}^{0.8} C_{SO4}^{0.4} \Theta^{T-20} \quad (2)$$

where

M_2 = Sulfide production rate coefficient

V = Stream flow velocity, m/h

C_{SO4} = Sulfate concentration, mg/L

In Thistlethwayte's model, sulfide generation also depends on the sulfate concentration and stream flow velocity. Their temperature coefficient ($\Theta = 1.139$) is significantly higher than that proposed by Pomeroy and Parkhurst.

While some other variations of these two models are available (ex. Boon and Lister, 1974) the components are essentially the same: H_2S evolution in a sewer under field conditions is determined by the organic strength of the wastewater, temperature, sulfate concentration in some cases, and stream velocity. In subsequent sections, the impact of these components is investigated in terms of a theoretical description of H_2S formation and the kinetics of the sewer system.

Reactions in a Sewer - An Overview

Figure 1 shows the classic depiction of a partially filled sewer, containing wastewater with a variety of organic and sulfur compounds. Commonly, the sewer is half full and the pipe velocity maintained at approximately 0.6 m/s. Silt and heavy organic particles deposit on the bottom, while bacterial growth develops on the walls of the sewer to form a biofilm or slime layer. This silt layer and biofilm provide an excellent environment for bacterial growth while protected from the velocity shear forces exerted by flowing wastewater. This model sewer contain several microenvironments: the space above the liquid is commonly filled with air with an abundance of oxygen; the liquid can be either aerobic or anaerobic, depending on the oxygen demand and reaeration rates; the silt and biofilm layers can also be aerobic or anaerobic.

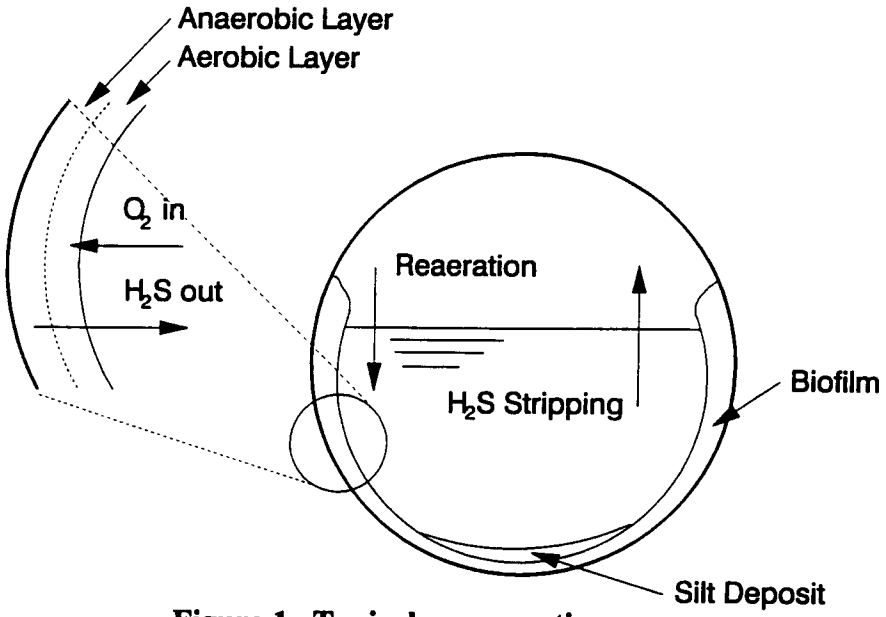


Figure 1. Typical sewer section.

The sulfur cycle in a sewer is fairly well understood. Sulfur compounds such as sulfate, SO_4^-, is reduced to H_2S by sulfur reducing bacteria in an environment depleted of oxygen, in the flowing wastewater or biofilm. H_2S in the liquid escapes as a gas into the air space, where reduced sulfur is oxidized by sulfur oxidizing bacteria to produce sulfuric acid.

This report focus on the production of H_2S. The following aspects are considered:

- The bacteriological factors controlling the growth of sulfur reducing bacteria, including inhibitors such as oxygen, metals, etc.
- The wastewater chemistry as it controls reactions between reduced sulfur and other constituents in the liquid, including precipitation, pH effects, etc.
- The transfer of H_2S from the liquid phase into the gas phase.

Sulfate Reducing Bacteria

This section discusses those environmental and nutritional factors that control the growth of sulfur reducing bacteria in wastewater, and the sequence of events required for bacterial H_2S production.

Organisms and Biochemistry

Sulfur reducing bacteria are obligate anaerobic bacteria that require not only the absence of oxygen, but also a low redox potential for growth. In the absence of the ideal environment, sulfide production will not occur. The sulfur reducing reaction can be depicted as follows:

$$\text{Organic substrate} + \text{Oxidized-S} \rightarrow CO_2 + H_2S \qquad (3)$$

Lactate is a commonly used organic substrate, while sulfate is the dominant oxidized sulfur source. Equation 3 then becomes:

$$2CH_3CHOHCOOH + SO_4^{=} \rightarrow 2CH_3COOH + S^{=} + 2H_2O + 2CO_2 \qquad (4)$$

According to equation 4, the organic substrate requirement for sulfate reduction is 5.6 mg lactate/mg $SO_4^{=}$-S. In terms of the oxygen equivalent (as COD) it therefore requires 6.0 mg COD/mg $SO_4^{=}$-S reduced, or also 6.0 mg COD/mg H_2S-S produced. SRBs are quite versatile and will use a variety of carbon sources as substrate as discussed in the next section.

In addition to organic substrate oxidation, several organisms contain the enzyme *dehydrogenase* which catalyze the following reaction to produce H_2S:

$$4H_2 + SO_4^{=} \rightarrow S^{=} + 4H_2O \qquad (5)$$

These reactions are quite reminiscent of the methane formation reactions encountered in anaerobic digestors.

Carbon Sources - Electron Donors

Sulfur reducing bacteria are quite versatile and can grow effectively on a number of carbon sources. Postgate (1984) proposed lactate as carbon source for a growth medium, but other carbon sources can also be utilized. This is important when we consider growth and H_2S production in sewers, since the organic constituents in the wastewater, typically expressed as BOD or COD, may or may not be available for bacterial growth if the organisms require a particular carbon compound for growth. Pomeroy and Bowlus (1946) suggested that BOD may not be an appropriate measure of available organic substrate for predicting H_2S production in sewers, since they observed much higher H_2S production in a wastewater containing citrus waste.

Lactate has been considered a prime carbon substrate for SRBs. However, studies into the impact of lactate on H_2S production have failed to show that high lactate levels *per se* in wastewater will enhance H_2S formation. Heukelekian (1948) investigated the impact of added lactate on H_2S production. In pure cultures, added lactate dramatically increased H_2S production. However, adding

lactate to sterilized wastewater inoculated with SRBs from pure culture, failed to produce H_2S. Nielsen and Hvitved-Jacobsen (1988) tested the ability of biofilms grown on various wastewaters to use different carbon source for SO_4^- reduction. They found that feeding lactate as sole carbon source resulted in only 30 to 50% of the H_2S production observed when feeding a control with the complex wastewater used for establishing the biofilm. This means that one single type of carbon source does not account for all H_2S formation.

Nielsen and Hvitved-Jacobsen (1988) conducted a study into the impact of selected organic compounds on SO_4^- reduction and H_2S production in a biofilm reactor. Four substrates were used to grow the biofilm: (A) domestic wastewater; (B) wastewater rich in protein compounds; (C) wastewater rich in carbohydrates; (D) a synthetic, lactate based wastewater. Once the biofilm was established, a synthetic feed was introduced containing only one carbon source and SO_4^- reduction rates determined. Figure 2 shows their results, where measured SO_4^- reduction rates are expressed as a percentage of the SO_4^- reduction rate when the growth substrate is used. Several important observations can be made:

- In almost all cases SO_4^- reduction rates for a specific carbon source is much slower than that of the complex substrate. SO_4^- reduction proceed optimally in the presence of the complex organic substrate used for biofilm growth.
- In the case of a wastewater with a particular characteristic (ex. carbohydrate rich), selected organics with that same characteristic (ex. glucose) has a more pronounced impact on SO_4^- reduction.
- Hydrogen had a dramatic impact on SO_4^- reduction, indicating *dehydrogenase* enzyme activity (equation 5) must be included in H_2S formation calculations.

While none of these conclusions are surprizing, their implication is very significant: it seems that the "natural" substrate present in a wastewater is also the optimal substrate for SRBs to produce H_2S. In other words, the organisms that will survive and grow in abundance in the sewer, will adapt to the carbon source in that wastewater and therefore be adapted to use that particular carbon source for SO_4^- reduction - irrespective of the actual carbon source.

The above conclusion seems rather surprizing in the light of general perceptions, such as, that "stale" wastewater in general is more prone to H_2S production. It may be, however, that H_2S production in these cases should be traced to other factors, such as increased SRB populations or the activity of other heterotrophic bacteria consuming oxygen and lowering the redox potential, as will be discussed in Sections "Environmental Impacts" and "Other Microorganisms". Note also that this conclusion does not imply that the H_2S production rate for various carbon sources will be the same - on the contrary, it will be very surprizing if various carbon sources does not yield significantly different H_2S production rates. However, a SRB population established growing on a given carbon source is likely to prefer that carbon source for H_2S production.

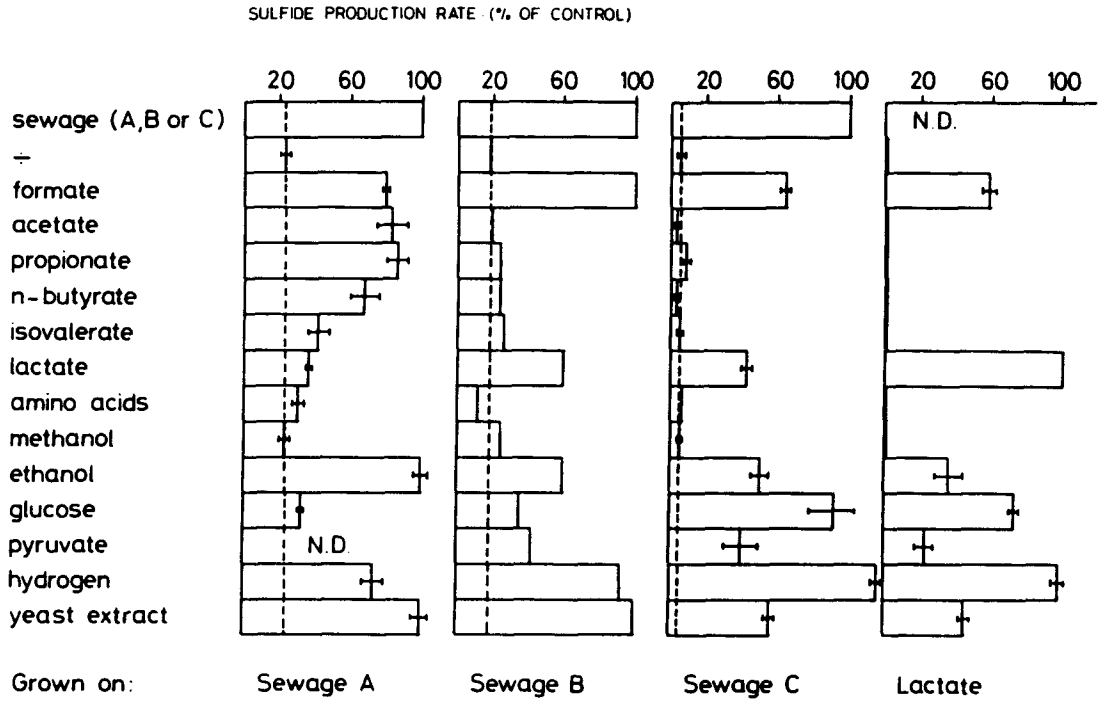


Figure 2. Sulfide production rates of different organic compounds in biofilms grown on four types of wastewaters. Rates are given as a percentage of the rate obtained on the substrate on which they were grown (Nielsen and Hvitved-Jacobsen, 1988).

The impact of substrate concentration on observed H_2S production in sewers is reflected by the models' dependency on BOD or COD. Equations 1 and 2 show that this dependance varies between 0.8 and first order - i.e. quite strong. According to equation 4, the stoichiometry depicts a direct relationship between SO_4^- reduction and organic content. An implication of this observation is that the carbon source may therefore become a **limiting** substrate.

Sulfur Sources - Electron Acceptors

Sulfate, SO_4^-, is abundantly available in sewage and is therefore generally not considered a limiting substrate (Pomeroy, 1956). Nielsen and Hvitved-Jacobsen (1988) concluded that, based on a mathematical model, SO_4^- will **not** be a limiting substrate in biofilms if the SO_4^- concentration exceeds 4-5 mg S/L. Since wastewater in general will contain several 100 mg SO_4^--S/L, H_2S production should be independent of the SO_4^- concentration. This finding is in agreement with the Pomeroy-Parkhurst model (equation 1), which shows no SO_4^- dependance. Thistlethwayte's model (equation 2) shows a 0.4 order dependency on SO_4^- concentration for H_2S production. Holder et al. (1985) explained this dependency on SO_4^- by a mass transfer limitation imposed on a zero order reaction, which will result in apparent 0.5-order reaction kinetics (see Section "Biofilm Kinetics").

Table 1 shows the standard electrode potential and half-reactions of several other compounds that can be used as terminal electron acceptor. The half reaction potential of these compounds show that an organism derives more energy when using oxygen or nitrate rather than sulfate as electron acceptor to explain in part why reduction of these compounds preceeds sulfate reduction. The standard electrode potentials for SO_4^-, SO_3^-, and $S_2O_3^-$ are of the same order of magnitude and the free energy available from the reaction will depend on the actual species concentrations. Pomeroy and Bowlus (1946) reported that sulfite (SO_3^-) reacted more rapidly than SO_4^- to produce H_2S. They postulated that this be attributed to the formation of thiosulfate, $S_2O_3^-$, as an intermediate by-product, which is then reduced to form H_2S. This postulate is in agreement with the finding of Rudolfs and Baumgartner (1932) than $S_2O_3^-$ decompose faster than either SO_4^- or SO_3^-.

Table 1. Redox Reactions of Importance to Understand the Biochemistry of Sulfur Reduction. Standard Electrode Potentials at 25 °C (Snoeyink and Jenkins, 1980; Benefield et al., 1982).

Reaction	pε°
$SO_4^= + 8H^+ + 6e^- \Leftrightarrow S_{(s)} + 4H_2O$	+6.0
$SO_4^= + 2H^+ + 2e^- \Leftrightarrow SO_3^= + H_2O$	-0.68
$SO_4^= + 9H^+ + 8e^- \Leftrightarrow HS^- + 4H_2O$	+4.13
$SO_3^= + 7H^+ + 6e^- \Leftrightarrow HS^- + 3H_2O$	5.89*
$S_2O_3^= + 8H^+ + 8e^- \Leftrightarrow 2HS^- + 3H_2O$	+3.38*
$O_{2(aq)} + 4H^+ + 4e^- \Leftrightarrow 2H_2O$	+21.5
$2NO_3^- + 12H^+ + 10e^- \Leftrightarrow N_{2(g)} + 6H_2O$	+21.0
$Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$	+13.0

* Calculated

Environmental Impacts

Redox Potential

Potentiometric electrodes are commonly used to measure the redox potential of a solution. These instruments measure the potential of an indicator electrode relative to that of a reference electrode, such as the commonly used saturated calomel electrode (using mercury ($Hg_{(l)}$), mercurous chloride ($Hg_2Cl_{2(s)}$), and potassium chloride (KCl)). The Nernst equation has the general form:

$$E = \text{Constant} + E^\circ - \frac{RT}{nF} \ln \frac{\{red\}}{\{ox\}} \qquad (6)$$

where

E = Potential of the cell, volt

E° = Standard potential of the cell, volt

R = Gas constant, 1.987 cal/deg-mole

T = Absolute temperature, °K

F = Faradys constant, 23,062 cal/volt-eq

n = Number of electrons transferred

{red} = Activity or concentration of the reduced species

{ox} = Activity or concentration of the oxidized species

The "constant" is a cell constant, which depends on the reference cell construction. Equation 6 indicates that the redox measurement will decrease as the solution become more "reduced" and increase as the solution become more "oxidized."

Redox measurements have been used as substitute for dissolved oxygen (DO) measurements in biological processes, such as the control of fermentation processes (Dahod, 1982). One of its advantages over traditional DO measurements is that redox measurements can detect negative numbers, thereby reducing the limitation imposed by the lower limit for DO probes while still indicating useful numbers.

Several investigators have looked at the importance of redox potential for sulfate reduction. Since the redox potential of the liquid also reflects other liquid constituents such as dissolved oxygen, nitrate, etc. it may be more applicable to identify the optimum sulfate reducing environment. El-Rayes (1988) found that the redox potential must be lowered to between 0 and -40 mV in order to initiate sulfide production. In addition, the H_2S production rate increased dramatically when the redox potential is lowered to -100 mV. Since nitrate was used in these tests to change the redox potential, El-Ryaes suggested that competition for substrate or intermediate denitrification byproducts may have inhibited H_2S production, rather than the redox potential *per se*. Table 1 shows that the available free energy for NO_3^- is far greater than with $SO_4^=$ as terminal electron acceptor so that we would expect denitrification to preceed sulfate reduction. Heukelekian (1946) concluded that redox potential is determining the onset of H_2S production, based on his experiments where H_2S was added to a solution to lower the

redox potential. He postulated that the onset of H_2S production is primarily determined by the activity of other organisms in the wastewater, which lowers the redox potential in the liquid, making H_2S production possible.

Temperature

Temperature plays a significant role in all biological reactions. Baumgartner (1934) found that H_2S production virtually ceased at 7 °C. Not only does an increase in temperature increase the rate of biochemical reactions, it also controls the growth rate of organisms, thus having a pronounced impact on the bacterial population density.

Sulfide production models often assume a $1.07^{(T-20)}$ factor for temperature impact. This "magic" number can be traced back to the Pomeroy and Bowlus (1946) report, which found a 7% increase in the **maximum** H_2S production rate. It is questionable whether the same temperature dependency can be expected for H_2S production at other than maximum H_2S production rates. For example, Baumgartner (1934) found little difference in H_2S production patterns for samples kept at 30 and 37.5 °C.

Other Microorganisms

The nutrient rich environment in a sewer provides ideal conditions for the growth of a whole host of bacteria. These organisms play an important role in creating an appropriate environment for H_2S production by removing potential inhibitors to H_2S production. Of primary importance are the following:

- **Aerobic organisms** that use O_2, NO_3^-, and other compounds as electron acceptor. It is well recognized that the presence of O_2 and NO_3^- will prevent H_2S production in sewers so that the removal rate of these compounds controls the onset of H_2S production. Aerobic organisms are therefore of great importance since they create a suitable environment for $SO_4^=$ reduction by removing O_2, NO_3^-, and other inhibitory compounds. Oxygen depletion by aerobic organisms may therefore be the key to sulfate reduction.

- **Fermentative organisms** that convert complex organic molecules to more readily accessible organic substrates. It was pointed out earlier (see Section "Carbon Sources - Electron Donors") that the actual organic substrate for $SO_4^=$ reduction is probably of less importance due to the versatility of SRBs. Furthermore, fermentative bacteria will only come to play when the redox potential is **already** favorable for H_2S production. However, fermentation which will proceed in the internal biofilm layers, produce fatty acids as byproduct. The fatty acids are the preferred substrate for many SRBs and readily biodegradable by aerobic organisms thus sustaining the aerobic activity in the sewer and preventing natural aeration from raising the DO enough to terminate H_2S production in the sewer.

The importance of these organisms can only be judged by using a comprehensive sewer model that will account for the uptake and growth rates of all the organisms involved. This model must consider sequential fermentation and degradation, as well as the "competative" reactions involving substitute electron acceptors such as O_2 and NO_3^-.

Sulfide Reactions

The mere production if $H_2S_{(aq)}$ in the wastewater itself, does not mean that H_2S will appear in the gas phase. This section first presents reactions between sulfur compounds and various constituents in the wastewater, and then address H_2S transfer from the liquid to the gas phase.

Weak Acid/Base Chemistry

H_2S is a diprotic weak acid, which exist in equilibrium with its conjugate bases according to the following equilibria:

$$H_2S \Leftrightarrow HS^- + H^+ \qquad pK_{a1} = 7.0 \qquad (7)$$

$$HS^- \Leftrightarrow S^= + H^+ \qquad pK_{a2} = 14.0 \qquad (8)$$

In addition, the dissociation of water is considered as follows:

$$H_2O \Leftrightarrow H^+ + OH^- \qquad pK_w = 14.0 \qquad (9)$$

Acid-base reactions proceed very rapidly to reach equilibrium. Consequently, as sulfide is produced by bacteria, it rapidly gains and loses protons to establish a new equilibrium with other sulfide species. It is therefore convenient to consider the **total** sulfide species in the liquid rather than specific, individual sulfide species, or to be precise the **total dissolved sulfide species**, $C_{d,s}$, as follows:

$$C_{d,s} = [H_2S_{(aq)}] + [HS^-] + [S^=] \qquad (10)$$

or

$$C_{d,s} = C_{H_2S_{aq}} + C_{HS^-} + C_{S^=} \qquad (11)$$

where [..] indicates the molar concentration of sulfide species and C_{xx} indicates the sulfide species concentration expressed in mg/L as S. It is important and convenient to express all sulfur species as S so that a direct conversion or addition of species is possible. In this report "mg/L as S" will be used as the default expression of sulfur species concentrations.

In order to assess the impact of sulfide reactions with other compounds in the wastewater, the specific sulfide species concentration in the water must be known. This can easily be calculated from basic chemistry principles using the definitions and reactions above. For convenience, the various species are expressed as a fraction of the total dissolved sulfide concentration as follows:

$$C_{H_2S_{aq}} = \alpha_0 C_{d,s} \qquad (12)$$

$$C_{HS^-} = \alpha_1 C_{d,s} \tag{13}$$

$$C_{S^=} = \alpha_2 C_{d,s} \tag{14}$$

where α_i is the fraction of the sulfide species that lost i number of protons and can readily be calculated as follows (Snoeyink and Jenkins, 1980):

$$\alpha_0 = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{15}$$

$$\alpha_1 = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{16}$$

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{17}$$

Note that the species fractions only depend on pH (and equilibrium constants, which have a slight temperature dependance). This means that once the pH of a solution is known, the actual sulfide species distribution can readily be calculated using equations 12 to 17. The solution pH has a dramatic impact on the sulfur species distribution as shown graphically in Figure 3. Note that:

- In order for sulfide to escape from the liquid, it needs to be available as $H_2S_{(aq)}$. $H_2S_{(aq)}$ is the major sulfide species only at relatively low pH, less than 7.0. This phenomenon is discussed at length in the Section entitled "Hydrogen Sulfide Stripping".
- Complexation and precipitation reactions often involves $S^=$, which is a significant species only at high pH, approaching 14. These reactions will therefore not proceed at optimum rates under normal conditions.

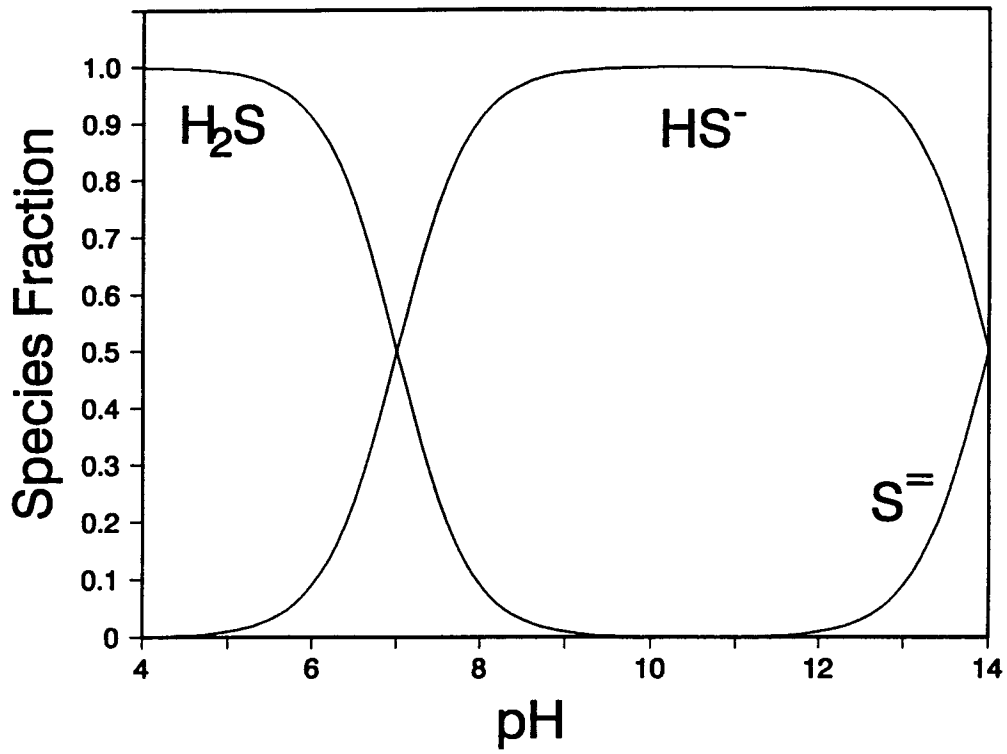


Figure 3. Sulfide species distribution as a function of pH (pK_{a1}= 7; pK_{a2} = 14).

Precipitation and Complexation of Sulfides

Sulfur compounds will readily form precipitants and complexes with various metals commonly found in wastewater. For example, sulfide precipitation with zinc is used in analytical tests to preserve sulfides in water and wastewater. Table 2 shows some of the precipitation reactions for sulfides.

Metal precipitants are able to reduce dissolved sulfide concentrations to levels where H_2S evolution can virtually be eliminated. Table 2 shows the total dissolved sulfide, $C_{d,s}$, concentration that will remain in solution in equilibrium with 1 mg/L of each metal, at pH 7. For example, at a residual of 1 mg Fe^{++}/L in solution, the corresponding $C_{d,s}$ is 0.014-0.18 mg S/L. $C_{d,s}$ concentrations are generally very low (a fraction of a mg/L at equilibrium) if a 1 mg/L residual metal concentration is achieved. However, the metal dose requirement is also substantial: usually 2 mg metal per mg S or more, indicating that fairly large doses of metal concentrations are required to reduce $C_{d,s}$.

The results in Table 2 indicate equilibrium conditions only. Precipitation reactions are sometimes slow to reach equilibrium. However, even if the reaction does not reach actual equilibrium, a partial equilibrium will still result in a very low sulfide concentration. Without increasing the metal concentration in wastewater by adding salts, precipitation reactions will most likely be controlled (limited) by the available metal concentration if a substantial amount of sulfides is produced. This means that sulfide precipitation will occur until the free metal concentration is depleted before $C_{d,s}$ will start to accumulate in the wastewater.

Table 2. Precipitants that will form with sulfide. Dissolved sulfide indicates the total dissolved sulfide concentration, $C_{d,s}$, at a metal concentration of 1 mg/L as metal and pH = 7.

Metal	Precipitant	pK_{so}	Total Dissolved Sulfide Concentration mg/L	Metal Requirement mg X/mg S
Fe^{++}	FeS	17.3[a] 18.40[c]	0.18 0.014	1.75
Fe^{+++}	Fe_2S_3	88[a,c]	4.3×10^{-15}	1.75
Zn^{++}	ZnS	21.5[a] 22.80[c]	1.3×10^{-5} 6.6×10^{-7}	2.04
Ag^{+}	Ag_2S	49.7[b]	1.5×10^{-28}	6.74
Mn^{++}	MnS	15.15[c]	24.92	1.72
Ni^{++}	NiS	20.52[c]	1.1×10^{-4}	1.83
Cd^{++}	CdS	28.00[c]	7.2×10^{-12}	3.51
Pb^{++}	PbS	28.15[c]	9.4×10^{-12}	6.47
Cu^{++}	CuS	36.10[c]	3.2×10^{-20}	1.98
Cu^{+}	Cu_2S	48.92[c]	6.6×10^{-7}	3.97

a. Snoeyink and Jenkins (1980)
b. Stumm and Morgan (1970)
c. Moeller and O'Conner (1972)

We have not investigated complex formation. Complex formation reactions with some metals (Zn^{++}, Cu^{++}, Cu^{+}) are relatively rapid and can potentially reduce $C_{d,s}$ by "tying up" some sulfide species in complexes. This will reduce the driving force to strip H_2S from the liquid and reduce H_2S production.

Chemical Sulfide Oxidation

Sulfide is spontaneously oxidized in the presence of oxygen in water, to produce $SO_4^{=}$, $S_2O_3^{=}$, or S (Chen and Morris, 1972) depending on the reaction condition:

$$HS^- + 2O_{2(aq)} \Leftrightarrow SO_4^{=} + H^+ \qquad (18)$$

$$2HS^- + 2O_{2(aq)} \Leftrightarrow S_2O_3^{=} + H_2O \qquad (19)$$

$$2HS^- + O_{2(aq)} + 2H^+ \Leftrightarrow 2S + 2H_2O \qquad (20)$$

These reactions can have an impact on the H_2S evolution rate from the sewer since the produced H_2S may not necessarily appear in the air space. Oxidation of H_2S can occur at any point where O_2 is present. For example, while H_2S may be produced in the inside layers of the biofilm, an aerobic layer at the biofilm surface or dissolved oxygen in the liquid may oxidize sulfides before it can be transported to the gas phase. The kinetics of the process must be determined to assess the impact of sulfide oxidation on H_2S production. Sulfide oxidation is generally slow, with a half-life on the order of days. However, several transition metals will catalyze the reaction. Chen and Morris (1970) reported that the time for oxidation of 0.01 M sulfide at pH 8.65 decreased from several days to a few minutes in the presence of 10^{-4} M Ni^{++}. Since metal and sulfide concentrations in wastewater are much lower, such a dramatic increase in oxidation rate is unlikely. Under most environmental conditions they found that sulfide oxidation proceeds slowly and that sulfide and oxygen can co-exist in water.

Mass Transfer Between Gas and Liquid Phase

Gerro and Stenstrom's report (Part III) discusses the factors controlling mass transfer between the liquid and gas phases. This discussion focuses primarily on the impact of mass transfer limitations on the production and evolution of H_2S into the gas phase.

Before corrosion can proceed, H_2S produced in the liquid phase must be transported into the gas phase. The mass transfer coefficient for gas transfer between phases depends largely on the degree of turbulence in the wastewater, temperature, and the species concentration in the liquid and gas phases. Mass transfer between a liquid and gas phase for an arbitrary species "x" can be expressed as follows:

$$N_x = (K_L a)_x (C_x^* - C_x) \qquad (21)$$

where

x = The species under consideration, such as O_2 or H_2S

N_x = Flux of species x into the liquid phase, g/m^2-h

$(K_L a)_x$ = Mass transfer coefficient for species x into the liquid, m/h

C_x = Concentration of species x in the liquid phase, g/m^3 (or mg/L)

C^*_x = Saturation concentration of species x in the liquid phase, in equilibrium with the gas phase concentration, g/m^3 (or mg/L). C^* is calculated using Henry's Law (equation 22).

$$C_x^* = H_x p_x \qquad (22)$$

where

p_x = Partial pressure of species x in the gas phase, atm

H_x = Henry's law coefficient for species x, mg/L-atm

Henry's Law coefficients are temperature dependant. These expressions for mass transfer can now be applied to H_2S stripping **from** the liquid and O_2 transfer from the gas **into** the liquid.

Hydrogen Sulfide Stripping

Hydrogen sulfide is a slightly soluble gas. In a sewer, H_2S is produced in the liquid phase and then transported into the gas phase. If we assume the concentration of H_2S in the gas phase is small (see Part III of this report) then C^*_{H2S} can be assumed to be zero. The general mass transfer equation is then simplified to:

$$N_{H2S} = -(K_L a)_{H2S} C_{H2S} \tag{23}$$

The negative sign indicates that the transfer is **from** the liquid **to** the gas phase which will cause a decrease in liquid phase concentration.

It is important to note that the transfer rate is dependant on the $H_2S_{(aq)}$ concentration, not the total dissolved sulfide species. Combining equations 23 and 12, the H_2S transfer rate can be written in terms of the total dissolved sulfide concentration:

$$N_{H2S} = -\alpha_0 (K_L a)_{H2S} C_{d,s} \tag{24}$$

The transfer H_2S rate from the liquid to gas phase is therefore highly dependant on pH (see Figure 3) and only at low pH (<< 7) will the transfer rate proceed at maximum. At pH 7, the H_2S transfer rate will be approximately 50% of the maximum rate. At high pH it is likely that the gas phase H_2S concentration will become totally controlled by the mass transfer rates, and equilibrium between the gas and liquid phases will probably not be established. However, even though the transfer rate is lower at pH > 7, it is not terminated and the potential for H_2S transfer remains the same.

Oxygen Transfer - Reaeration

The DO in the wastewater has a significant and controlling influence on H_2S production since H_2S production does not occur while O_2 is present. Oxygen is also a slightly soluble gas, but unlike H_2S, it is primarily transported **from** the gas phase **into** the liquid phase. Aerobic bacteria in the wastewater consumes O_2 for metabolism and reduces the DO to virtually zero, when H_2S production will commence. If we assume the DO in the liquid phase is small (approximately zero) then C^*_{O2} controls the mass transfer and the general mass transfer equation is simplified to:

$$N_{O2} = +(K_L a)_{O2} C^*_{O2} \tag{25}$$

or

$$N_{O2} = +(K_L a)_{O2} H_{O2} p_{O2} \tag{26}$$

The positive sign indicates that O_2 transfer is **from** the gas **to** the liquid phase. This simplified expression for reaeration may not be sufficiently accurate to model the sewer due to the importance of the O_2 balance and the need to calculate the DO in the wastewater accurately. It serves here only to illustrate the dominant factors or driving forces for reaeration.

If we assume that the oxygen concentration in the gas phase remains essentially constant (p_{O2} = 0.21 atm) then the reaeration rate becomes solely dependent on the mass transfer coefficient, $(K_La)_{O2}$. The mass transfer coefficient is controlled by the flow velocity, depth of flow, and temperature (see Gerro and Stenstrom's report, Part III).

Mass Transfer Between Liquid Phase and Biofilm

Biofilm Description

The biofilm in a sewer contributes significantly to H_2S production in sewers (Holder et al. 1985; Nielsen and Hvitved-Jacobsen, 1988; Pomeroy and Bowlus, 1946; Holder, 1986; El-Rayes, 1988). This is commonly attributed to two factors: a high SRB population in the biofilm, and an ideal environment for H_2S production.

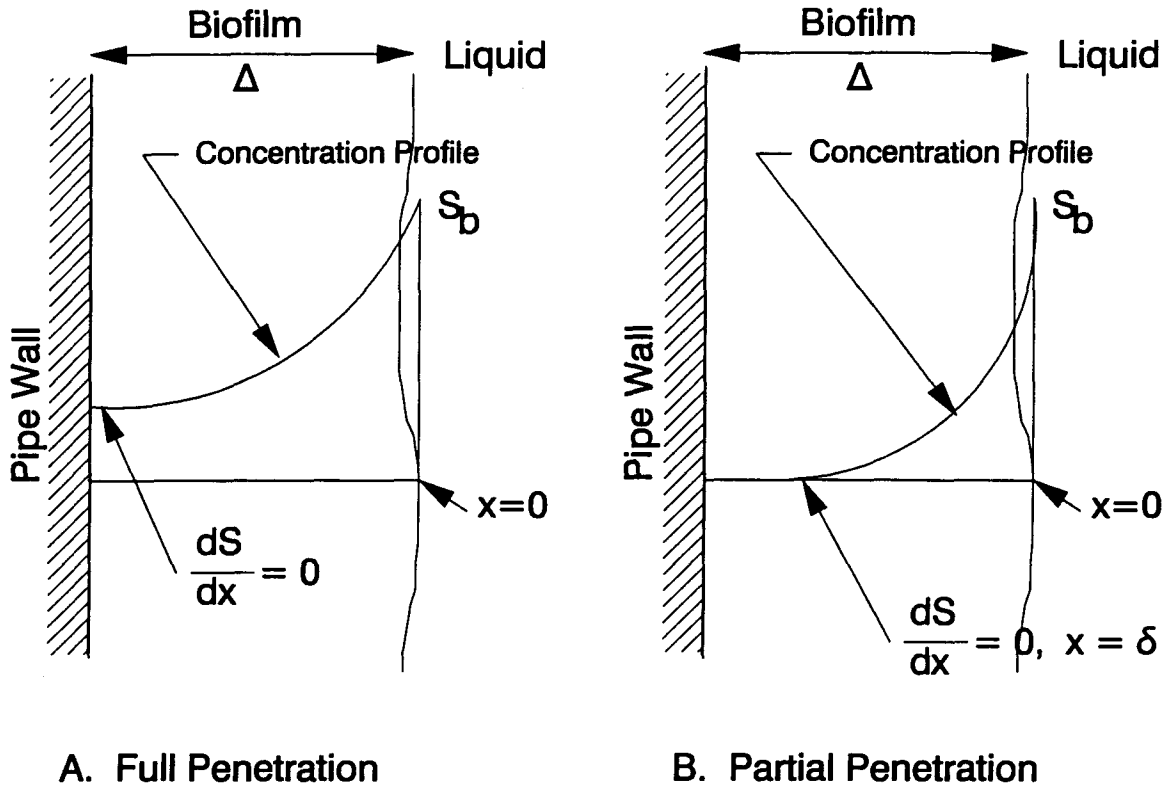
The bacterial population in the biofilm is significantly greater than that in the bulk liquid (see Part II of this report; Heukelekian, 1948). This large population on the pipe wall can be attributed to the stationary surface which prevents bacteria from washing away and allow for a significant population to develop in the biofilm. Additionally, the liquid's slower velocity at the pipe surface facilitate bacterial adhesion and create a niche for bacterial growth.

The environment inside the biofilm is ideal for H_2S production. Diffusional resistances limit oxygen transfer into the biofilm, so that an anaerobic layer develops at the pipe surface. The biofilm (Figure 1) is considered to contain several layers ranging from possibly aerobic on the liquid side, to anaerobic on the pipe side. The actual distribution of oxygen inside the biofilm is determined by the availability of nutrients in the bulk liquid and the reaction rates in the biofilm itself. Before proceeding with this discussion, it is important to investigate biofilm kinetics.

Biofilm Kinetics

Reaction rate expressions are commonly derived for homogeneous reactions. These rate expressions therefore describe the rate at which a particular reaction will proceed in an environment where mass transfer is **not** limited. Furthermore, the reactions are considered to be homogeneous, i.e. the potential for a reaction is the same at any location inside the liquid. Even though few field scale reactions fall into this strict definition, homogenous reaction rate expressions are used for many practical applications. Homogeneous reaction rate expressions can be applied to determine biofilm kinetics, as have been studied for areas such as trickling filters. We will use these descriptions for H_2S production in sewers.

Biofilms in a sewer grow an a reasonable flat surface. The biofilm kinetics can therefore be approximated by a flat plate geometry. Figure 4 shows a model describing substrate transfer into a biofilm. The process is mathematically described as follows:



A. Full Penetration B. Partial Penetration

Figure 4. Boundary conditions for biofilm kinetics for complete and partial substrate penetration.

$$\frac{\partial C_{f,x}}{\partial t} = D_x \frac{\partial^2 C_{f,x}}{\partial x^2} + r_{i,x} \tag{27}$$

where

$C_{f,x}$ = Concentration of species x in the film, mg/L

t = Time, h

D_x = Diffusion coefficient of species x into the biofilm, m^2/h

x = Distance into the biofilm, m

$r_{i,x}$ = Intrinsic reaction rate for species x, i.e. the homogeneous reaction rate excluding mass transfer limitations, mg/L-h.

Assuming steady state, equation 27 can be simplified to:

$$D_x \frac{d^2 C_{f,x}}{dx^2} = -r_{i,x} \tag{28}$$

The Monod type reaction rate expression, is commonly used to describe substrate removal rates for biological systems:

$$r_{i,x} = \frac{k_{max} C_x}{K_s + C_x} \tag{29}$$

where

k_{max} = Maximum reaction rate, mg/L-h

C_x = Concentration of species x, mg/L

K_s = Half saturation coefficient, mg/L.

Equation 29 indicates that at low concentrations ($C_x << K_s$), the reaction rate becomes linearly proportional to the substrate concentration, i.e first order. At high substrate concentrations ($C_x >> K_s$), the reaction rate become independent of the substrate concentration, i.e. zero order. The impact of first and zero order kinetics will therefore be investigated.

Boundary Conditions

The boundary conditions for solving equation 28 is depicted in Figure 4 as follows:

- The substrate concentration at the liquid surface of the biofilm is equal to the bulk substrate concentration in the wastewater - i.e. assuming a negligible liquid film resistance:

$$\text{At } x = 0, \qquad C_f = C_b \tag{30}$$

- The substrate concentration profile gradient at the pipe wall is zero - i.e. there is no substrate flux into the wall:

$$\text{At } x = \Delta, \qquad \frac{dC_f}{dx} = 0 \tag{31}$$

These boundary conditions are applicable for most reaction cases, except for zero order kinetics. Since zero order kinetics will mathematically allow the reaction to proceed even when the substrate concentration reaches zero, the solution of equation 28 can generate negative concentration values and two cases needs to be considered: complete substrate penetration of the biofilm, and partial substrate penetration into the biofilm. For complete substrate penetration, the boundary conditions in equations 30 and 31 are applicable. However, for partial substrate penetration, an additional boundary condition is imposed, namely:

- When the substrate concentration reaches zero, the concentration gradient must also be zero to prevent further penetration of substrate (this distance is referred to as the penetration depth, δ):

$$\text{At } C = 0 \qquad x = \delta \tag{32}$$

$$\text{and} \qquad \frac{dC_f}{dx} = 0 \tag{33}$$

Apparent Reaction Rate Expressions

The apparent reaction rate expression gives the rate at which substrate is removed from the bulk solution and enters the biofilm, expressed in terms of the bulk liquid concentration, i.e. concentration at the film surface, C_b. The apparent substrate removal rate can be determined from the solution of equation 28, which gives the substrate concentration profile inside the biofilm as a function of depth into the film. Once the substrate concentration profile in known, the substrate flux into the film at the surface (N_x), which represents the substrate removal rate, can be determined as:

$$N_x = -D_x \frac{dC_{f,x}}{dx}\bigg|_{x=0} \tag{34}$$

N_x is a "surface reaction rate" with units of g/m^2-h, but can be converted to an apparent volumetric reaction surface reaction rate for a sewer by multiplying the rate with the surface area to volume ratio, i.e. the inverse of the hydraulic radius. The apparent volumetric reaction rate, $r_{a,x}$, to describe disappearance of species x from the liquid into the biofilm is therefore:

$$r_{a,x} = -\frac{D_x}{R}\frac{dC_{f,x}}{dx}\bigg|_{x=0} \tag{35}$$

The expressions for the surface flux N_x for first and zero order kinetics are summarized in Table 3 (Harremoes, 1978; Neethling, 1988).

Two parameters are introduced to quantify the degree of diffusional resistance: the Thiele modulus, and the effectiveness factor. The Thiele modulus (ϕ) can be interpreted as the ratio between the reaction rate and diffusion rate. A large Thiele modulus indicates a rapid reaction rate compared to the diffusion rate, and consequently a process limited by diffusion. The effectiveness factor (η) gives the ratio between the actual reaction rate and the reaction rate if diffusional limitations are completely removed. When $\eta = 1$, no diffusional limitation exist.

Equation 40A shows that for an intrinsic first order reaction rate expression, the apparent reaction rate will also be first order in terms of the bulk substrate concentration. That means that the reaction in the sewer itself can be modeled as a first order reaction, but using a reaction rate constant reduced by the effectiveness factor to account for the diffusional limitation in the biofilm. Zero order reaction kinetics results in two descriptions (equation 40B and 40C): for full penetration, the apparent reaction rate in also zero order, but for partial penetration, the apparent reaction rate expression in half order.

The impact of diffusional resistance should be taken into consideration when H_2S production in a sewer is determined. For practical applications, the reaction is expected to approximate zero, half, or first order kinetics depending on the intrinsic reaction rate expression and the degree on diffusional resistance, with reaction rate constants adjusted to account for the diffusional limitation. Equations 1 and 2 show that H_2S production in field studies is strongly affected by the BOD concentration (first and 0.8 order respectively). This dependency can be explained in terms of first order intrinsic biofilm

Table 3. Summary of apparent reaction rate expressions for zero and first order intrinsic reaction rates.

Identifier		Solution for Reaction Order			Eqn
		A. First	B. Zero (Full)	C. Zero (Partial)	
Intrinsic Reaction Rate Expression	r_f	$-k_{f1}C_f$	$-k_{f0}$	$-k_{f0}$	(36)
Thiele Modulus	ϕ^2	$\frac{k_{f1}\Delta^2}{D}$	$\frac{k_{f0}\Delta^2}{DC_b}$	$\frac{k_{f0}\Delta^2}{DC_b}$	(37)
Penetration Depth	δ	Δ, Full	Δ, Full	$\sqrt{\frac{2DC_b}{k_{f0}\Delta^2}} = \sqrt{\frac{2}{\phi^2}}$	(38)
Flux	N	$\eta k_{f1}\Delta C_b$	$k_{f0}\Delta$	$\sqrt{2Dk_{f0}}C_b^{0.5}$	(39)
Apparent Reaction Rate	r_a	$\frac{\eta k_{f1}\Delta C_b}{R}$	$\frac{k_{f0}\Delta}{R}$	$\frac{\sqrt{2Dk_{f0}}C_b^{0.5}}{R}$	(40)
Effectiveness Factor	η	$\frac{\tanh\phi}{\phi}$	1.0	$1-\delta$	(41)

where

η = Effectiveness factor, -

ϕ = Thiele modulus, -

Δ = Biofilm depth, m

kinetics, or intermediate kinetics (somewhere between first and zero order) as in equation 29, with a mass transfer resistance imposed on the reaction. In addition, liquid phase H_2S production may change the overall H_2S kinetics.

Since the sulfate concentration in a sewer is very high (commonly several hundred mg/L) the reaction is expected to follow zero order kinetics. The results of Nielsen and Hvitved-Jacobsen (1988) confirmed that SO_4^- will hardly ever be a limiting substrate and the Pomeroy-Parkhurst model (equation 1) exclude SO_4^- as model parameter, thus supporting this hypothesis. However, since Thisthlethwyate's model predicts that H_2S production follows 0.4-order kinetics, Holder (1986) suggested that it be attributed to partial penetration of the biofilm as described by equation 40C.

Kinetic Considerations for a Sewer Pipe Flow Model

A sewer can be modeled in terms of the physical flow and transport of mass, coupled with appropriate reaction rate expressions. Two types of reactions should be considered: rapid reactions, which can be assumed to be essentially in equilibrium, and slow reactions that must include appropriate kinetics rate expressions. In addition, reactions in both the liquid and biofilm must be included. For a comprehensive and more complete model, gas phase reactions and gas convection should be added. However, since we are primarily interested in the H_2S production rates the gas phase will be assumed to be a non-reactive sink for H_2S.

> At this point, the kinetic model has not been completely developed in terms of the pipe flow model and the relative reaction rates. The focus of the work to date has been to assess the impact of various liquid phase components on the H_2S production rate, which is essential information needed to formulate and apply the model. Additional effort is needed to calibrate and test the model, which we hope to undertake during the next year.

The following sections describe the relationship between various components of the sewer model (sulfide, sulfate, BOD/COD, DO, etc.), the reactions in which the species are consumed or produced, and their impact on bacterial growth.

Growth of Sulfur Reducing Bacteria

The growth of bacteria can commonly be described by Monod type kinetics. In most models, substrate removal and endproduct production are considered to be proportional to the growth rate of bacteria. The increase in bacterial numbers can then be calculated and the corresponding removal/production rates determined.

Steady state models greatly simplify bacterial kinetics. Assuming steady state for the sewer means that *concentrations along the pipe is time invariant, i.e. remain the same at all times.* This means that we can neglect the actual increase in bacterial numbers due to bacterial growth, since at steady state the increase in bacterial numbers (due to growth and seeding from upstream) equals the loss in bacterial numbers (due to cell decay and washout downstream).

Even though bacterial number remains constant at steady state, the actual bacterial density remains dependent on the growth kinetics. Also, the rate of substrate removal/byproduct production is dependent on the actual steady state growth rate. The following factors affect SRB activity:

- Dissolved oxygen concentration.
- Impact of growth inhibitors.
- Organic substrate concentration.

Note that an inhibition of the SRB activity will lead to a corresponding inhibition of sulfide production.

Growth of Aerobic Bacteria

The activities of other oxygen consuming or aerobic bacteria are vital to a complete understanding of the sewer pipe ecosystem. While these organisms do not directly contribute to H_2S production, they are primarily responsible for creating a suitable environment for SRB growth. The primary characteristics to be considered for these organisms are their impact and dependency on:

- Dissolved oxygen.
- Organic substrate.
- Inhibition by metals and other inhibitors.

Dissolved Sulfide Reactions

Dissolved sulfide species distribution proceeds rapidly to establish the acid-base equilibrium. Acid-base reactions are therefore considered to be in equilibrium. All aqueous sulfide species can therefore be accounted for by using total dissolved sulfide concentration, $C_{d,s}$, and pH as variables. The individual sulfide species can directly be calculated using the α-factors (equations 12 to 17).

The following reactions cause an **increase** in total dissolved sulfide species, $C_{d,s}$:

- Bacterial reduction of reduced sulfur, primarily $SO_4^=$, in the liquid phase.
- Bacterial reduction of reduced sulfur, primarily $SO_4^=$, in the biofilm.

The following reactions cause an **decrease** in total dissolved sulfide species, $C_{d,s}$:

- Precipitation by metals, etc.
- Complex formation with metals.
- Mass transfer from the liquid to the gas phase.
- Chemical or biological oxidation of sulfide.

Total Sulfide Species

Metals in the wastewater can impact H_2S production in two ways: as inhibitor (or sometimes stimulant) of bacterial growth, and as participant in chemical reactions. Metals will effectively "tie up" produced sulfides to form combined sulfides, due to:

- Precipitation of sulfides
- Complex formation.

For simplicity, these reactions can be considered to be either rapid or slow. By assuming a slow reaction the impact of metals can be ignored, or by assuming rapid reactions, the metal reactions are assumed to reach equilibrium instantaneously. Table 2 shows that equilibrium of many metal precipitants will lead to very low residual concentrations, so that precipitation may, for all practical purposes, be considered to go to completion for the limiting compound (normally the metal).

The total sulfide concentration in the wastewater consists therefore of two components: **dissolved** sulfides, which accounts for the reactive sulfide species that participate in reactions with metals and are stripped from the liquid, and **combined** sulfide, which represents precipitated and complexed sulfide species:

$$C_{t,s} = C_{d,s} + C_{c,s} \tag{42}$$

where

$C_{t,s}$ = Total sulfide concentration, mg/L as S

$C_{d,s}$ = Dissolved sulfide concentration, mg/L as S

$C_{c,s}$ = Combined sulfide concentration, mg/L as S

Dissolved Oxygen

Dissolved oxygen in the wastewater will practically eliminate H_2S production. The following activities must be considered to determine DO concentration in the liquid and biofilm:

- Oxygen consumption by aerobic organisms
- Reaeration from the gas phase
- Chemical oxidation of reduced sulfur compounds
- DO profiles in the biofilm.

Organic Substrate

Organic substrate is commonly measured by the BOD or COD concentration. As pointed out in Section "Carbon Sources - Electron Donors", SRBs are extremely versatile and can use many different carbon sources. While lumped parameters such as BOD or COD may not give the actual growth nutrient concentration, it may still be an adequate indicator of the growth nutrient concentration. The following factors have an impact on the organic substrate concentration:

- Sulfur reducing bacterial growth
- Aerobic organisms growth
- Fermentor activity.

Prolonged exposure to an anaerobic environment can lead to the formation of volatile fatty acids, which can impact H_2S production in two ways: (1) Volatile fatty acids have been shown to be an optimum carbon substrate for SRB activity. (2) If the wastewater subsequently enters an pipe section where oxygen transfer is increased, the presence of the volatile acids, which are generally more rapidly degraded by aerobic organisms, will lead to an increase in aerobic activity and hence increased oxygen uptake. The net result is that it may be impossible to maintain aerobic conditions in the aerated pipe section, leading to favorable conditions for SRB growth.

Inhibitors

Inhibitors will cause a reduction in the bacterial activity. Its impact will therefore be included in the bacterial growth kinetics.

Reported Sulfide Production Studies

This section discusses H_2S production studies, specifically its implications for sulfide production kinetics. Many studies measured H_2S production or SO_4^- removal in laboratory studies, which resemble the H2SPP test used in the experiments presented in this report. This discussion focuses on the results of studies reported by Rudolfs and Baumgartner (1932), Baumgartner (1934), Pomeroy and Bowlus (1946), Heukelekian (1948), and Elliassen et al. (1949).

Shape of Sulfide Production Curve

Sulfide production rates proceed with a definite S-shape curve reaching a plateau after several days (typically more that 10 days). Many variations of the S-shape curve are observed, but virtually all H_2S production curves can fit to *a part of the S shape curve* or perhaps several S-shaped curves. Figure 5 shows typical H_2S production curves. Some cases show the top half on the S-shape only, indicating a first order production in terms of the remaining potential for H_2S production. Pomeroy and Bowlus (1946) speculated that the S-shape of the H_2S production curve can be explained in terms of successive nutrients being used to produce H_2S. Some of their results showed a very pronounced 2-S-shape curve, with a definite plateau between the two S-shape curves.

Lag Period

While some studies showed an immediate production of H_2S, many others showed a definite lag period before H_2S appeared. Typically, this lag period is 1-2 days, with longer periods at lower temperatures. Heukelekian (1948) suggested that the lag period is caused by two factors: absence of a suitable food supply at the onset of the test, or time required to create a suitable redox environment for H_2S production to occur. Pomeroy and Bowlus (1946) found several hours delay which they attributed to a time needed to "develop active cultures" for sulfide production.

In summary: a lag period is often observed before evolution of H_2S becomes apparent. This delay can be attributed to the time needed to establish:

- A significant SRB culture
- The ideal environment
- A suitable carbon source
- Other sulfide reactions preceeding evolution of H_2S.

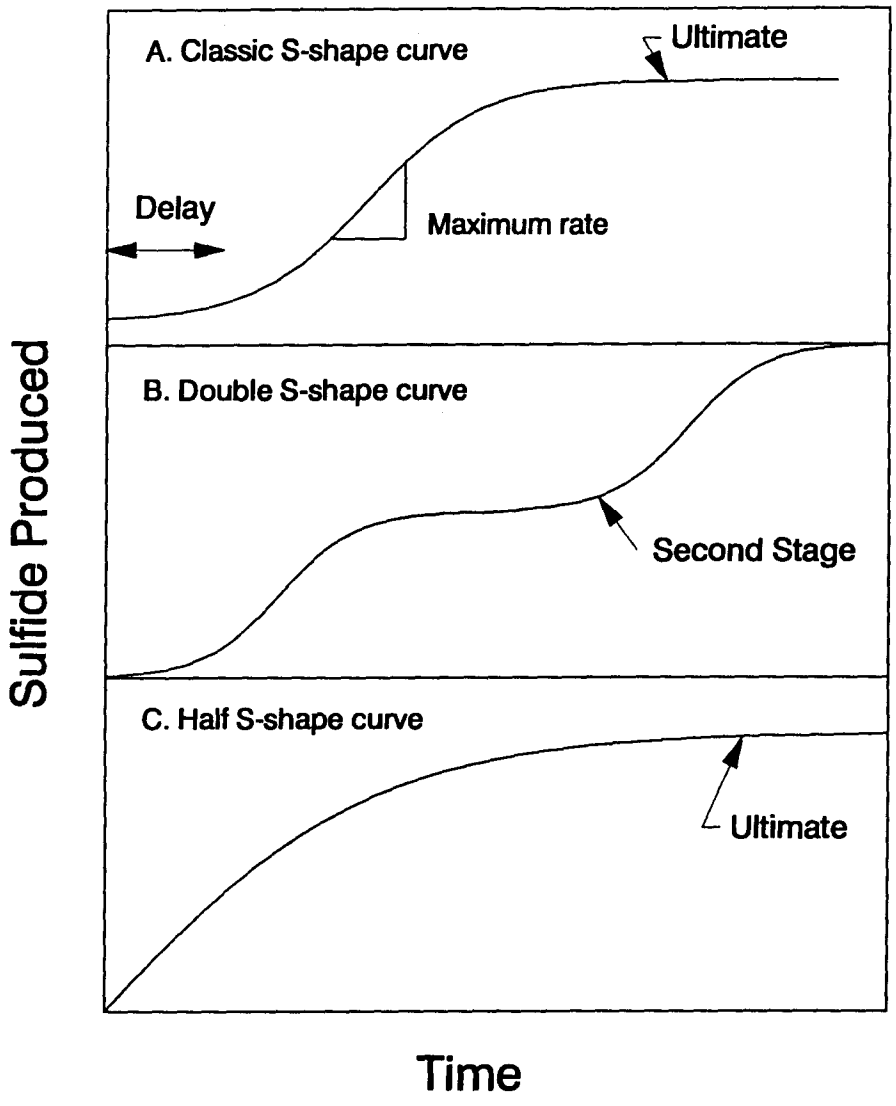


Figure 5. S-shape curves typically observed during sulfide production. (A) Typical curve showing lag phase and ultimate sulfide production. (B) Double S-shape curve showing two phases of sulfide production. (C) Curve without lag phase

Correlation Between Sulfate Reduction and Sulfide Production

Sulfates are abundantly available in wastewater and $SO_4^=$ reduction is the primary source of H_2S. However, many tests showed that other sulfur compounds also contribute to H_2S production (Baumgartner, 1934; Pomeroy and Bowlus, 1946). Both these studies suggested that the additional H_2S production be attributed to organic sulfur compounds, or perhaps thiosulfate, which is sometimes available in significant amounts and react more readily than $SO_4^=$.

Impact of Seeding

Not surprisingly, seeding will increase the H_2S production dramatically. Increased H_2S production of samples seeded with "stale" wastewater can be attributed to factors other than increased bacterial numbers. Stale wastewater may contain organic substrates or other compounds that facilitate in rapidly establishing an environment suitable for H_2S production. Baumgartner's (1934) tests showed that H_2S production still followed the characteristic S-shape curve after seeding but at increased rates.

Reaction Precedence - A Summary Model

The foregoing discussion on H_2S production can be summarized in a conceptual model for sulfide production in a sewer, which includes the following sequential events:

- Sulfur reducing bacteria grow to establish a large population, especially in the biofilm near the pipe surface.
- Reactions proceed to remove dissolved oxygen, nitrates, etc. and create a suitable environment for SRBs to thrive.
- When the redox potential is reduced sufficiently, H_2S production starts.
- The production of H_2S follows an S-shaped curve, finally reaching a plateau. However, it is unclear what causes a limit on H_2S production.
- Acid base reactions proceed rapidly to establish an equilibrium for the dissolved sulfide species ($H_2S_{(aq)}$, HS^-, and $S^=$).
- Precipitation reactions occur, causing a lag between the onset of H_2S production and the appearance of dissolved sulfide in the liquid. Note that since acid-base reactions are more rapid than precipitation, some stripping of H_2S will occur at this stage, but the built-up of dissolved sulfide in the liquid is expected to be small.
- Once dissolved sulfides appear in solution, mass transfer of $H_2S_{(aq)}$ proceed in to the gas phase.

MATERIALS AND METHODS

The experimental research reported here focuses on the results obtained using the H_2S Production Potential (H2SPP) test. The test is designed to measure the potential for H_2S formation in the laboratory for wastewater samples collected from sewers. The wastewater includes all constituents normally present in the wastewater and all potential reactions will therefore proceed as expected in an actual sewer. The one notable exception is the difficulty to obtain and simulate the impact of a biofilm. Some attempts are presented to include elevated SRB densities in the tests and to quantify the results.

H2SPP Test Protocol

The H2SPP test measures the potential of a wastewater sample to produce H_2S that can escape into the gas phase and be oxidized to H_2SO_4. The test resembles the classic Biochemical Oxygen

Demand (BOD) test by simply measuring the evolution of H_2S from a sample. H_2S generated by the sample is captured in a solution containing zinc acetate, which is subsequently analyzed for H_2S. Rudolfs and Baumgartner (1932) and Baumgartner (1934) describe similar tests for determining H_2S production. Their procedure is virtually identical to the same procedure discussed here.

The sample is placed in a container to allow bacterial reduction of sulfur compounds to H_2S. After the selected contact time, H_2S is stripped from the solution by first lowering the pH to convert all sulfide to $H_2S_{(aq)}$ and then bubbling $N_{2(g)}$ through the sample. The N_2 gas leaving the sample is collected and bubbled through a zinc acetate solution (pH 10) to capture the sulfide. In order to obtain useful results, a 100% capture efficiency must be achieved in the experimental setup. The impact of pH, sample volume, and the zinc acetate concentration on capture efficiency were investigated. The procedures in *Standard Methods* (APHA, 1985) for capture and preservation of sulfide samples was found adequate to ensure sulfide capture.

Various physical setups for the H2SPP tests were investigated to optimize purge time and capture efficiency. Four H_2S capture configurations (Figure 6) using various combinations of flasks and graduate cylinders were tested. Configuration B (Figure 6) was used to test the capture efficiency of flasks. A solution of sodium sulfide was placed in the "sample" flask and then purged to determine the capture efficiency. Results in Table 4 show that the efficiency for 3 capture flasks in series using a purge time of 20 minutes is very good. Less than 20% H_2S escapes the first flask. However, it also indicates that mass transfer must be overcome in order to increase the capture efficiency for a single capture flasc. This hypothesis was tested using cylinders as both capture and sample vessels (Figure 6D). The resulting capture efficiency (Table 5) confirm our hypothesis where about 90% or better capture was obtained in 10 minutes purge time.

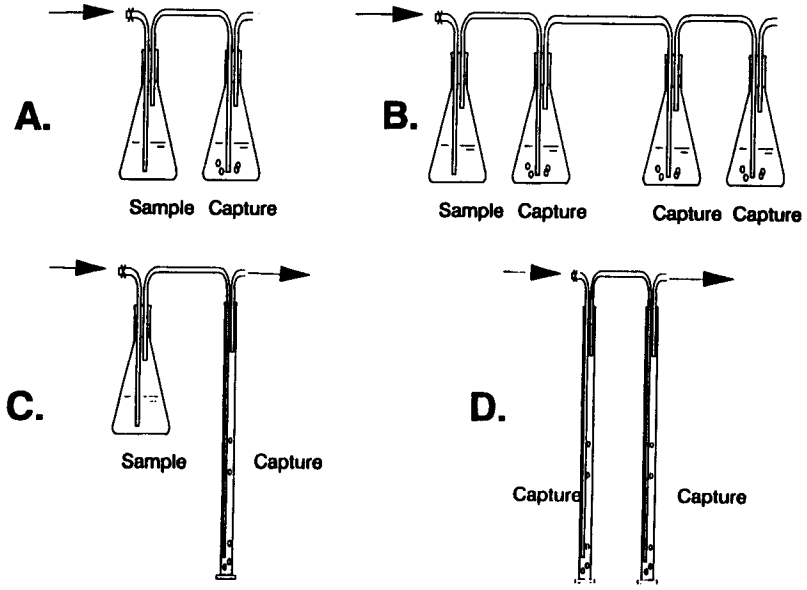


Figure 6. Capture configurations for H2SPP test.

Table 4. Hydrogen sulfide capture efficiency in a series of flasks.

Sample	Volume mL	Concentration mg H_2S-S/L	Mass mg S	Capture %
Sample 1 (Initial 6.6 mg S)				
1	100	53.4	5.34	81
2	100	6.4	0.64	10
3	100	1.2	0.12	2
Remaining	200	3.5	0.70	10
Total			6.80	103
Sample 2 (Initial 6.72 mg S)				
1	100	56.2	5.62	84
2	100	8.4	0.84	13
3	100	1.6	0.16	3
Remaining	200	2.8	0.56	8
Total			7.18	108

Table 5. Hydrogen sulfide capture efficiency in a cylinder.

Sample	Purge Time min	Mass mg H_2S-S	Capture %
Initial	10	65.5	-
Capture		59.4	91
Remaining		4.0	6
Total		63.4	97
Initial	10	79.5	-
Capture		70.0	88
Remaining		7.6	10
Total		77.6	98
Initial	20	6.8	
Capture		6.9	101
Remaining		0.4	5
Total		7.3	106

The following test procedure is therefore used to determine the H2SPP:

1. Place 200 mL sample in a 250 mL cylinder.

2. Place 250 mL distilled water in a second 250 mL cylinder, add 5 drops 6N NaOH to raise pH above 10, and add 10 drops 2N zinc acetate.

3. Connect piping between sample and capture flascs.

4. Incubate sample for desired period.

5. Add 7 drops 6N HCl to the sample flasc to lower pH below 3.

6. Purge for 10 minutes with N_2 gas.

7. Measure the H_2S concentration in the capture volume according to *Standard Methods* (Method 428A) and calculate the H2SPP. Express the results as mg H_2S-S/L based on the sample volume.

This procedure is virtually identical to that described by Rudolfs and Baumgartner (1932). The major differences are: the pH is lowered in the H2SPP test before purging to ensure that all sulfide is converted to H_2S to enhance the stripping efficiency. They did not lower the pH but continued purging the sample for 30 to 60 minutes "depending on the amount of sulfide present." In addition, they used CO_2 gas for purging, whereas we used N_2.

H2SPP Test Kinetics

Two approaches can be followed to analyze H2SPP data: Previous tests (see Section "Shape of Sulfide Production Curve") indicated that H_2S production typically follows an S-shaped curve. First, if we assume that the initial slow production of H_2S is attributed to a lag phase and this lag is eliminated during data analysis, then the process can be described by first order kinetics in terms of the remaining potential for H_2S formation (as in the BOD test). Alternatively, since the most important part of the reaction for sewer kinetics is the first 12 or 24 hours, the peak H_2S production rate as determined by the maximum slope of the H_2S production curve could be used as measure of the H_2S production potential in the sewer. Pomeroy and Bowlus (1946) used the maximum H_2S production rate in their paper.

First Order Kinetics

In order to determine the ultimate, or maximum, H2SPP, collected data were analyzed in a similar way as the classic BOD time series analysis. Assume a first order model with respect to the remaining H2SPP:

$$r_s = -kS \tag{43}$$

where

r_s = Reaction rate for H_2S production, mg S/L-hr

k = Reaction rate constant, hr^{-1}

S = H2SPP remaining, mg S/L

Applying equation 43 to a batch reactor between time 0 and time=t, the H2SPP remaining is expressed as:

$$S = S_u e^{-kt} \qquad (44)$$

where

S_u = Ultimate H2SPP, mg S/L

t = Time, d

The data collected for the collected samples were analyzed using Thomas' (1950) slope method which is commonly used to determine BOD kinetic constants. The analysis gave quite good correlations in many cases as shown in Figure 7.

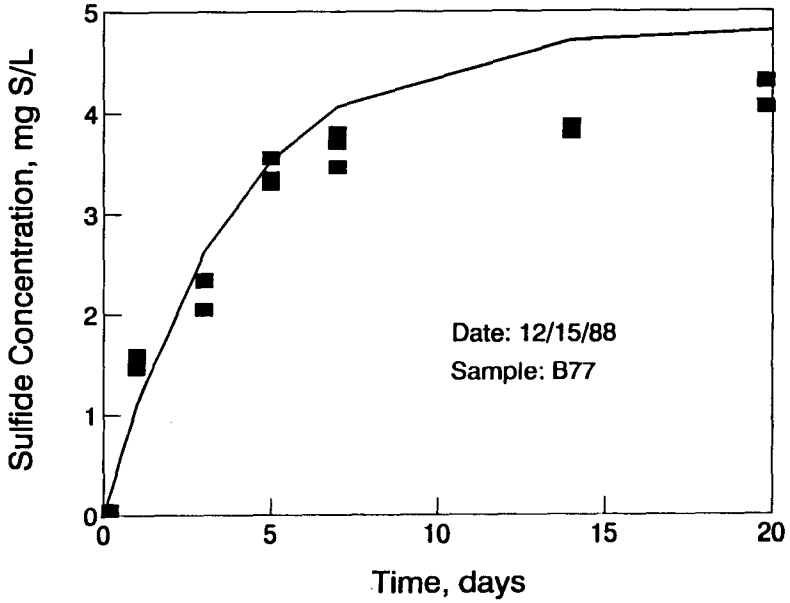


Figure 7. H2SPP analysis for manhole B77. Sample collected on 12/15/88. Reaction rate constant, k = 0.26 d^{-1}, S_u = 4.83 mg H_2S-S/L.

The first order approach can therefore be used with reasonable success to approximate H_2S production. Correlation coefficients for many data sets are generally over 95% and data reproduction is good. As with BOD analyses, a 7-day H2SPP can be used as "standard" test time. This will give sufficient time to produce measurable amounts of H_2S in the wastewater.

Maximum H_2S Production Rate

The maximum H_2S production rate can be determined by calculating the slope of the H_2S versus time graph at the steepest section of the S-curve. These results should correlate with the kinetic coefficient determined using first order kinetics described above. Note that the maximum H_2S production rate represents a single point in time and does not give a fundamental kinetic description of the process. Since the maximum slope gives the peak H_2S production rate, it can be viewed as an upper limit for H_2S production.

Sewer Sampling

Samples were collected from sewers six times during the year (Table 7) at manholes in two sewer lines. Manholes B77 and B78 are located in a heavily corroded sewer, while manhole E30 is located in a non-corroded sewer.

Metal Addition for H2SPP Tests

In order to assess the impact of wastewater constituents on H_2S production, a mix of four metal compounds were added to a wastewater sample and the H2SPP determined. The concentrations of the four metal compounds in wastewater decreased rather substantially from 1973 to 1987 as shown in Table 8. Since the actual concentration of these compounds vary significantly in wastewater, a typical concentration was chosen to represent the approximate metal concentration. The metal mix was added to the wastewater sample, which mean that the true species concentration (Table 8) is the initial wastewater concentration (which was not measured) plus the added amount. These concentration values are therefore only an approximation of what was present in the sample during the test. However, the measured H2SPP when compared to the control, will give an indication of the impact of the mix on H_2S production.

Table 7. Sample dates and locations.

Date	Location
9/22/88	B77
11/10/88	B77
12/15/88	B77
12/15/88	E30
2/9/89	B78
5/3/89	B78

Table 8. Concentration of items showing the largest change when comparing the 1973/4 and 1987 wastewater composition.

Compounds	Concentration, mg/L		
	1973/4	1987	Select as typical 1973
Cr (total)	0.9	0.2	1.0
Cu^{++}	0.6	0.2	0.6
CN^{-}	0.4	0.02	0.5
Pb^{++}	0.4	0.1	0.5

RESULTS AND DISCUSSION

Initial H_2S in Collected Samples

All samples had a significant residual H_2S concentration - i.e. at time zero during the H2SPP test. This indicates that H_2S production was occurring in the wastewater before the test was started. However, in order to evaluate the system kinetics, the initial (t=0) H_2S concentration was subtracted from the measured H_2S produced to establish a new baseline. Samples with added biofilm contained a very significant amount of residual H_2S - in some cases over 50 mg S/L at t=0! Comparing this value with the produced H_2S (usually less than 10 mg S/L) we see the importance of the initial H_2S in the sample.

The high residual H_2S concentration in the sample is very significant for biofilm samples. In the case of liquid samples, it is less important since the initial values were generally quite low. For biofilm samples it indicates that a high H_2S concentration is trapped in the biofilm layers of the sewers. This H_2S will escape at some point in time and, even if H_2S production is controlled, the residual H_2S currently present in the biofilm will still escape at some point. It also underlines the importance of the biofilm in H_2S production in sewers.

H2SPP of Wastewater

Table 9 summarizes the H2SPP results for liquid samples. As expected, location B77 and B78, which is in a heavily corroded pipeline, show the highest ultimate H2SPP and generally the highest rate of H_2S production. Except for the 5/3/89 sample which also showed a poor correlation for the first order model, data from the corroded sewer are in general agreement: the reaction rate constant exceeds 0.2 d^{-1} with an ultimate H2SPP of 4-5 mg/L. The sample that was collected from a non-corroded pipe, E30, showed a rate constant of 0.16 d^{-1} and S_u of 3.37 mg/L. While the ultimate H2SPP for both samples are surprisingly close, the rate at which it is approached, is quite different.

Table 9. H2SPP Analysis for Liquid Samples.

Sample Date	Location	k d^{-1}	S_u mg H_2S-S/L	Max Rate mg/L-d
9/22/88	B77	0.27	4.72	1.25
11/10/88	B77	0.26	4.78	1.45
12/15/88	B77	0.26	4.83	1.45
2/9/89	B77	0.20	3.99	0.85
5/3/89	B78	0.09*	10.52	1.67
12/15/88	E30	0.16*	3.37	0.62

* = Indicate correlation coefficient below 0.9.

The maximum H_2S production rates in Table 9 agrees in general with the observations from the kinetic first order model: the corroded sewer has a maximum H_2S production rate of 1-2 mg/L-d, while the H_2S production in the non-corroded sewer is less that 1 mg/L-d. This finding, combined with the rate constants found in the first order analysis, has a great significance for H_2S production in sewers. It is very unlikely that the ultimate H2SPP potential will ever be exhausted in an actual sewer since the travel time in a typical sewer line is far too short. However, the rate at which H_2S is produced will dramatically affect the H_2S concentration in the wastewater and subsequently, the air space. These tests clearly showed that the H_2S production rate is far greater in the liquid wastewater in the corroded sewer than in the non-corroded sewer.

Impact of Biofilm on H2SPP

In order to assess the impact of the biofilm on H_2S production, scrapings from the sewer pipes were added to the liquid sample. Scrapings were collected at manholes B77 and B78 and stored in sample bottles flushed with N_2 gas. After resuspending the biofilm in O_2-free water, the suspension was added to wastewater samples and the H2SPP measured.

The results in Table 10 are quite surprising: it seems that the biofilm addition had only a small, and even a negative impact on the observed H_2S production kinetics. Ultimate H2SPP values remained essentially the same when compared to the control sample (without biofilm added). However, the first order model kinetic rate constant, k, increased significantly for the added biofilm, while the correlation coefficient was very low. At the same time the maximum rate decreased!

Added biofilm apparently reduced the maximum H_2S production rate! It is difficult to explain this result without additional experiments where actual SRB concentrations are measured. In addition, samples with added biofilm had a large initial H_2S concentration trapped in the biofilm itself which increased the noise and scatter in the collected data.

Table 10. H2SPP Analysis for Samples with added Biofilm.

Date	Sample Location	Type	k d^{-1}	S_u mg H_2S-S/L	Max Rate mg/L-d
2/9/89	B77	L	0.20	3.99	0.85
2/9/89	B77	L+B	0.25*	3.18	0.37
5/3/89	B78	L	0.09*	10.52	1.67
5/3/89	B78	L+B	0.16*	9.27	0.91

L = Liquid Sample
B = Biofilm added
* = Indicate correlation coefficient below 0.9.

Impact of Added Mixture

The combined impact of Cr^{+++}, Cu^{++}, CN^-, and Pb^{++} on H2SPP was investigated in samples from the corroded sewer manhole B78. The results are shown in Table 11.

Table 11. Impact of Added Metals on H2SPP.

Date	Sample Location	Type	k d-1	S_u mg H2S-S/L	Max Rate mg/L-d
2/9/89	B77	L	0.20	3.99	0.85
2/9/89	B77	L+M	-0.03*	-2.47	0.15
5/3/89	B78	L	0.09*	10.52	1.67
5/3/89	B78	L+M	-0.04*	-13.24	1.00
2/9/89	B77	L+B	0.25*	3.18	0.37
2/9/89	B77	L+B+M	0.20	2.31	0.31
5/3/89	B78	L+B	0.16*	9.27	0.91
5/3/89	B78	L+B+M	0.17	5.94	0.53

L = Liquid sample
B = Biofilm added
M = Metals added
* = Indicate correlation coefficient below 0.9.

Adding metals to samples affected H_2S production dramatically. The first order model gives rather poor correlations and may not be appropriate for the data. The negative reaction rate constant and negative S_u indicate that H_2S production did not follow the anticipated decreasing rate response,

but rather an increasing rate, meaning that the model was a poor fit for the observed data. Both liquid samples with metals showed this poor correlation. The increased H_2S production rate is indicative of the first part of the classic S shaped curve.

The maximum H_2S production rates give results that are much easier to interpret. Adding the mix to samples reduced the maximum H_2S production rate significantly. Liquid H_2S production rates decreased between 40 and 80% and biofilm rates between 16 and 42% after adding the mix. This reduction is quite significant since the actual H_2S production rate is of great importance in the sewer model to determine the amount of H_2S generated during the travel time to the treatment plant.

Metals can reduce the H2SPP in two ways: by direct inhibition of SRB, or by chemical reactions with dissolved sulfides. This study did not attempt to determine the exact mode of action. A more encompassing study needs to be conducted to determine the mechanism in which metals reduce H_2S production rates. In the tests performed so far, the H_2S production proceeded at an increased rate, following the first stage of the traditional S shaped curve. This may indicate either an initial inhibition, that is overcome in later stages, or an initial reaction between H_2S and added metals to form precipitates, thus preventing H_2S evolution from the liquid.

SIGNIFICANCE OF RESULTS

This report describes a kinetic model for H_2S production in sewers. The model includes bacterial sulfur reduction in the wastewater and biofilm, and the impact of chemical reactions and mass transfer on the evolution of H_2S from the liquid into the air space. A proper understanding of the H_2S production kinetics in the sewer is of great importance.

H_2S production in wastewater samples follows a typical S-shape curve. Initially H_2S evolution is slow due to low SRB numbers, potential inhibitors (such as DO or NO_3^-), or reactions between liquid compounds and dissolved sulfides. As time progresses, the rate increases to reach a maximum, followed by a reduction in rate possible due to a substrate limitation, end-product inhibition, or some other unknown factor.

The maximum H_2S production rate and lag time before H_2S evolution occurs is of great significance in predicting and describing H_2S evolution from wastewater in a typical sewer. If the lag period is significant, the wastewater may reach the treatment plant before conditions in the pipe is conducive to H_2S production. Or, if the H_2S production rate is reduced significantly by additives, the H_2S concentration in the liquid may be sufficiently reduced to prevent H_2S evolution from the liquid in significant quantities.

The ultimate significance of the reaction rate kinetics and impact of metals or waste activated sludge on H_2S production rates can be evaluated using the proposed kinetic sewer model. However, in order to use the model, reaction rates that account for added inhibitors, DO, and added aerobic organisms must be determined.

Waste activated sludge added to the sewer at upstream treatment plants may have a significant impact on H_2S production. The added waste activated sludge contain large quantities of active aerobic bacteria, which will rapidly consume the available oxygen to generate favorable conditions in the sewer for H_2S production.

Results so far showed that metals have a significant impact on H_2S production. Both the first order reaction rate constant and the maximum H_2S production rate decrease significantly when metals are added to the solution. In addition, it seems that there is an increase in the lag period before H_2S production occur. Both these factors will reduce the H_2S production in a flowing sewer, where only a limited amount of time is available for H_2S production and evolution.

NOMENCLATURE

C^*_x = Saturation concentration of species x in the liquid phase, in equilibrium with the gas phase concentration, g/m^3 (or mg/L). C^* is calculated using Henry's Law.

C_{BOD} = BOD concentration in wastewater, mg/L as S

$C_{c,s}$ = Combined sulfide concentration, mg/L as S

$C_{d,s}$ = Dissolved sulfide concentration, mg/L as S

$C_{f,x}$ = Concentration of species x in the film, mg/L

C_{SO4} = Sulfate concentration, mg/L as S

$C_{t,s}$ = Total sulfide concentration, mg/L as S

C_x = Concentration of species x, mg/L

D_x = Diffusion coefficient of species x into the biofilm, m^2/h

E = Potential of the cell, volt

E° = Standard potential of the cell, volt

F = Faradys constant, 23,062 cal/volt-eq

H_x = Henry's law coefficient for species x, mg/L-atm

k_{max} = Maximum reaction rate, mg/L-h

$(K_La)_x$ = Mass transfer coefficient for species x into the liquid, m/h

K_s = Half saturation coefficient, mg/L.

M_1 = Effective sulfide flux coefficient for sulfide generated in slime, m/h

M_2 = Sulfide production rate coefficient

N_x = Flux of species x **into** the liquid phase, g/m^2-h

n	=	Number of electrons transfered
p_x	=	Partial pressure of species x in the gas phase, atm
$r_{i,x}$	=	Intrinsic reaction rate for species x, i.e. the homogeneous reaction rate excluding mass transfer limitations, mg/L-h.
r_s	=	Rate of sulfide generation in the biofilm, g/m^2-h
R	=	Gas constant, 1.987 cal/deg-mole
T	=	Absolute temperature, °K
t	=	Time, h
V	=	Stream flow velocity, m/h
x	=	Distance into the biofilm, m
x	=	The species under consideration, such as O_2 or H_2S (when used as subscript)
{ox}	=	Activity or concentration of the oxidized species
{red}	=	Activity or concentration of the reduced species
Δ	=	Biofilm depth, m
η	=	Effectiveness factor, -
Θ	=	Temperature coefficient, usually $\Theta = 1.07$
ϕ	=	Thiele modulus, -

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APPENDIX A. DATA

Appendix A summarizes the H2SPP data collected during the study period. Manholes B77 and B78 are in a heavily corroded pipeline, while E30 is not corroded. Data in Table A-1 were adjusted to give zero H2SPP at t=0. Tables A-2 and A-3 includes actual measurements as well as corrected (for t=0) and model calculated values.

Table A-1. Averaged H2SPP values for sewage samples.

Time	Sample Location			
days	B77 9/22/88	B77 11/10/88	B77 12/15/88	E30 12/15/88
0	0.00	0.00	0.00	0.00
1	1.27	1.42	1.54	0.31
3	2.72	2.33	2.25	1.77
5	3.33	3.31	3.40	2.16
7	3.62	3.69	3.66	2.50
14	3.84	3.83	3.84	2.68
20	3.95	4.14	4.22	2.91

Table A-2 H2SPP data for samples collected 2/9/89.

	Liquid			Metal			Biofilm+Metal			Biofilm		
k =	0.204			-0.034			0.202			0.250		
Su =	3.987			-2.475			2.306			3.175		
R^2 =	0.933			0.196			0.991			0.840		
Time days	Measure	Calc	Model	Measure	Calc	Model	Measure	Calc	Model	Measure	Calc	Model
0	1.26	0	0.00	1.3	0	0.00	6.84 ->5.8	0	0.00	6.67 ->5.8	0	0.00
1	1.9	0.64	0.74	1.4	0.1	0.09	6.22	0.42	0.42	6.84	1.04	0.70
3	3.5	2.24	1.82	1.5	0.2	0.26	6.84	1.04	1.05	7.29	1.49	1.68
5	3.8	2.54	2.55	1.8	0.5	0.46	7.20	1.40	1.46	7.56	1.76	2.27
7	4.09	2.83	3.03	2.0	0.7	0.66	7.64	1.84	1.74	8.18	2.38	2.62
14	4.8	3.54	3.76	2.79	1.49	1.50	7.82	2.02	2.17	8.91	3.11	3.08

Measure = Experimentally determined H_2S concentration

Calc = Adjusted H_2S concentration values applying a t=0 correction.

Model = Model predicted H_2S concentrations using the estimated kinetics coefficients.

Table A-3 H2SPP data for samples collected 5/3/89.

	Liquid			Metal			Biofilm+Metal			Biofilm		
k =	0.0914			-0.037			0.173			0.164		
Su =	10.534			-13.242			5.942			9.268		
R^2 =	0.346			0.042			0.931			0.741		
Time days	Measure	Calc	Model	Measure	Calc	Model	Measure	Calc	Model	Measure	Calc	Model
0	4.5	0	0.00	4.1	0	0.00	50.6	0	0.00	51	0	0.00
1	5.1	0.6	0.92	4.38	0.28	0.51	51.7	1.1	0.94	53	2	1.40
3	7.9	3.4	2.53	6.3	2.2	1.59	52.7	2.1	2.40	53.8	2.8	3.59
5	9.3	4.8	3.86	8.1	4.0	2.75	53.8	3.2	3.43	55.5	4.5	5.18
7	10.0	5.5	4.98	9.7	5.6	4.00	54.9	4.3	4.17	57.3	6.3	6.32
14	11.1	6.6	7.60	10.9	6.8	9.21	55.9	5.3	5.41	59.6	8.6	8.33

Measure = Experimentally determined H_2S concentration
Calc = Adjusted H_2S concentration values applying a t=0 correction.
Model = Model predicted H_2S concentrations using the estimated kinetics coefficients.

PART II. SULFATE-REDUCING BACTERIA IN CONCRETE SEWER PIPES*

In sewage effluent contained by concrete sewer pipes during transport to the waste treatment facility, sulfate-reducing bacteria (SRB) are responsible for production of the sewer gas sulfide and are a major factor in microbial concrete corrosion. Although SRB's are strictly anaerobic, they are ubiquitous and are found even in aerobic environments. They show considerable adaptability in terms of temperature and salinity, tolerating temperatures from below -5° to 75 °C, pH value ranging from 5 to 9.5 and salinity up to 18% (Jorgensen, 1977). They may also be oxygen toleranct; Desulfobacter postgatei and Desulfovibrio species are known to be oxygen-resistant (Hardy, 1981; Cypionka, 1985). Cypionka et al, 1985, reported that the following SRB's, Desulfovibrio vulgaris, Desulfovibrio baarsii, Desulfobacter postgatei, Desulfobulbus propionicus, Desulfococcus multivorans, Desulfonema limicola, Desulfosarcina variabilis and Desulforomonas acetoxidans, used thiosulfate or sulfur as electron acceptors and exhibited oxygen-dependent growth in sulfate- and sulfur-free medium. They form thiosulfate or sulfur by continuously regenerating them in a cycling process from sulfide by autoxidation. Our studies are focused on the SRB and their physiology in both pure and mixed culture systems under strictly anaerobic conditions. We developed a reliable medium and culture conditions for enumerating SRB's by MPN analysis of mixed culture inocula taken from natural samples. This culture protocol was also assessed by using axenic cultures of laboratory strains of SRB's. Because of the superiority of this medium, we have used it for isolation of three strains of SRB's from cultures originally inoculated with biofilm from a corroding sewer pipe and have begun their characterization. As model systems for the inhibition of sulfate reduction of SRB, we established stable enrichment cultures using lactate as a single sulfidogenic substrate. These enrichment cultures were used as microcosms to simulate the sewer pipe environment for sulfide-inhibition experiments. We summarize here our experimental studies on the isolation of SRB, evaluation of media and experiments on inhibition of sulfate reduction.

MATERIALS AND METHODS

Media and Enumeration Techniques: We reviewed the composition of various published media most commonly used in the isolation and growth of SRB's. Postgate's Medium B and Pfennig's enrichment medium were selected for comparison with alpha medium which was developed in our own laboratory. Table 1 compares the composition of the three media. Most-Probable-Number (MPN) of the biofilm sample obtained from site #B78 were evaluated in these media and the results were compared (Table 3). The medium which gave the highest bacterial count was used in the subsequent experiments. Throughout these studies we employed the techniques of Hungate (Hungate, 1969) as modified by Bryant (Bryant, 1972) for the culture of strictly anaerobic microorganisms.

*R.A. Mah

Table 1. Constituents of Alpha Medium, Postgate Medium B and Pfennig's Medium for Enumeration of SRB (MPN)*.

ALPHA MEDIUM		MEDIUM B (PG)		PFENNIG'S MEDIUM	
NH_4Cl	1.0	NH_4Cl	1.0	NH_4Cl	1.0
$CaCl_2.2H_2O$	0.5	$CaSO_4$	1.0	$CaCl_2.2H_2O$	0.1
$K_2HPO_4.3H_2O$	0.4	KH_2PO_4	0.5	K_2HPO_4	0.5
$FeSO_4.7H_2O$	0.5	$FeSO_4.7H_2O$	0.5	$FeSO_4.7H_2O$	0.5
$MgCl_2.6H_2O$	1.0	$MgSO_4.7H_2O$	2.0	$MgSO_4.7H_2O$	2.0
Na_2SO_4	1.0	Na lactate	2.2	Na_2SO_4	1.0
Na lactate	2.2	Yeast extract	1.0	Na lactate	2.2
Yeast extract	1.0	Resazurin	0.5	Yeast extract	1.0
Resazurin	0.5	Ascorbic acid	0.1	Resazurin	0.5
Ascorbic acid	0.1	Nathioglycollate	0.1	Ascorbic acid	0.1
Na thioglycollate	0.1			Nathioglycollate	0.1
$NaHCO_3$	4.0				
$MgSO_4.7H_2O$	2.0				
Trace mineral**	10 ml.				

* Ingredients, g per liter

** Trace mineral solution (g/L)

H_2SeO_3 0.01, $MnCl_2.4H_2O$ 0.1, $FeSO_4.7H_2O$ 0.1, $CoCl_2.6H_2O$ 0.15, $ZnCl_2$ 0.1, H_3BO_3 0.01 $NaMoO_4.2H_2O$ 0.01, $CuCl_2.2H_2O$ 0.02, $NiSO_4.6H_2O$ 0.02, $AlCl_3.6H_2O$ 0.04, Disodium EDTA dihydrate 0.5, $NaWo_4$ 0.03.

The method for the indirect enumeration of SRB's was the Most-Probable-Number (MPN) technique using anaerobic alpha media (Table 1), $FeSO_4.7H_2O$ was used for differentiation because ferrous salts formed a black precipitate of FeS when sulfide was formed and imparted a distinctive blackening of the media indicating the present of SRB's. The method for the isolation and direct enumeration of SRB's consisted of inoculating samples of serial dilutions of bacterial cultures into molten agar media containing ferrous ion for the detection of SRB's in anaerobic roll-tubes. The media were solidified on the inner walls of the tubes and colonies of SRB's that grew were identified by their black coloration. Pure cultures of the most abundant SRB's were isolated from samples taken from the highest dilution cultures of the MPN determination experiments. The strains were isolated by inoculating enrichment medium solidified with 1.5% purified agar and transferring colonies of SRB to fresh medium. This process was repeated until only one colony type was observed, and then the process was repeated three more times. Culture purity was verified by microscopic observation, only one cell type was observed, and by inoculating complex medium without a sulfidogenic substrate; no growth in this medium indicated that no heterotrophic contaminants were present.

Enumeration of SRB in The Concrete Sewers: The numbers of SRB's in the samples of sewage and biofilm were determined by the MPN technique. Sewer and biofilm samples were collected at Compton, CA on 25 August 1988, from manhole #B78, a site where concrete corrosion is very severe, and manhole #E30 which is considered a clean, non-corroding pipe segment. The bottles containing water samples were filled and capped so no air was entrapped and anaerobic conditions were maintained. The biofilm samples were scraped from the sides of the pipe with the bottle mouth and the headspace of the bottles was flushed with pure nitrogen gas to exclude air. Biofilm samples were diluted with the culture medium for inoculation of MPN experiments.

Inhibition of Sulfate Reduction Experiments: To test for inhibition of sulfate reduction by oxyanion group VI elements, chromate, tungstate, selenate and molybdate, we added the oxyanions at varying concentrations to freshly inoculated cultures of two SRB enrichment cultures. The SRB enrichments were initiated by inoculating samples of sewage (Sample #1) and biofilm (Sample #2) from site #B78 severe concrete corrosion. The enrichment cultures were grown as batch cultures with lactate as substrate; a 2.5% inoculum was transferred routinely to fresh medium every 7-10 days since December 1988.

The enrichment alpha medium (Table 2) was modified from the MPN alpha medium by replacing $FeSO_4.7H_2O$ and $MgSO_4.7H_2O$ with Na_2SO_4 as a sole sulfate source; $CaCl_2.2H_2O$ was decreased in concentration to 0.1 g/L in order to avoid black precipitation of FeS and to reduce interference from calcium salts while measuring the bacterial growth and sulfide concentration. Na_2S, a reducing agent, was also used in the enrichment medium to reduce the redox potential low enough to initiate growth of SRB's.

Table 2. Constituents of Alpha Medium for Inhibitor Experiments (Enrichment Medium).

Ingredients	g/L
NH_4Cl	1.0
$CaCl_2.2H_2O$	0.1
$MgCl_2.6H_2O$	1.0
K_2HPO_4	0.4
Na_2SO_4	1.4
$NaHCO_3$	4.0
Na lactate	2.2
Yeast extract	0.5
Resazurin	0.5
$Na_2S.9H_2O$	0.24
Trace mineral solution	10.0 ml.

An untreated control culture inoculated with the same sample was incubated for the same period of time and analyzed for sulfide production. In every case, the control sample metabolized all of the available sulfate and converted it to sulfide as measured by the methylene blue method (Trüper and Schlegel, 1964). The oxyanionic inhibitors were prepared anaerobically, the pH was adjusted to 7.0 and sterilized by autoclaving before use. A 5% inoculum of a late logarithmically grown culture was used; the estimated number of cells in this innoculum was $1\text{-}1.6 \times 10^8$ organisms/ml. All cultures were incubated at 37 °C for a minimum of 7-10 days and analyzed for sulfide production periodically.

RESULTS AND DISCUSSION

The mineral composition of the alpha medium was based on a standard mixture of inorganic salts normally employed for culture of other anaerobic bacteria in our laboratory. It differed significantly from the medium of Postgate and Pfennig by addition of a trace mineral solution and by the addition of sufficient quantities of bicarbonate-CO_2 to maintain the buffering capacity of the medium at pH 7.0 ± 0.2. These differences, and the use of the Hungate technique, most likely accounted for the improved reproducibility of our method and the more consistent replication of data compared to media used by other researchers (Grossman, 1953; Postgate,1959; Iverson, 1966). Our MPN experiments using alpha medium yielded two to three fold higher counts than the other media (Experiment I, Table 3). In subsequent experiments, comparing alpha medium and Postgate's medium B using the same anaerobic techniques, there was no difference statistically between these two media. However, alpha medium always yielded higher counts on the average with a more consistency in the replica (Experiment II, Table 3).

Table 3. Comparing MPN Results of Biofilm Sample Site #B78 in Alpha Medium, Postgate Medium B and Pfennig's Medium.

Type of medium	MPN ml^{-1}
Experiment I:	
Alpha	3.4×10^8
Postgate's B	2.6×10^8
Pfenning's	1.0×10^8
Experiment II:	
Alpha	#1 6.0×10^7
	#2 1.4×10^8
	#3 1.4×10^8
	average = $1.1 \pm 0.4 \times 10^8$
Postgate's	#1 6.0×10^7
	#2 6.0×10^7
	#3 1.6×10^8
	average = $0.9 \pm 0.5 \times 10^8$

ENUMERATION OF SRB

Strain G.11 of genus Desulfovibrio, the H2 utilizing sulfate reducer, was used to compare the roll tube colony counting and MPN methods to determine which technique gives the higher estimation of numbers of bacteria. Different types of substrates were also used in order to observe the maximum count and the time period that gave the positive result. The results are summarized in Table 4:

Table 4. MPN and Roll Tube Study of Strain G.11.

Experiment	Substrate	# days*	MPN/ml.	RT/ml.
#1	H_2	MPN 7 days RT 35 days	2.2×10^7	1.0×10^7
#2	H_2	MPN 13 days RT 35 days	2.6×10^7	2.1×10^7
#3	H_2	MPN 9 days	3.4×10^8	-
	Lactate	MPN 12 days RT 33 days	3.4×10^8	1.7×10^8
	H_2 + Lactate	MPN 9 days	3.4×10^8	-
#4	Lactate	MPN 9 days	3.4×10^8	-
	Lactate	MPN 9 days	4.4×10^8	-

* Number of days when positive results observed without further changes.

We compared colony counting and MPN methods (Table 4) to determine which technique gave the most rapid results, highest consistency, and the best estimation of numbers of bacteria. The MPN method was faster than the colony counting method. Maximum counts in the MPN method were reached in less than 10 days; roll tubes took more than 4 weeks. The MPN method also gave higher viable counts from all samples tested; the difference was about 50% higher numbers with the MPN method.

Results from a literature review showed that lactate is used by the vast majority of SRB's. This includes the most recently discovered strains which are fatty-acid oxidizing SRB's. Therefore, sodium lactate was used as the single sulfidogenic substrate. Table 5 shows the MPN of lactate-oxidizing SRB in the sewage and biofilm samples of the two sites. The pH of the water sample from site #B78 was 7 ± 0.2 and the temperature was 31 °C. The characteristics for site #E30 were pH 7.5 ± 0.2 and the temperature 27.5 °C. There were 3.5 times as many SRB in the biofilm of the corroding pipe than in the non-corroded pipe biofilm and 5.6 times as many SRB in the sewage sample of the corroding pipe than in the non-corroded pipe. However, these numbers are only a guide line for the numbers of SRB

with which we are dealing; that figure could vary widely depending on the thickness of the biofilm, the flow/sulfate concentration of the sewage, the date, time, site, and season of sampling. Numbers of bacteria do not necessarily reflect microbial activity, however, we cannot expect rapid sulfate reduction rates in locations with small populations. Nevertheless, we expected that the clean sewer (manhole #E30) would have fewer numbers of SRB's; yet, the MPN numbers were still in the same range.

Table 5. MPN of 4 Sewage Samples, Collected on August 25, 1988.

Site #	Sample type	Total sulfides*	MPN g^{-1} TVS^{-1}
B 78	water	1.3 mM	5.2×10^9
B 78	biofilm	-	2.7×10^{10}
E 30	water	0.2 mM	9.2×10^8
E 30	biofilm	-	7.6×10^9

* Amount of sulfides present in the collected liquid samples.

Microscopic examination of cells from the 3 colonies isolated from biofilm sample site #B78 are morphologically indistinguishable from each other. They are rods, straight, motile, some with pointed ends and occur singly and in pairs. They stained gram negative. The colonies in the roll tube were black and varied in size ranging from 0.5 to 5 mm. in diameter; they were well circumscribed with a clear zone surrounding the colony. Some colonies developed clear zones at the centers when the roll tubes were left in the incubator longer than 4 weeks. All isolated colonies were able to grow at 20-37 °C, with the optimal temperature at 37 °C; in pH 6.5 to 8; they used lactate, propionate and ethanol as their substrates.

Our studies indicated that these sulfate-reducers belonged to the genus Desulfobulbus. We would like to complete our work on characterization of these SRB and to confirm that they are the majority of sulfate-reducers present in the sample and in the sewage.

Tables 6-9 show the effect of molybdate, selenate, chromate and tungstate on sulfide production of the enrichment cultures, sewage and biofilm sample site #B78. Total irreversible inhibition of sulfate reduction was observed at 0.25 mM (~35 ppm) selenate (SeO_4:SO_4 = 1:40) and 90% inhibition at 0.10 mM (~14 ppm) selenate (SeO_4:SO_4 = 1:100), indicating a highly specific effect of selenate to sulfate reduction. Experiments on selenate and sulfate reduction by cell suspensions of Desulfovibrio desulfuricans subsp. aestuarii showed similar results with ours that SRB were incapable of reducing either selenate or sulfate when the selenate/sulfate ratio was 1:50 and irreversible inhibition occurred at high selenate concentration (Zehr, 1987). The highly specific effect of selenate is probably due to the fact that the selenate analog adenosine-5'-phosphoselenate has a greater stability than the molybdate or tungstate analog of adenosine-5'-phosphosulfate (Wilson, 1958). The molecular size of sulfate and selenate is also similar but molybdate is bigger and has therefore more difficulty entering the cell and coming into contact with ATP sulfurylase, the enzyme in the first step of sulfate reduction (Postgate, 1952).

Table 6. Effect of Molybdate on Sulfied Production, After 48 Hours Incubation at 37 °C., of the enrichment cultures, Sewage and Biofilm Samples Site # B78.

Na_2SO_4 (mM)	$Na_2MoO_4.2H_2O$ (mM)	Sulfides (mM)*	
		Sewage	Biofilm
10	-	7.03 ± .04	7.01 ± .27
10	0.10	4.66 ± .07	3.99 ± .28
10	0.25	3.59 ± .49	3.92 ± .38
10	0.50	1.61 ± .08	3.51 ± .18
10	1.00	1.20 ± .05	1.23 ± .13

* Average of 5 replica ± (max-min/2).

All inhibitor experiments were done in the alpha enrichment medium containing 1 mM of sodium sulfide as a reducing agent. Sulfide concentration in the liquid medium was determined by methylene blue method adapted from Trüper and Schlegel (1946). Measurement of sulfide depends much on pH of the medium. At pH7 (pH of the medium) pK of $H_2S \Leftrightarrow HS^- + H^+$ is about 7. Therefore, it is assumed that approximately 50% of sulfide will be in the liquid phase and another 50% in the gas phase. All inhibitor experiments were repeated at least twice to determine the reliability of the results and all were shown the similar results.

Table 7. Effect of Selenate on Sulfide Production, After 48 Hours Incubation at 37 °C, of the Enrichment Cultures, Sewage and Biofilm Samples Site # B78.

Na_2SO_4 (mM)	Na_2SeO_4 (mM)	Sulfides (mM)*	
		Sewage	Biofilm
10	-	6.87 ± .16	6.71 ± .17
10	0.10	1.14 ± .11	0.99 ± .16
10	0.25	0.76 ± .14	0.79 ± .21
10	0.50	0.68 ± .07	0.63 ± .02
10	1.00	0.59 ± .11	0.64 ± .12

* Average of 3 replica ± (max-min/2).

Table 8. Effect of Chromate on Sulfide Production, After 48 Hours Incubation at 37 °C, of the Enrichment Cultures, Sewage and Biofilm Samples Site # B78

Na_2SO_4 (mM)	Na_2CrO_4 (mM)	Sulfides (mM)*	
		Sewage	Biofilm
10	-	6.83 ± .60	7.10 ± .29
10	0.10	6.88 ± .59	6.57 ± .55
10	0.25	6.85 ± .44	6.95 ± .40
10	0.50	6.77 ± .75	6.75 ± .59
10	1.00	0.91 ± .21	0.78 ± .18

* Average of 5 replica ± (max-min/2).

Table 9. Effect of Tungstate on Sulfide Production, After 48 Hours Incubation at 37 °C., of the Enrichment Cultures, Sewage and Biofilm Samples Site # B78.

Na_2SO_4 (mM)	Na_2WO_4 (mM)	Sulfides (mM)*	
		Sewage	Biofilm
10	-	5.76 ± .21	5.76 ± .34
10	1.00	5.66 ± .36	5.78 ± .29
10	2.50	2.96 ± .04	1.32 ± .19
10	5.00	0.67 ± .03	0.76 ± .06
10	10.0	0.51 ± .06	0.46 ± .04

* Average of 5 replica ± (max-min/2).

Figures 1-12 show the sulfide production over the entire period of observation of sample #1 (sewage), #2 (biofilm) and pure cultures, colony 1 and 2 isolated from the biofilm sample of site #B78. Except for molybdate, the effect of the inhibitors was similar in both samples for all four elements tested. In the case of molybdate, the biofilm inoculated enrichment was more resistant than the sewage effluent enrichment. A concentration of at least 1.0 mM sodium molybdate was required to inhibit the biofilm enrichment whereas 0.5 mM sodium molybdate was already sufficient to inhibit the sewage effluent culture. This finding indicates that there are population differences between the two enrichment cultures. The minimum inhibitory concentration of selenate in pure cultures is also lower than in the enrichment cultures (mixed populations) Table 10, indicating more resistance to selenate in the heterogenous microbial populations. Molybdate, chromate and tungstate all inhibited sulfate reduction at much higher concentrations than selenate.

Table 10. Minimum Inhibitory Concentration (MIC) of Oxyanions Group VI Tested on the Enrichment Cultures.

Substance	MIC* mM (ppm)	Culture**	Inhibitor: SO_4
SeO_4	0.25 (~35)	Sewage and biofilm samples, site #B78	1:40
	0.1 (~14)	2 Isolated pure - cultures (colony #1 and #2)	1:100
MoO_4	0.5 (~80)	Sewage sample, site #B78	1:20
	1.0 (~160)	Biofilm sample, site #B78 and isolated pure cultures (colony #1, #2 and #3)	1:10
CrO_4	1.0 (~116)	Sewage and biofilm samples, site # B78	1:10
WO_4	5.0 (~1240)	Sewage and biofilm samples, site # B78	1:2

* Sulfide production was approximate totally inhibited within the first 48 hours.

** A 5% inoculum of a late logarithmically grown was used; the estimated number of cells(MPN) in the inoculum was 1-1.6 x 10^8 organisms/ml. All cultures were incubated at 37 °C for 7-10 days.

The application of oxyanion, particularly selenate (MIC ~35 ppm) to inhibit sulfide production in the sewage or as a pretreatment in industries with high sulfate sewage before dumping the sewage into the public sewers, would need further studies in terms of a bigger scale experiment, a future field study, and a biodegradation of selenate itself as well as its chemical interactions with other compounds and metals.

Minimum inhibitory concentration of microbicides and bacteriostatic substances are usually influenced by many factors such as the nature of the medium in which the substance is tested, the strains of tested SRB's, pure culture or mixed population, inoculation size, the presence of salts or heavy metals, the temperature, the amount of the sulfate pool and the presence of electron donors, such as hydrogen, n-butanol, ethanol, propanol, etc. which stimulate the rate of sulfate reduction (Ingvorsen, 1981; Postgate, 1952; Postgate, 1984).

The recent isolation of two new species of Desulfovibrio capable of utilizing higher fatty acids up to eighteen carbons (Widdel, 1981) and the description (Pfennig, 1981; Widdel, 1982) of five new genera of SRB, Desulfobacter, Desulfosarcina, Desulfonema, Desulfobulbus, and Desulfococcus that are morphologically and nutritionally diverse has completely destroyed the concept that the SRB are a small and highly specialized group with a limited metabolic versatility. This physiological diversity of SRB's was observed in our pure cultures isolated from the biofilm sample, site #B78.

Therefore, the control of sulfide production and concrete corrosion may be specific to each locale with the majority of resident SRB's enriched by local selective factor of pH, temperature, substrate availability, presence or absence of heavy metals, in situ combinations of oxyanions, etc.

PROPOSAL TO LA COUNTY ON SRB

Our previous studies indicate that sulfate-reducing bacteria belonging to the genus Desulfobulbus rather than to the more commonly occurring Desulfovibrio predominate in all sewage samples thus far examined. This ecological study needs further verification on additional samples, and we propose to do further viable counts on freshly sampled sewage to establish this finding. This verification is important in the design for inhibition of sulfide production experiments. The genus Desulfobulbus is capable of using propionate as well as lactate as electron donor and carbon source. They also are able to use other inorganic compounds such as nitrate as electron donors. In other words they can use much wider variety of compounds as electron donors and carbon sources. In addition to examining the numerical importance of Desulfobulbus, we also propose to study the effect of the following sulfate-reducing inhibitors on both pure cultures of the most numerous sulfate-reducer isolated from the sewage samples and on natural mixed cultures of unenriched sewage samples:

1. Arquad 16 50%* (N,N,N-Trimethyl-1-hexadecanaminium chloride)
2. Arquad S 50%* (Trimethylsoya alkyl quaternary ammonium chlorides)
3. Arquad 2C 75%* (Dicoco alkyldimethyl quaternary ammonium chlorides)
4. Hibitane (Chlorhexidine acetate)

* Arquads are quaternary ammonia compounds, widely used in the textile industry as an antistatic agent, in pesticide/herbicide formulations, in cosmetic formulations as an ingredient in hair conditioners, toiletries and fragrances, etc.

These compounds were selected from a list of sulfate-inhibitors compiled by Postgate (1984) from publications reported by several research groups. The studies were performed on pure cultures of Desulfovibrio or Desulfotomaculum or on mixed, impure cultures. We selected the above compounds because of their low minimum inhibitory concentrations (ranging from 0.1 to 50 μg/ml) and the wide use of the Arquad compounds.

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Fig.1 Sulfide Production by Sample #1

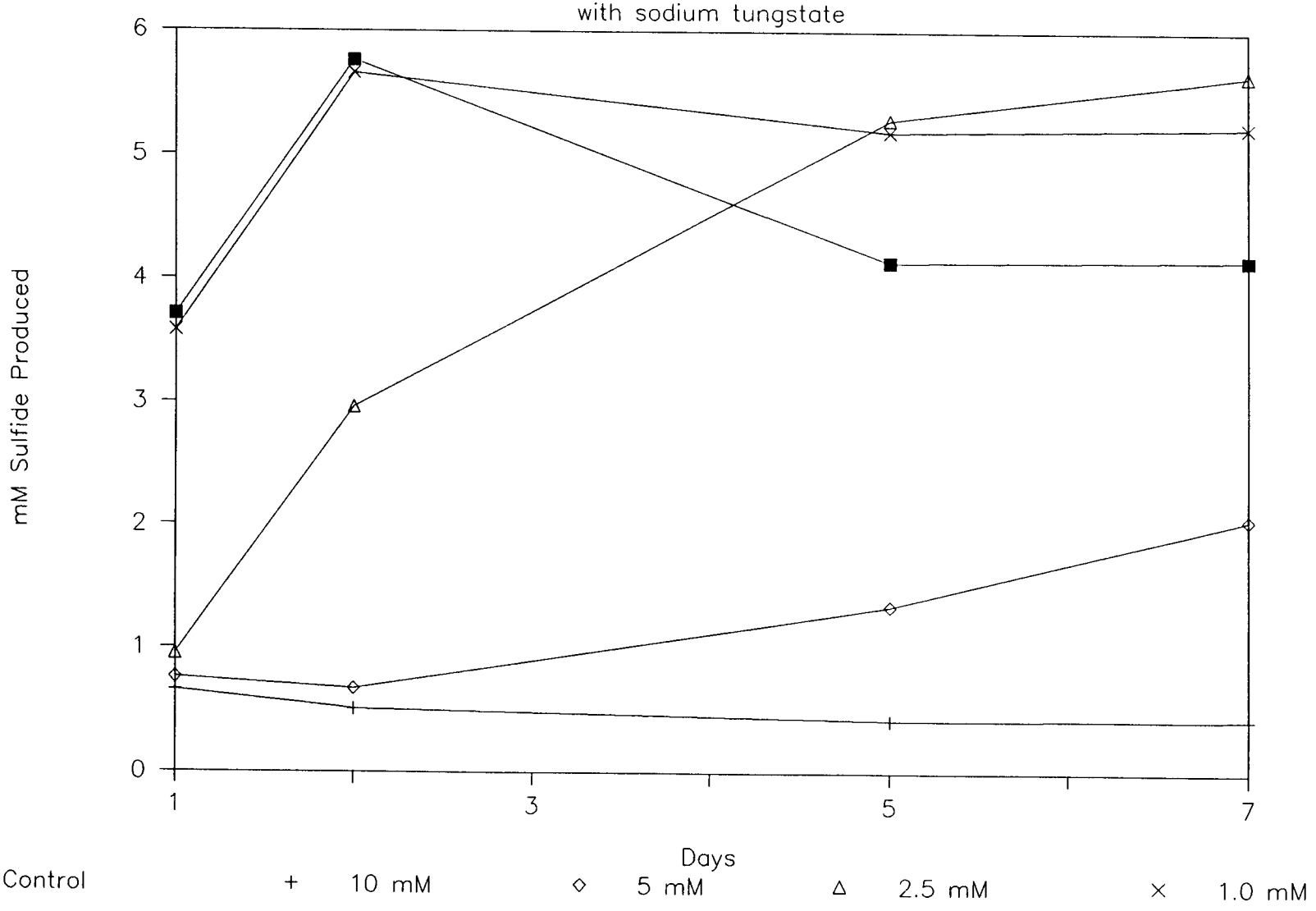

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Fig. 2 Sulfide Production by Sample 2

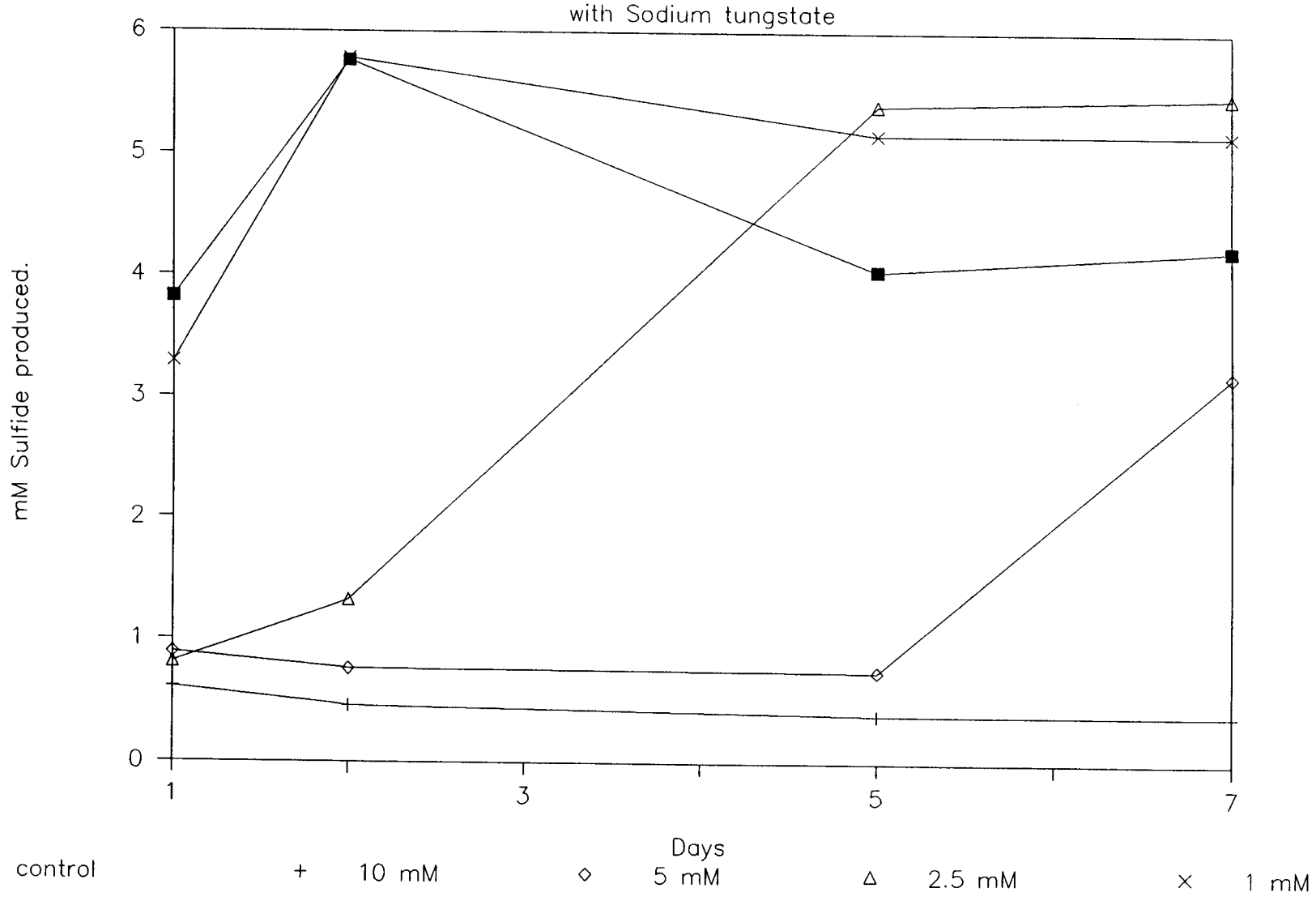


Fig. 3 Sulfide Production by Sample #1

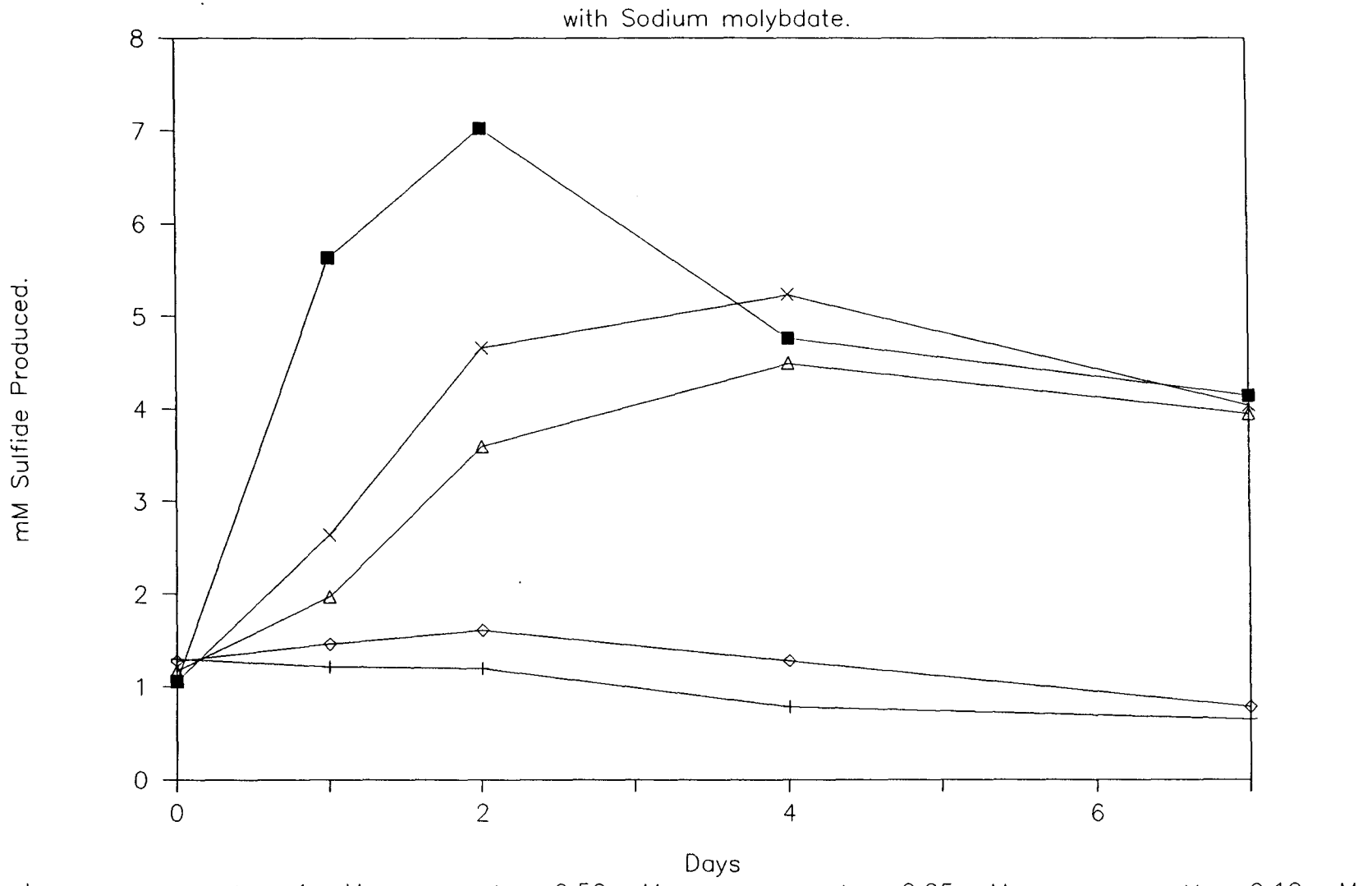


Fig.4 Sulfide Production by Sample #2

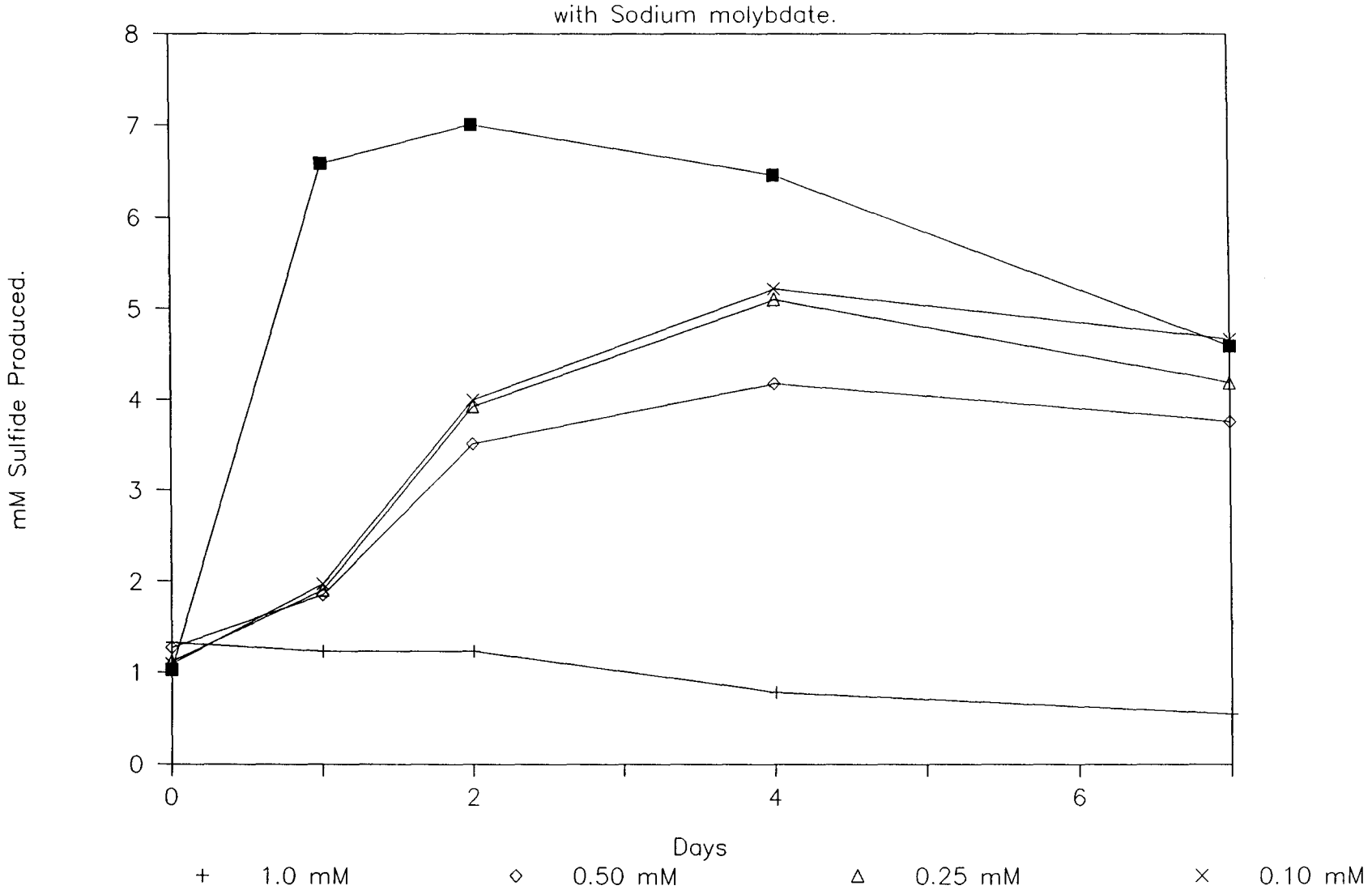


Fig.5 Sulfide Production by Sample # 1

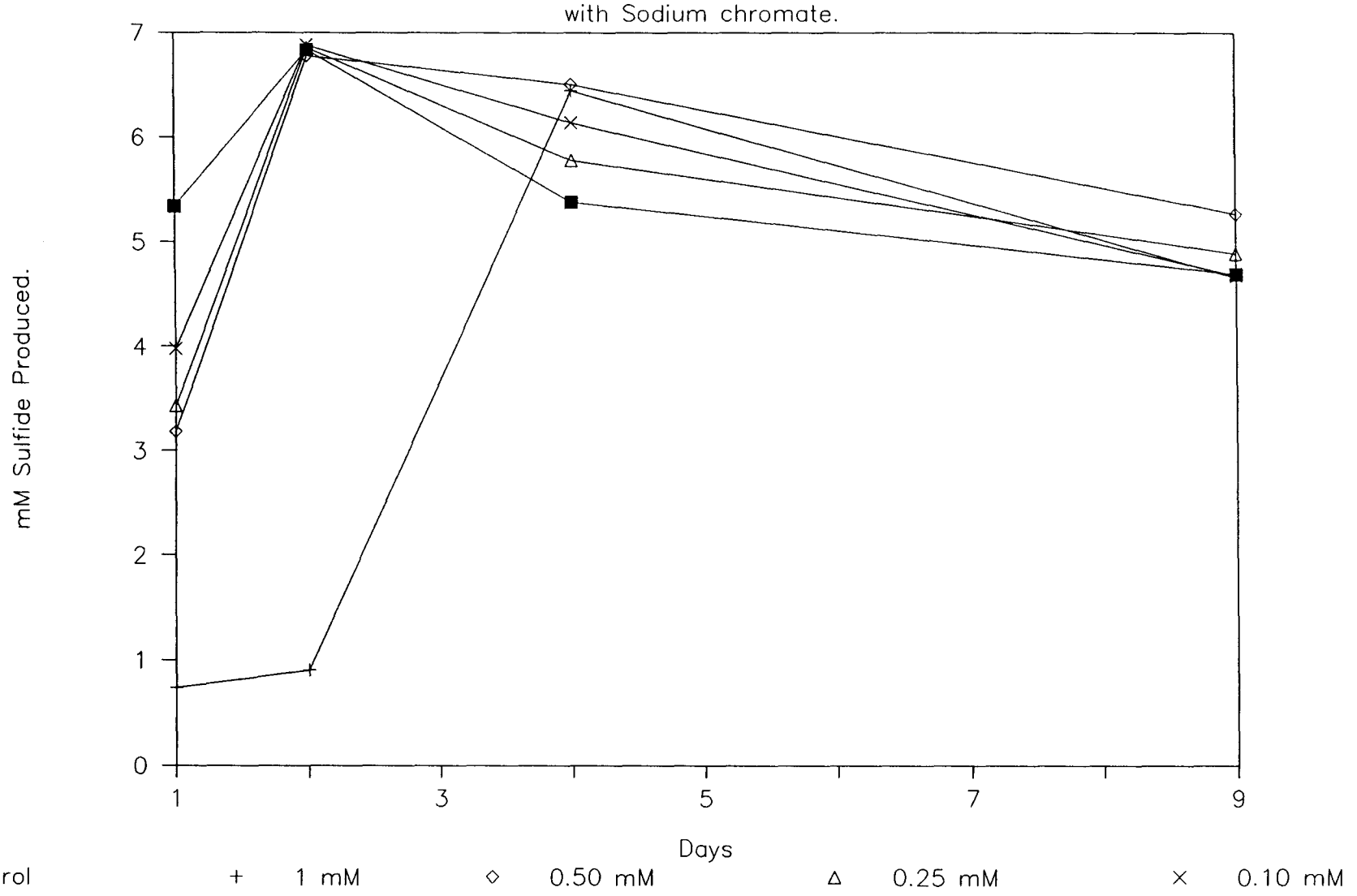


Fig.6 Sulfide Production by Sample # 2

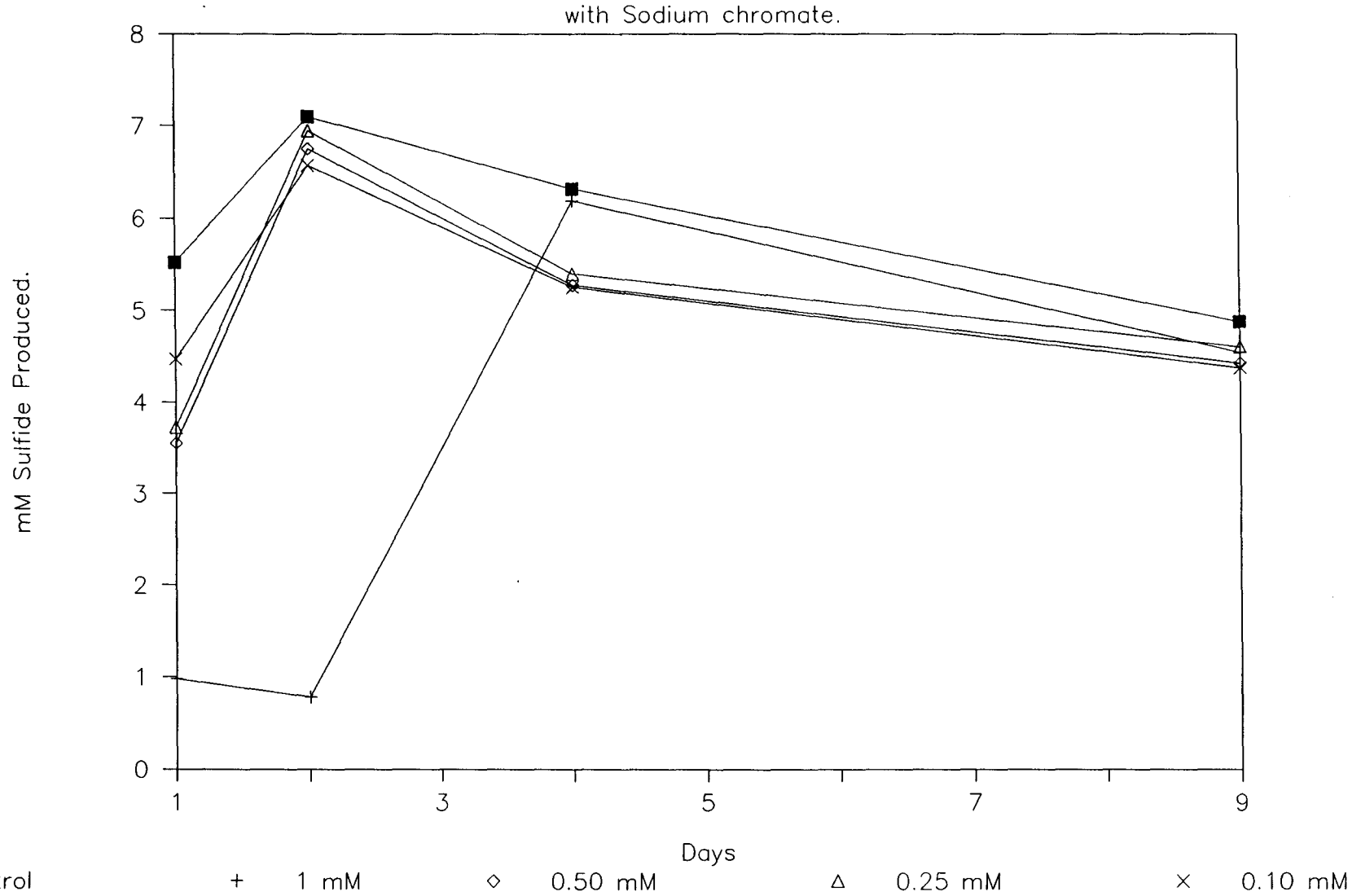


Fig.7 Sulfide Production by Sample # 1

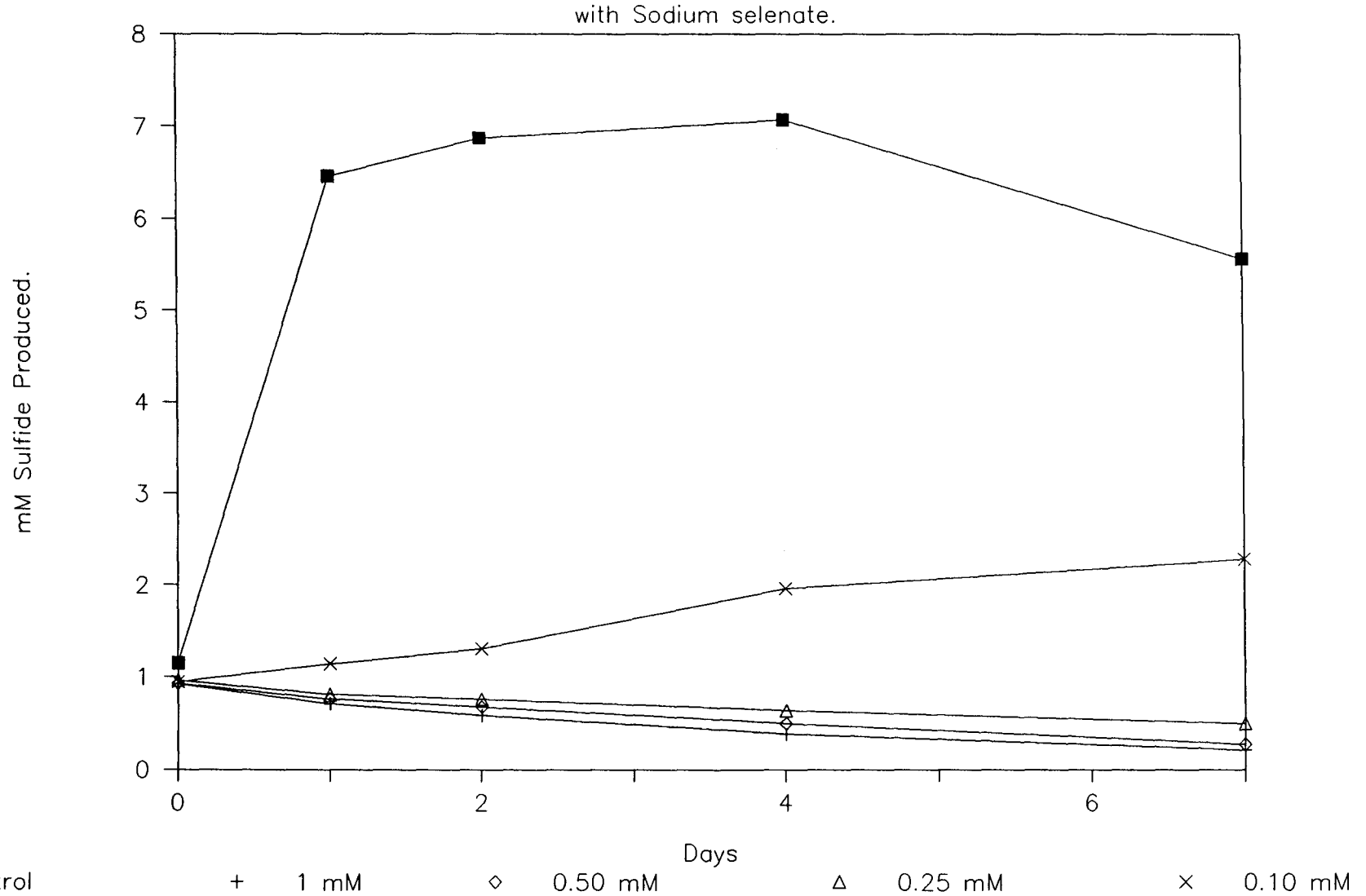


Fig.8 Sulfide Production by Sample # 2

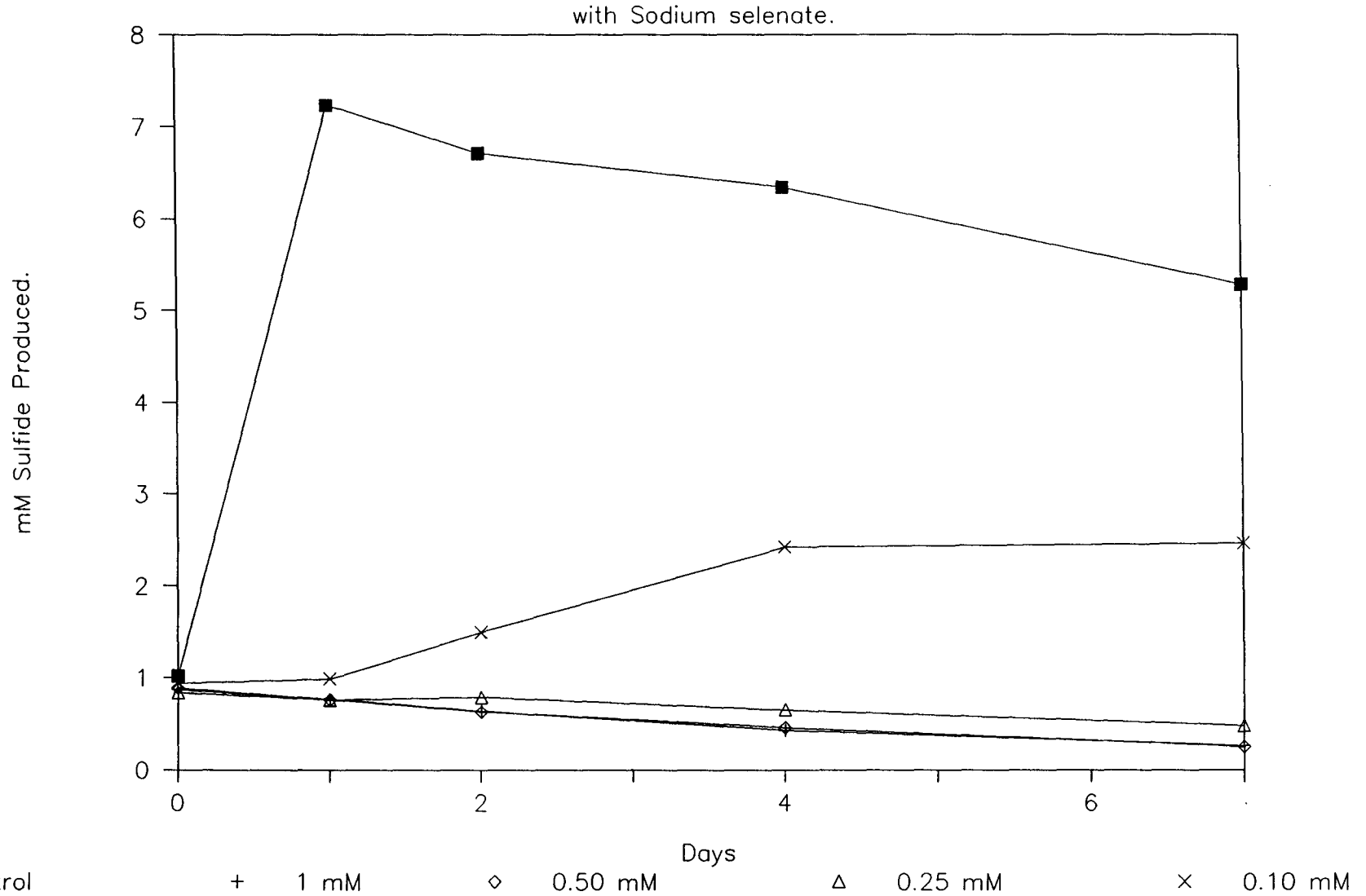


Figure9:Sulfide Production of Colony #1

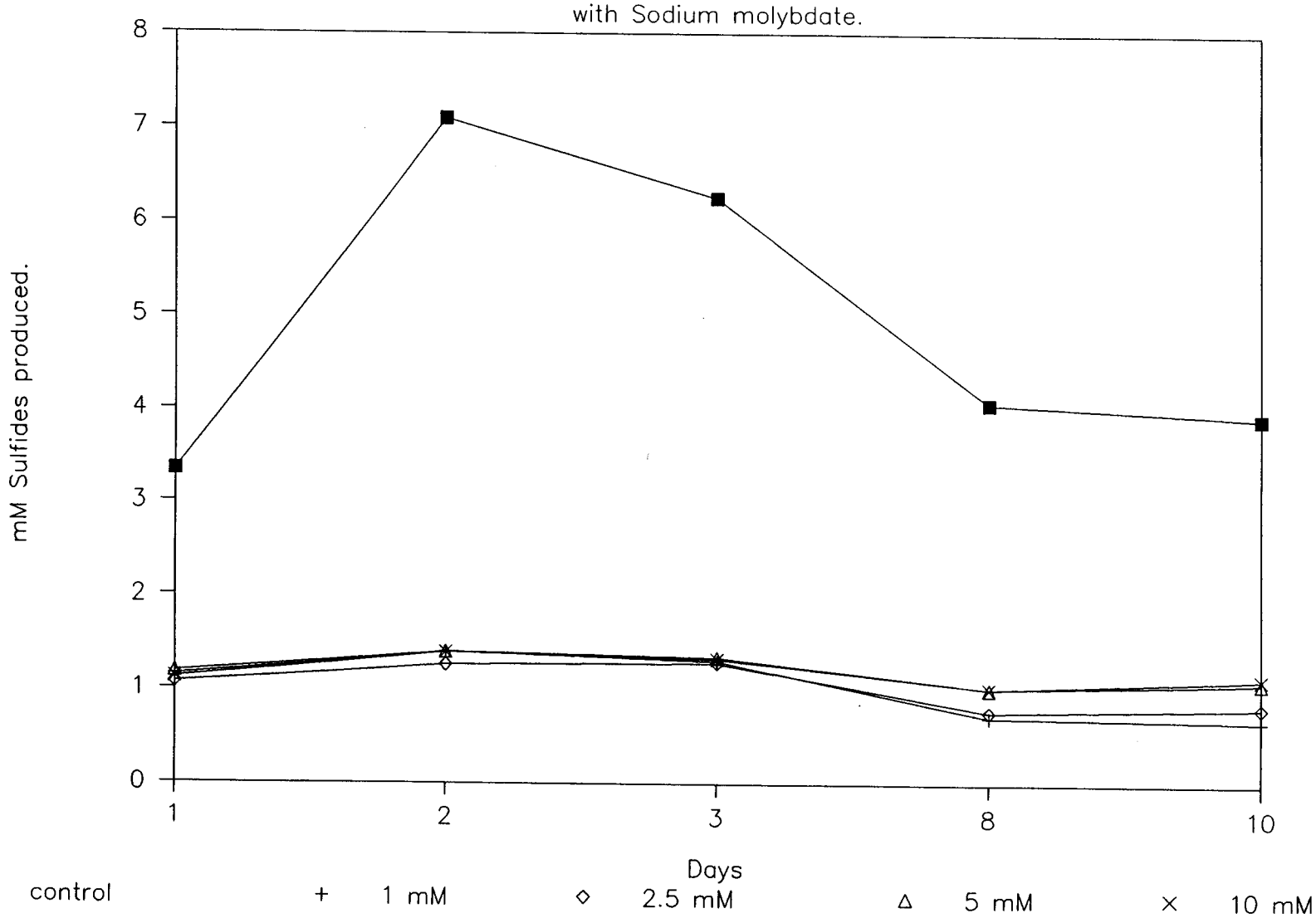


Figure10:Sulfide Production of Colony#2

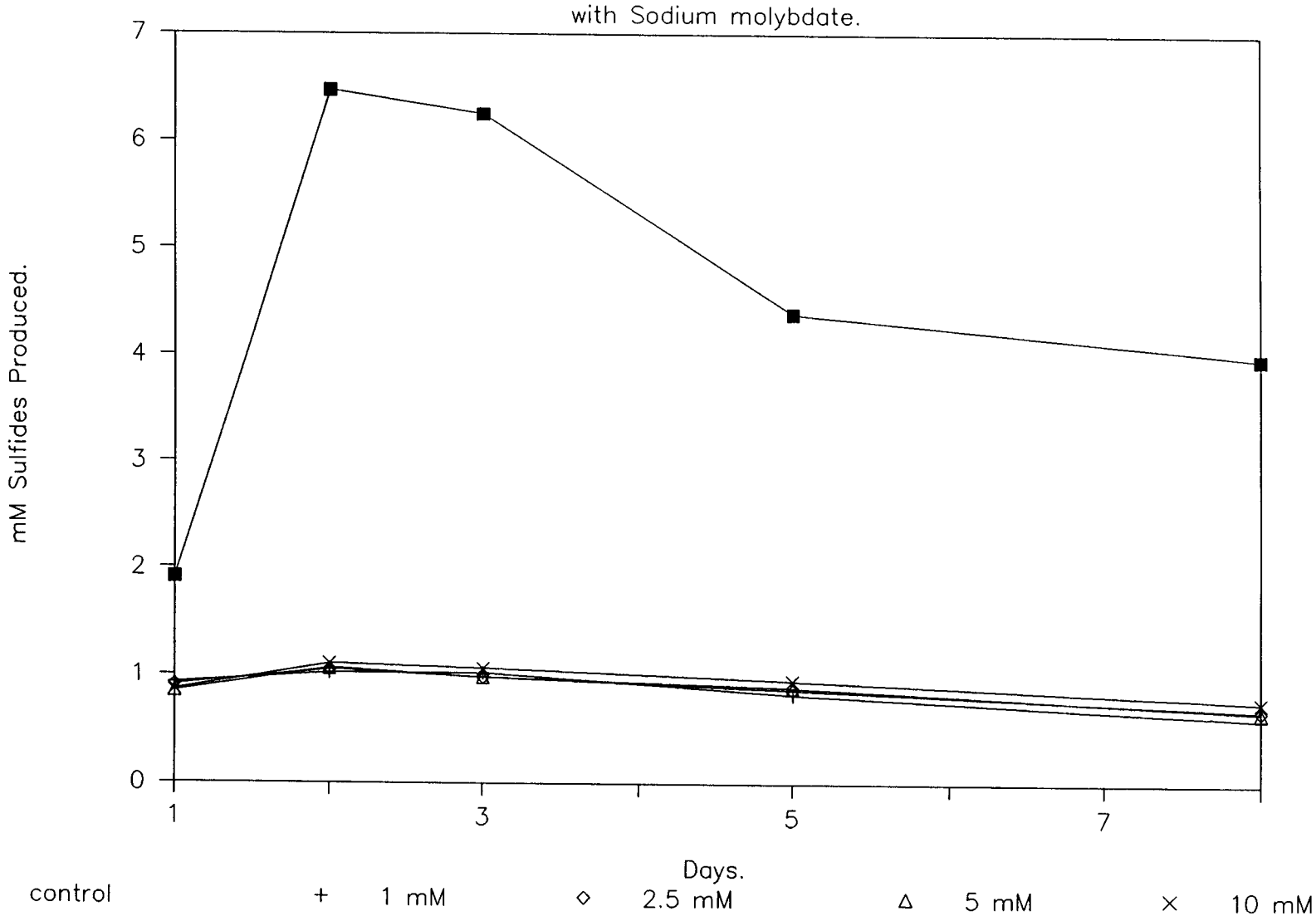


Figure11:Sulfide Production of Colony#1

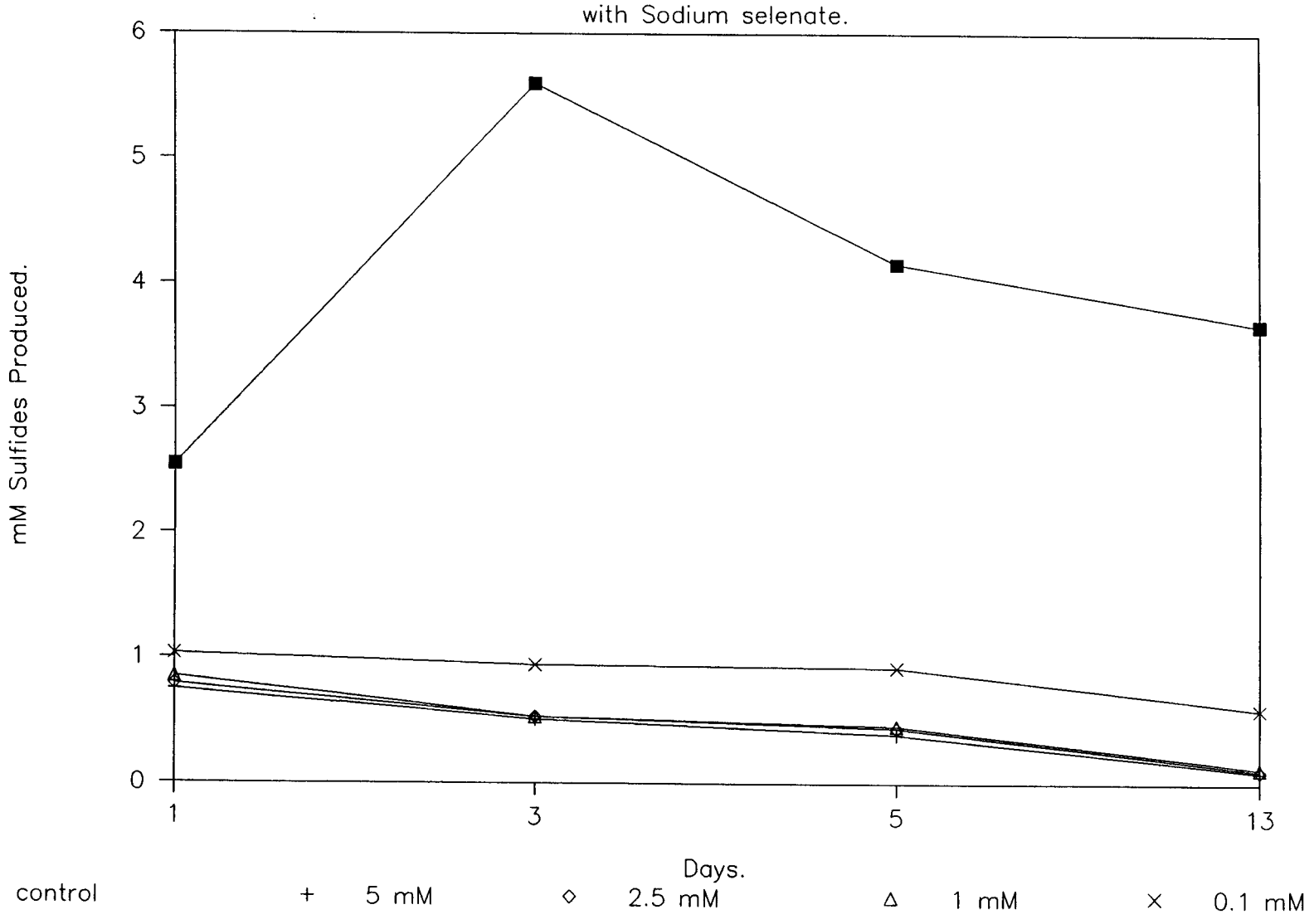
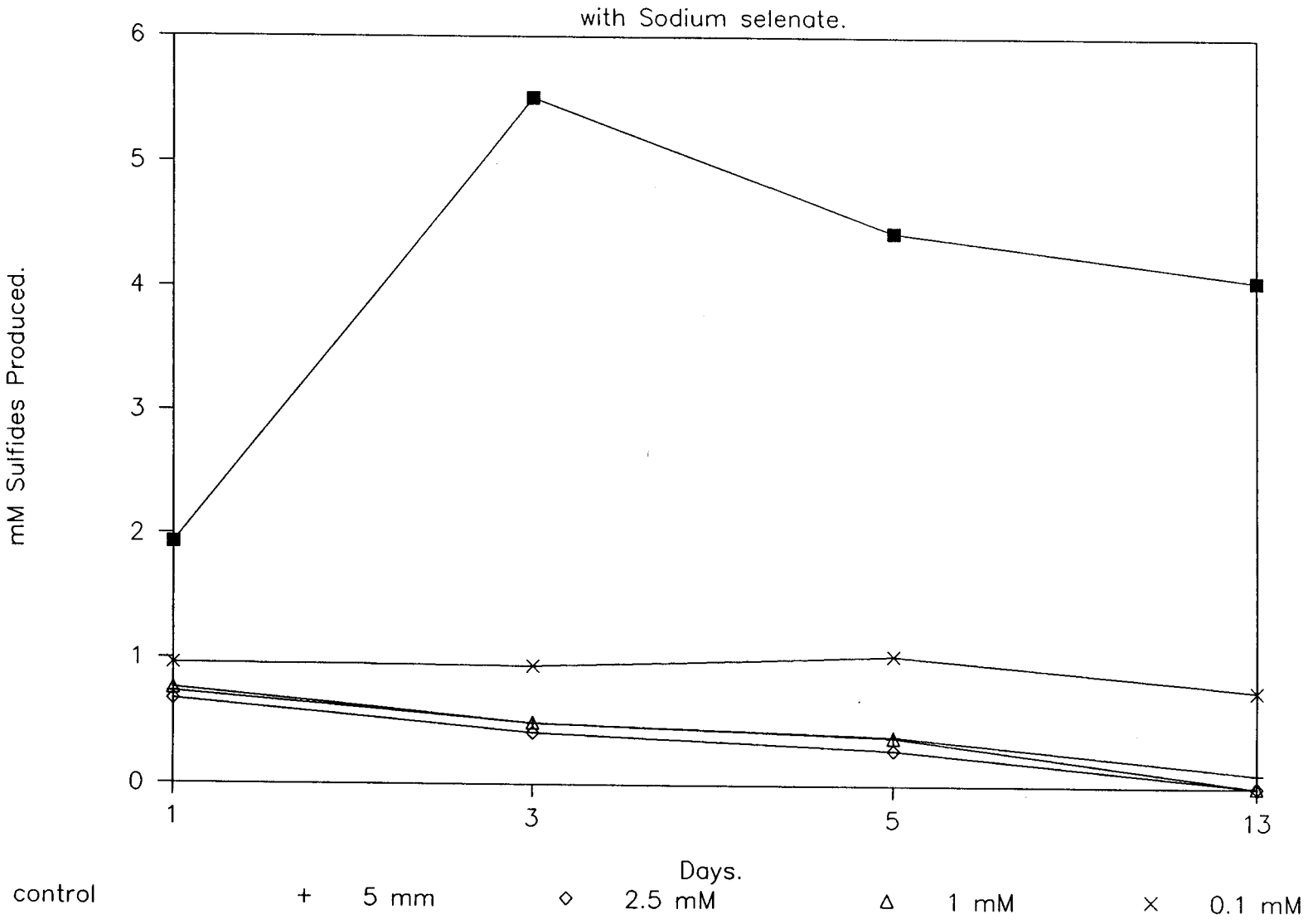


Figure12:Sulfide Production of Colony#2



PART III. ESTIMATION VOLATILIZATION OF REDUCED SULFUR COMPOUNDS

The release of volatile reduced sulfur containing compounds (VSCs) from untreated wastewaters and during wastewater treatment is a known side effect of wastewater collection and treatment. In the past interest was focused primarily on H_2S emissions and its malodorous qualities and high toxicity, which caused health and safety problems for operation and maintenance personnel. It was observed, however, as early as 1900 (Olmstead and Hamlin) that concrete sewers showed signs of rapid corrosion. This phenomenon was most frequently observed in wastewater collection systems in warm climates. Investigators assumed that H_2S, formed by decomposition of organic material or by sulfate reduction in the wastewater, escaped into the sewer atmosphere where it was oxidized to sulfuric acid.

The occurrence of concrete corrosion in wastewater collection systems in colder climates in the late 70s prompted further research. The high sulfur content in detergents and increased protein content of wastewaters might enhance production of volatile sulfur compounds (VSCs) in wastewaters during transport (Sand and Bock, 1984; Milde et al., 1983).

It has been known since the early 70s (Okita, 1969; Thistlethwayte and Goleb, 1972) that H_2S is not the only VSC in the atmosphere or in wastewater. Thistlethwayte found that in addition to H_2S, methylmercaptan (MMC) and dimethylsulfide (DMS) were the predominant sulfur containing species in sewer gas, and that wastewater composition strongly affects the type and concentration of VSCs. It is conceivable that these organic volatile sulfur compounds (OVSCs) have contributed to the total sulfur deposition on the pipe walls and may be responsible for at least part of the H_2SO_4 formation that finally leads to corrosion.

In order to assess the contribution of OVSCs to concrete corrosion in wastewater collection systems two sets of questions must be answered:

1. What are the sources of the VSCs in sewer gases? What are their respective rates of production, mass transfer rates to the gas phase, and mechanisms for deposition on pipe walls? How do environmental conditions affect those rates?

2. Are all of these VSCs easily oxidized in sewer gas or on the pipe walls to form H_2SO_4?

This report will exclusively address the first set of questions, with a strong emphasis on mass transfer; however, it should be indicated that in the process of performing this research several contradictory references addressing the second set of questions were found, and that experimental evidence seems contradictory. Sand (1987) reports that a mixed culture of

thiobacilli that were found on pipe walls were not able to oxidize methylmercaptan, whereas Sivela and Sundmann (1974) found that a thiobacillus strain was able to oxidize MMC, DMS, and dimethyldisulfide (DMDS) in a culture medium. A more definitive answer as to the conditions where OVSCs might be oxidized to H_2SO_4 on pipe walls is essential in order to assess their significance for corrosion.

This report addresses the literature on the occurrence of VCS's in sewage and its source and reviews mass transfer theory and develops the theoretical basis for a numerically based model to calculate stripping of VSCs from wastewater collection systems. It also describes the selected procedures and the specifics of the computer model.

The remainder of this report is divided into four sections. Section 1 addresses the literature on the occurrence of VSCs in sewages and its source. Section 2 reviews mass transfer theory and develops the theoretical basis for a numerically based model to calculate stripping of VSCs from wastewater collection systems. Section 3 describes the selected procedures and Section 4 describes the specifics of the computer model.

OCCURRENCE AND SOURCES OF VSCs

Monitoring Results for VSCs

Various measurements of the concentration of the major VSCs in sewer gas, or in the vicinity of sewers, suggest that the most predominant species are H_2S, MMC, DMS, and DMDS. Some of these compound's physical and chemical properties are listed in Table 1. Our review suggests that there is no simple or known relationship describing their relative abundance. Thistlethwayte and Goleb (1972) found mostly H_2S in sewer gas above mixed municipal sewage at a site in Sydney, Australia. Concentrations were 0.2 to 10 ppmv. OVSCs totaled 10 to 50 ppbv with most of it being MMC with some DMS. The authors concluded, that for this particular site, the OVSCs/H_2S ratio ranged from 1:50 to 1:100. Other gas samples collected from wastewater treatment systems carrying discharges from a large kraft pulp mill, and from other industries including the manufacture of dairy products, showed H_2S and mercaptan levels of hundreds of ppmv. A wastewater collection system near Melbourne, containing highly septic mixed municipal sewage, showed high H_2S levels and an OVSCs/H_2S ratio ranging from 1:5 to 1:10.

Koenig et al., (1980) report only DMS and dimethyltrisulfide in sewer gas. After intensive purging of municipal sewage at 80°C they found a third OVSC, dimethyltetrasulfide. The occurrence of dimethyltrisulfide and dimenthyltetrasulfide as predominant OVSCs has not been reported by any other researchers. Their findings might have been influenced by the purging procedure.

Monitoring data of ambient air for VSCs in the vicinity of several sewage transport and treatment facilities in Finland were provided by Kangas et al. (1986). They found, somewhat contradictory to Thistlethwayte, that around pumping stations, where ambient air is probably most similar to sewer gas, MMC and DMS were as abundant as H_2S. Concentrations for all three species averaged about 50 ppbv. Around screens and aeration basins MMC was in general more prevalent than H_2S. DMDS could not be detected in any of the samples.

Comparison of the two studies and other references suggests that the relative significance of each of the VSCs or OVSCs in sewer gas depends on the specific source of a wastewater and the conditions of its transport. The use of different analytical procedures may have contributed to the variation in the results.

Sources of VSC in Wastewater Treatment Systems

Several sources with specifically high emissions of OVSCs were found in the literature. Okita (1969) reports MMC (5.6 ppbv) and DMS (3.5 ppbv) to be predominant over H_2S (0.66 ppbv) in ambient air in an oil refinery in Japan. Ambient air in a pulp mill contained 57 ppbv of MMC and 2.8 ppbv of DMS, with no H_2S being reported. Pulp mills are an important source of VSCs in air, as well as in wastewater, and are frequently cited in the literature. Sivela and Sundmann (1974) mention that "condensates of sulfate cellulose mills contain high concentrations of H_2S, MMC, DMS and DMDS. These toxic and malodorous waste products are formed from the methoxy groups of lignin in the pulping process."

Oil refinery wastewater can be another source of VSCs in wastewater collection systems. Jenkins et al. (1980) report that various mercaptans were found in the wastewater from refineries and headspace gas. He also reports that MMC is produced by the decomposition of heavier organosulfur compounds, such as hexylmercaptan, during activated sludge treatment.

A very important source of sulfur in wastewater are the sulfur containing amino acids methionine and cysteine. They can occur in high concentrations in wastewater from food processing industries (meat, fish, dairy) and are common in domestic wastewater. Pohl and Bock (1983) report that MMC, DMS, and DMDS were produced by the bacterial degradation of methionine. H_2S was not reported. Cultures of E.coli, Proteus vulgaris, Pseudomonas

aeruginosa, Clostridium tetani have been shown to produce methylmercaptan but not H_2S from methionine (Salsbury and Merricks, 1975). Alternatively from cysteine they can produce H_2S. cysteine (Salsbury and Merricks, 1975). Relative rates of production for each of the VSCs will depend strongly on the presence of the appropriate strains of bacteria which can utilize them under the prevailing oxygen and substrate concentrations.

The prevailing opinion among environmental engineers is that the major production of H_2S in wastewater results because of the use of $SO_4^=$ as an electron acceptor in anoxic or anaerobic environments. Domestic water use generally increases the sulfate content of wastewaters by 15-30 mg/l (Metcalf and Eddy, 1979). Sea water intrusions into groundwater supplies can also result in increased sulfate levels. Industrial discharge of SO_4 from neutralization processes is yet another sulfate source.

Finally, anionic surfactants with a sulfonate group as the hydrophilic component are normally used in laundry detergents, with linear-alkyl-sulfonates (LAS) being the major representatives. No information on typical sulfonate concentrations in sewage and on the fate of the sulfur were found. However, their use in large quantities suggests that they are a major sulfur source in municipal wastewaters.

From the previous discussion it can be concluded that:

1. In addition to H_2S several organic volatile sulfur compounds are frequently found in wastewater and sewage gas, predominantly methylmercaptan, dimethylsulfide, and dimethyldisulfide. Concentrations and relative abundances of these four VSCs in sewer gas and ambient air in the vicinity of sewage transport and treatment facilities varies considerably.

2. Sulfur containing compounds that may serve as precursors for VSCs can enter wastewater collection systems from a variety of sources with the major ones being:

    a. Oil refineries, with special concern for mercaptans,

    b. Pulp mills, with high concentrations of VSCs in the sulfate cellulose mill condensates,

    c. Sulfonates that are used in large quantities in detergents,

    d. Amino acids, coming from domestic sources, as well as food processing industries, and

    e. Sulfates from mineral pickup and industrial sources.

3. Overall production rates of the various VSCs will depend on

a. the presence of one or more suitable precursors, and

b. the environmental conditions with respect to the needs of the VSC producing bacteria.

MASS TRANSFER

The exchange of volatile compounds between the liquid and gas phases is of major importance in wastewater treatment applications. Efficient absorption of oxygen from the atmosphere through instream reaeration or in biological treatment processes is essential in order to satisfy the BOD of wastewaters. For that reason research has historically focussed on the question of how to measure and predict oxygen transfer rates accurately. While improving aeration in activated sludge processes is still of high priority in wastewater engineering, current interest in the interphase exchange processes over the last decade has focussed on stripping of VOCs that are commonly found in municipal and industrial wastewaters.

In this section several theoretical methods to describe interphase mass transfer will be reviewed and discussed in light of the available experimental evidence. These predictions will be made in order to develop the numerical transfer model.

Mass Transfer Models

Various theoretical models have been proposed to describe the volatilization of a chemical from a water body, open to the atmosphere. Comparative summaries of these models and discussion of their merits under varying conditions have been presented by Smith et al. (1980), Dobbins (1964), and Lyman et al. (1982). The theory most commonly used in the literature is the classical Lewis and Whitman two-film mass transfer model, as improved by Liss and Slater (1974).

For the two film model to be applicable a number of assumptions are required. The bulk liquid is assumed to be well mixed, with a thin layer on the surface in which concentration gradient of a solute is established. The bulk gas above the liquid is also assumed to be well mixed, and a thin air layer in contact with the liquid surface displays another concentration gradient. Thus, diffusion and transport in the bulk liquid or gas is not rate-limiting. At the interface between these two layers a concentration discontinuity occurs, and at equilibrium the ratio of concentrations across it is assumed to equal the Henry's law constant. Transfer through both films occurs through molecular diffusion.

Under these assumptions mass transfer of a chemical between water and atmosphere is given by

$$N = \frac{Cg - \frac{HC_l}{RT}}{\frac{1}{k_g} + \frac{H}{RTk_l}} \quad (1)$$

where:

N	=	flux (g/cm^2s)
k_g, k_l	=	gas- and liquid-phase exchange coefficients, respectively (cm/s)
H	=	Henry's law constant ($atm.m^3/mol$)
C_g, C_l	=	bulk concentrations in gas and liquid phase, respectively (g/cm^3)

The exchange coefficient k_i are related to the molecular diffusivities in both films, D_i (cm^2/s) by

$$k_i = D_i/z_i \quad (2)$$

where z_1 = film thickness (cm)

The overall mass transfer coefficients for the gas phase (K_g) and liquid phase (K_L) can be defined as:

$$1/K_G = 1/k_g + H/RTk_l \quad (3)$$

$$1/K_L = 1/k_l + RT/Hk_g \quad (4)$$

Substitution of (3) and (4) in (1) yields:

$$N = K_G(C_g - C_lH/RT) = K_L(C_gRT/H - C_l) \quad (5)$$

Finally, the stripping or absorption rate constant for a given water body can be defined as

$$K_v = K_L/L \quad (6)$$

with the depth L (cm), which equals the interfacial area, A, divided by the liquid volume.

Assuming its background atmospheric level to be negligible the bulk concentration of the compound in the water at any time t than can be written as

$$C = C_0 e^{-K_v t} \tag{7}$$

where

C_0 = initial concentration at t = 0
C = concentration at time t

Stripping of Highly Volatile Compounds

Smith et al. (1981) have shown that for compounds of high volatility ($H > 4 \times 10^{-3}$ atm.m^3/mol) the rate of stripping or absorption is almost completely controlled by liquid film diffusion. In this case (4) reduces to

$$K_L = k_l = D_l/z_l \tag{8}$$

The subscript l can be dropped since only one diffusivity is controlling. The form of this equation is familiar. With different initial conditions, and remaining K_v as $K_L a$, the standard ASCE oxygen transfer equation is obtained.

For two highly volatile compounds the two film theory predicts that the ratio of their stripping or absorption rates will be equal to the ratio of their molecular diffusivities in water:

$$K_v^x/K_v^y = D^x/D^y \tag{9}$$

where x,y denotes compound types.

Based on the assumption that volatilization from and sorption by water bodies show, under otherwise identical conditions, the same rate constants, Tsivoglou (1968) first used equation (9) as basis of the tracer technique for measuring the stream reaeration rate. Although his considerations do not explicitly refer to the two-film theory, they are based on the same essential assumption, i.e. that changes in the degree of turbulent mixing will not affect the ratio of the mass transfer coefficients of the tracer compound to the unknown compound.

The plausibility of a stationary surface film as required in the two-film model was discussed by Dobbins (1962). He reviewed the relevant stripping and absorption theories and their underlying assumptions and compared their prediction with results from volatilization experiments. Unlike the two film model, penetration theories assume a periodic turnover of the total water volume by turbulent mixing. Between two turnovers, transport of the gas is achieved by diffusion. Danckwertz's (1970) modified penetration theory refined this concept. He introduced

a renewal factor r which is defined as the average frequency at which any particular vertical element is mixed. He then assumed that there is no correlation between the time for which any vertical element has been exposed to the gas and its chance of being mixed, the distribution of ages across the area of the interface being a completely random function. Applying this model to a finite depth of liquid, L, it can be shown that

$$K_L = (Dr)^{1/2} \tanh(rL^2/D)^{1/2} \tag{10}$$

While film and penetration theories seem incompatible at first, Dobbins combined them into a model in which a surface layer, whose actual existence for water bodies is indicated by surface phenomena such as surface tension, maintains its existence only in a statistical sense. The film is assumed to be always present, with the liquid being continuously exchanged for liquid from layers beneath the surface at some renewal rate, r. The mathematical description combines some random exchange function with the boundary conditions of a liquid film of finite thickness, L. This model yields for the transfer coefficient

$$K_L = (Dr)^{1/2} \coth(rL^2/D)^{1/2} \tag{11}$$

It basically results in K_L being a function of D^n, with n depending on the mixing conditions. In equation (11), as the value of r approaches zero. the value of K_L approaches D/L, as it should for the steady-state condition. For high renewal rates, K_L becomes equal to $(Dr)^{1/2}$. Thus, the results of the film and modified renewal theories can be viewed as being special cases of equation (11), representing its lower and upper limits with n = 1 and n = 1/2, respectively.

This section has reviewed mass transfer theory with particular emphasis on using it to describe a tracer. Two conclusions are noteworthy.

1. The ratio of transfer coefficients for two compounds will not only depend on the ratio of their diffusivities but requires incorporation of an exponent n, that reflects the stability of the surface layer. Equation (9) therefore must be rewritten as

$$K_v^x/K_v^y = (D^x/D^y)^n \tag{12}$$

   As the surface layer becomes more stable, n approaches 1.

2. Even if the ratio of the K_L is known for two compounds under lab conditions, it can only be expected to be equal to the K_L-ratio under particular field conditions if mixing conditions in field and lab were the same.

This is not always the case. As these conclusions somewhat restrict the applicability of the simple tracing theory, some authors have decided to omit their discussion altogether. Other researchers, such as Roberts et al. (1983) and Smith et al. (1980), have attempted to study the effects of turbulent mixing on the relationship between transfer coefficient and molecular diffusivity experimentally. Their results will be discussed below.

Stripping of Intermediate and Low Volatility Compounds

It must be kept in mind that both models were derived assuming that the considered chemicals were highly volatile, i.e. the volatilization rate is controlled by mass transfer in the liquid phase. Smith et al. (1981) have expanded volatilization models in order to apply them to compounds of low ($H < 10^{-5}$ atm.m^3/mol) and intermediate ($10^{-5} < H < 4 \times 10^{-3}$ atm.m^3/mol) volatility. In both cases mass transfer resistance in the gas phase will become of increasing importance. Examples are chlorinated compounds of low vapor pressure, high molecular weight compounds, such as PCBs and DDT. For volatile compounds the ratio of the unknown stripping or absorption rate (e.g. K_L^x) to the known stripping rate (e.g. K_L^y) is the ratio of their diffusivities as follows:

$$K_L^x/K_L^y = (D_l^x/D_l^y)^n \tag{13}$$

For compounds of low volatility whose transport is completely limited by transport in the gas phase, the ratio of their transfer coefficients is similar and is expressed as

$$K_L^x/K_L^y = (D_g^x/D_g^y)^m \tag{14}$$

Note that the diffusivities are for the gas phase.

As in the case of liquid controlled volatilization, the exponent m characterizes the stability of the gas phase boundary layer and is basically a function of wind velocity. A convenient choice for the tracer y in this case is water, because its evaporation rate is controlled entirely by gas phase mass transfer resistance, since the concentration of water does not change during evaporation. In summary, mass transfer coefficients for compounds whose volatilization is determined by both liquid and gas phase resistance can be related to the liquid and gas phase diffusivities of oxygen and water, respectively, by

$$K_L^C = (1/k_l^O A + RT/Hk_g^W B)^{-1} \tag{15}$$

where the indices C,O, and W refer to the volatile compound of interest C, oxygen, and water, respectively. A and B should be defined as

$$A = (D_l^C/D_l^O)^n \tag{16}$$

$$B = (D_g^C/D_g^O)^m \tag{17}$$

Comparison of Smith's experimental results with this theory will be presented later.

In addition to predicting the exact relationship between transfer rates and molecular diffusivities, the theoretical calculation of D_L itself is the second challenge for volatilization modelers. Lab measurements are either missing, inaccurate or not comparable for the two compounds. Several expressions have been proposed for the relation between D_L and simple molecular properties, such as the molecular weight and the molar volume at the boiling point.

Calculation of Molecular Diffusivities

A variety of methods to predict diffusion coefficients have been tried in the past. Reid and Sherwood (1977) have reviewed the literature on the prediction of diffusion coefficients and have discussed the limitations of these approaches in light of existing experimental evidence. In general, most of the correlations are based on simple physical models containing some adjustment parameters that are determined empirically in order to fit existing data.

The most basic relation between D and some molecular property of the solute is the Stokes-Einstein equation

$$D = RT/6\eta_B r_A \tag{18}$$

where η_B is the viscosity of the solvent and r_A the radius of the spherical solute molecule. This simple inverse proportionality between D and r_A will be valid only for large spherical molecules. Molecules of di- and triatomic gases and most of the low molecular organics found in wastewater do not fulfill this requirement. Unfortunately, Reid and Sherwood failed to present and discuss the theoretical assumptions underlying the various correlations.

Two other correlations that are frequently used in the literature should be mentioned. Liss and Slater (1974) have proposed

$$D^x/D^y = (m^x/m^y)^{1/2} \tag{19}$$

with D being the diffusivities in the phase by which mass transfer is controlled and m being the molecular weight of compounds x and y, respectively. This approximation is, according to Smith et al. (1974) based on Graham's law of effusion which is valid only for molecules effusing in a vacuum where there is no resistance to diffusion. Unfortunately neither he, nor the authors who used it, have rigorously verified or defended the model.

Another commonly used method relates D to the solute molar volume at its normal boiling point, V_b (cm^3mol^{-1}). It is based on the Othmer-Thakar relation

$$D_l = \frac{14x10^{-5}}{\mu_w^{1.1} V_b^{0.6}} \tag{20}$$

where μ_w is the viscosity of water (cP).

Naturally the usefulness of all these models for the theoretical prediction of diffusivities is limited by the simplifying assumptions about the physical processes involved or the properties of the chemicals under consideration. Smith et al. (1980) however, state "that for most compounds the estimates of the ratio of mass-transport coefficients based on molecular diameters or the square root of the molecular weights are within a factor of 2 of the ratio of diffusion coefficients."

This statement is supported by an analysis of experimental results by Hayduk and Laudie (1974). They collected diffusivity data for a wide range of compounds and compared them to several of the commonly used correlations, such as the Wilke-Chang (1955) and the Othmer-Thakar equations. Their findings indicate that for a variety of inorganic gases and organic compounds the constant in the original Othmer-Thakar correlation could slightly be adjusted in order to provide the best fit of the available experimental data. Predicted values in general did not deviate more than just a few percent from the measured ones.

To summarize the results of the above discussed theoretical considerations on mass exchange processes between atmosphere and open water bodies it can be said that:

1. Mass transfer coefficients for volatile compounds are a function of the molecular diffusivity in the liquid phase, corrected by an exponent that reflects the stability of the surface layer. For less volatile compounds resistance to diffusion through the gas phase will become important and atmospheric turbulence will act as a correcting exponent on the gas diffusivity of the compound as well.

2. Several correlations which attempt to improve the simple Stokes-Einstein model exist, and relate molecular diffusivities to compound-specific parameters.

From these theoretical results it can be concluded that it should be acceptable.

1. To predict mass transfer of a specific compound using a tracer compound as long as the (mixing) conditions of the required lab experiments and in the field are identical or at least known.

2. These predictions must not necessarily be based on lab experiments but the knowledge of elementary molecular properties of the two compounds.

The next section reviews the relevant literature and summary examples which verify or refine the previously discussed theories.

Experimental Verification

The previously discussed considerations raise basically two questions that have been addressed by researchers:

1. Can the stripping rate for one compound be predicted for a wide range of temperature and mixing conditions, as suggested in equations (15-17)?

2. How well do lab results for diffusivities compare with values predicted on the base of molecular properties?

Unfortunately, several researchers have not attempted to answer these questions separately, but have instead compared ratios of volatilization rates for two compounds directly to the ratios of e.g. their molecular weights. This is likely to have been caused by experimental problems in determining diffusivities somewhat accurately. As a result, disagreement of theory and experiment in this case can be caused by inadequacies in each of the steps and does not allow the assumptions and models to be verified.

In the following review the results of the most relevant studies included in the bibliography are briefly discussed. Those references which are not discussed in detail either provide additional experimental support, or address specific applications of mass transfer processes in water and wastewater treatment which are only marginally related to this work.

Tsivoglou (1968) used radioactive Krypton-85 as a tracer for oxygen. Calculation of the reaeration rate for various subreaches of a river was based on former lab results which indicated that $K_L(Kr\text{-}85)/K_L(0_2)$ was independent of the degree of turbulence and temperature. Tsivoglou does not report in this study the experimental conditions of those tests but merely indicates a low variation of the obtained ratios $(K_L(Kr)/K_L(0_2)) = 0.83$ with a standard deviation of 0.04. Reaeration capacity of a particular reach is then estimated from the measured volatilization rates of Kr-85 and compared to the predictions of two models for mass transfer under environmental conditions (O'Connor and Dobbins, 1958). Reproducibility of the obtained K_L for each of the examined subreaches obviously was excellent. More recent work (Boyle et al, in press) comparing the radiotracer method and the best available oxygen transfer methods has reduced the variability to ± 0.02. This indicates that the assumptions used to develop the tracer theory are valid and that mixing/temperature effects are less than ± 0.02 ($\pm 2.5\%$).

Dobbins (1962) measured absorption rates for H_2, He, O_2, N_2, and propane in water at 20°C. His primary goal was to investigate the impact of variations in mixing conditions on the ratio of K_L for two compounds, in order to verify equation (11). Some of his results are shown in Figure 1. They suggest that the ratio of the volatilization rates of He and N_2 decreases with

increased mixing, which is likely to reduce the stability of the surface layer. Dobbins claims that equation (11) best fits the experimental data. Fitting allowed him to determine his theory's parameters, i.e. the renewal rate r and the film thickness L, and finally to estimate the exponent n as a function of the renewal rate, as shown in Figure 2. The case of n = 1, i.e. the two-film-theory could not be verified for fundamental reasons: it would require rpm = 0, as can be seen in Figure 1. In this case, however, the assumption of complete mixing of the bulk of the water, would be violated. This suggests that lab results will always describe a case with $n < 1$.

Two comments should be made about Dobbins results:

1. The ones he presented are based only on the He/N_2-pair. In this case agreement with his theory seems to be good. It is not clear, however, if this result can be extended to other compounds.

2. The results show that there is no necessary relationship between the value of K_L and the energy input to the system. Instead, the position of the mixer relative to the surface can vary K_L considerably, with the energy input being constant. The energy input again is a function of mixer speed and stroke as well.

Rathbun (1978) tried to develop a nonradioactive tracer for the prediction of reaeration rates. He conducted a series of lab experiments, using ethylene and propane as tracers and compared their volatilization rates with the absorption rate for oxygen under various experimental conditions. His findings indicate, somewhat contradictory to Dobbins' results, that the ratio of the mass transfer coefficients is significantly affected by mixer speed, nor do changes in temperature or the presence of contaminants (phenol, detergent, oil film) etc. change the ratio. However, in generalizing these results to pairs of any two compounds, one has to be careful. Figures 3-4 clearly show that there is considerable scattering of the K_L-ratios as a function of $K_L(O_2)$. Attempting to fit the data using Dobbins' correlation, which Rathbun did not reference, might have provided a better correlation.

Even more important is the fact that the K_L for all three compounds are similar, i.e. their ratios are close to unity. This means that even the effect of an exponent n = 1/2, representing high turnover rates for the surface layer in Dobbins model, will hardly be detectable, considering the scattering of data. There might not even be a contradiction between Tsivoglou's/Rathbun's and Dobbins' results. They simply used tracers with different degrees of similarity to the "partner." This suggests the following conclusion:

> Volatile compounds with similar resistances in the liquid phase will experience a much smaller impact on the ratio of the K_L than those with molecular diffusivities that are different by a factor of two or so. If one wants to eliminate nonquantifiable effects of

turbulence on the K_L-ratio, a wise choice for a tracer therefore is a compound with a lab volatilization rate as close as possible to the compound for which a field volatilization rate has to be determined.

Smith et al. (1980) comprehensively discussed volatilization of high volatility compounds. They measured K_v^C/K_v^O-ratios for several VOCs, benzene and some of the chlorinated aliphatics most common in drinking and wastewater. They found that for a given compound the ratio does not vary significantly with the oxygen reaeration rate, which is used to parameterize mixing conditions. Temperature, salinity and surfactant concentration did not appear to have an effect. The results are shown in Figures 5 and 6. They seem at first to prove the validity of the two-film theory. Smith is, however, aware of Dobbins' work and assumes that film renewal might be important even at the lowest stirring rate. It might have been worthwhile in this case to check if a nonlinear fit of the data yielded a "better" result, i.e. a decrease of n with increasing turbulence. This is supported by the findings, shown in Table 1 and Figure 7. If one calculates diffusivities for the VOCs based on the Othmer-Thakar relation (20) and compares them to the measured K_v-ratios, a log-log fit (Figure 7) suggests that

$$K_v^C/K_v^O = (D^c/D^O)^{0.61} = (V_b^O/V_b^c)^{0.37} \tag{21}$$

Although this correction incorporates two models (volatilization and molecular diffusion) and does independent verification, it suggests that a combination of Dobbins and Othmer-Thakar theories may be adequate for the given compounds. This interpretation is further supported by the above reference to the excellent fit of experimental data with Othmer-Thakar prediction. Applying these results to Smith concludes that for nonturbulent natural bodies of water, such as lakes and ponds, that equation 22 adequately considers the turbulence under lab conditions (1.7 = 1/0.6).

$$(K_v^C/K_v^O)_{env} = (K_v^C/K_v^O)_{lab}^{1.6} = (D^C/D^O)_{est} \tag{22}$$

For rivers or other turbulent water bodies equation 23 may give the best results.

$$(K_v^C/K_v^O)_{env} = (K_v^C/K_v^O)_{lab} = (D^C/D^O)_{est}^{0.6} \tag{23}$$

Finally, comparison of the data in Table 1 suggests that in general diffusivities based on molar volume fit the measured volatilization rates better than those obtained from molecular weights.

Smith et al. (1981) also attempted to verify their model on the volatilization of intermediate and low volatility chemicals from water that resulted in equations (15-17). Although data for naphthalene and anthracene were reported to fit the model well, a larger data base would be needed to confirm their assumptions.

Experimental results by Roberts and Dandliker (1983), support the major results presented so far. They were interested in the removal of VOCs from drinking water and studied volatilization rates as a function of power input. In addition to determining that stripping is a function of power input, they concluded the following:

1. K_L^x/K_L^O-ratios for the studied low molecular chlorinated VOCs are very similar. They do not vary significantly with turbulence, range around 0.6 and compare well with Smith's (1980) results.

2. By fitting calculated diffusivities using the Wilke-Chang correlation and comparing their ratios to the K_L-ratios measured in the lab, with the exception of chloroform, they found an overall "best-fit" diffusivity exponent n of approximately 0.62. This is in good agreement with Smith's results and indicates that surface renewal was important over the whole range of mixing conditions. This is intuitively supported by their experimental equipment which was comprised of a turbine positioned at the water surface and a paddle positioned at the bottom of the vessel. Even at the lowest stirring rate the assumption of a steady-state film may be unrealistic.

As with Smith's data the question remains: why doesn't n decrease with power input? Figure 8 suggests the relation, if it exists, could be obscured by the scatter.

Summary

The purpose of this section was to provide a review of existing mass transfer models in order to determine the most suitable model for describing stripping of VSCs as a function of some other compound, such as oxygen or krypton. The following conclusions are made:

1. The most appropriate model to describe mass transfer under lab conditions appears to be Dobbins' correlation.

2. Molecular diffusivities can be predicted quite accurately by several correlations. The most appropriate ones for a wide range of compounds appear to be Othmer-Thakar and the Wilke-Chang relations, requiring the knowledge of the molar volume at the normal boiling point and/or the molecular weight of the solvent. The predictions should be accurate to within ±10-15%.

3. Stripping or absorption rates for a given compound under specific environmental conditions can be estimated using tracers. Estimates can be based on lab experiments of the K_L-ratio or the ratio of the measured or calculated diffusivities. This method can probably be applied, as well, to compounds of intermediate and low volatility compounds, but requires the use of two tracers. In general the use of tracers requires that they are carefully chosen, to avoid spurious results, such as adsorption to solids or biodegradation.

4. To minimize the influence of different mixing conditions on tracer accuracy, a tracer with a D_L similar to that of the compound of interest should be selected. Multiple tracers, could be used to characterize mixing conditions of a homogeneous subreach and may assist with mass transfer predictions.

5. This literature review provides a useful data base for many of the compounds that may be found in wastewater collection systems. In particular the emission of potentially hazardous compounds, such as TCE and PCE, during transport and treatment has recently attracted interest from state and local agencies that regulate air quality. Estimates for total emissions of these compounds from the collection systems usually have not taken advantage of predictive models such as these being discussed herein. More accurate estimates might be required in the near future. Data and modelling tools provided by the literature reviewed in this report may be helpful in that respect.

CALCULATING VSC TRANSFER COEFFICIENTS

In a previous section various models that attempt to predict volatilization rates as a function of a compound's physical properties and parameters in the presence of varying conditions were reviewed. In this section these models will be combined in order to predict mass transfer rates for a given VSC in wastewater collection systems. Since very few mass transfer measurements have been actually performed in collection systems, it is assumed that the model must require only the following information: compound type and properties (e.g. as shown in Table 1), wastewater flow rate, slope, geometry, and pipe material (e.g. friction factor).

The approach follows the previous thesis of using a tracer. Therefore the mass transfer coefficient for oxygen in wastewater flowing in a sewer will be estimated using previously developed correlations.

It was stated previously that the O'Connor-Dobbins equation appears to best predict the reaeration coefficient, k_2, for a given condition in a river or in flowing water. Equations (24) and (25) show the relationships in English and SI units, respectively.

$$k_2^{20} = 5.91\ V^{0.5}/H^{1.5} \tag{24}$$

$$k_2^{20} = 1.77\ V^{0.5}/H^{1.5} \tag{25}$$

where k_2^{20} is the reaeration coefficient at 20° in $days^{-1}$, V is the mean velocity in feet/s or m/s, respectively, and H is the average depth in feet or m.

The Manning equation relates the mean velocity in an open channel to its slope, S, its hydraulic radius R, (cross-sectional area divided by wetted perimeter), and a roughness coefficient, n, which depends on the channel material. It is applicable only when the channel slope is less than about 0.1 with H and n being constant, which are reasonable assumptions for individual reaches in a wastewater collection system. Equations 26 and 27 show the Manning equation for English and SI units, respectively.

$$V = \frac{1.49\, R^{0.67}\, S^{0.5}}{n} \tag{26}$$

$$V = \frac{1.0\, R^{0.67}\, S^{0.5}}{n} \tag{27}$$

Combining these two equations for English and SI units yields

$$k_s^{20} = \frac{7.21\, R^{0.33}\, S^{0.25}}{n^{0.5}\, H^{1.5}} \tag{28}$$

$$k_s^{20} = \frac{1.77\, R^{0.33}\, S^{0.25}}{n^{0.5}\, H^{1.5}} \tag{29}$$

R and H are functions of the depth of water in the pipe, h, and its geometry. In the case of a pipe with circular cross section it is therefore possible and convenient to express the ratios $R^{1/3}/H^{3/2}$ in terms of h and the pipe's inner radius, r. Incorporating this information yields

$$k_2^{20} = \frac{20.41\, f(x)\, S^{0.25}}{n^{0.5}\, r^{1.17}} \tag{30}$$

where

$$f(x) = \frac{(1-x^2)^{0.75}}{(\frac{\pi}{180}\,\mathrm{Arccos}(x) - x\,(1-x^2)^{0.5})^{1.17}\,(\frac{2\pi}{180}\,\mathrm{Arccos}(x))^{0.33}} \tag{31}$$

where $x = (r-h)/r$

in which

r = sewer pipe internal radius
h = height of flowing wastewater

In a previous section it was shown that a tracer compound can be used to estimate volatilization rates for other compounds. from the same sewer portion. It was shown that for a compound i

$$\frac{k_{2s}}{k_2} = \left[\frac{D_i}{D_{02}}\right]^n \tag{32}$$

where the exponent n ($0.5 < n < 1$) is a function of turbulence in the flowing wastewater.

Strictly speaking this relationship is applicable only for highly volatile compounds, i.e. those with $H > 10^{-3}$ atm.mol m^2 for which mass transfer is almost completely limited by diffusion in the water. Literature values of Henry's law constant were available for H_2S and dimethylsulfide only; however, the high vapor pressures of methylmercaptan and dimethyldisulfide will, together with their lower solubility in water (as compared to H_2S), should result in similar Henry's law constants. Therefore the relationship should be valid for all the VSCs of importance.

Literature estimates of molecular diffusivities for the VSCs were not available, and a reliable and convenient estimation method has to be used. This process requires an accurate relationship between D and some molecular property, such as the molecular volume at the boiling point, V_b. As discussed previously, the Wilke-Chang and Othmer-Thakar correlations have been successfully used in predicting diffusivities over a wide range of compounds. They will both be used to calculate D for the four VSCs, along with their "updated" versions reported by Hayduk and Laudie (1974), as follows:

$$D = \frac{14 \times 10^{-5}}{\mu^{1.1} V_b^{0.6}} \tag{33}$$

$$D = \frac{13.26 \times 10^{-5}}{\mu^{1.4} V_b^{0.589}} \tag{34}$$

The two Othmer-Thakar relations are shown in equations 34 and 35.

$$D = \frac{7.4 \times 10^{-8} (2.6M_2)^{0.5} T}{\mu V_b^{0.6}} \tag{35}$$

$$D = \frac{7.4 \times 10^{-8} (2.26M_2)^{0.5} T}{\mu V_b^{0.6}} \tag{36}$$

V_b is the molar volume at the boiling point in cm^3, μ is the viscosity of water in cp, T is temperature in degree K, and M_2 is the molecular weight of the solvent, i.e. water, in grams. The molecular diffusivity of the volatile compound in water, D, is in cm^2/s.

Both relations require knowledge of the molar volume at the boiling point. V_b is known experimentally for H_2S and must be estimated for other compounds. The methods of LeBas and Schroeder, as described by Reid (1977) both were used. Agreement among the methods was good in general, as can be seen from Table 2. The average of the two values was then used to calculate D from the "original" and the "corrected" versions of the Wilke-Chang and the Othmer-Thakar relations.

Based on the calculated diffusivities, the volatilization rates for the four VSCs can be estimated, given the diffusivity for oxygen in water at the same temperature. The diffusivity of oxygen was calculated using a molar volume of $V_b = 27.9$ cm^3/mol, and the mean of the updated Wilke-Chang and the two versions of Othmer-Thakar correlations to obtain the value of 1.85 x 10^{-5} cm^2/s at 20°C.

As D_{ox}/D_i deviates significantly from unit for the heavier VSCs, the appropriate choice of the exponent n in equation (32) becomes more important. Smith (1980) and Roberts (1983) both found a value of 0.62 in lab experiments over a wide range of turbulence (n = 0.62. Unfortunately the symbol "n" is used throughout the literature for this coefficient. This "n" should be be confused with Mannings "n"). These results were obtained from tests with several VOCs. Their molecular diffusivities in water covered approximately the same range as the organic VSCs studied herein. Comparison of the specific surfaces in the lab experiments and those used to calculate mass transfer in wastewater collection systems shows that the corresponding K_2 in sewers lie well within the range of experimental K_La, suggesting the applicability of the lab results to the sewer conditions.

Combining the previous equations the mass transfer rates for VSCs can be written as

$$K_L a_s^{20} = \frac{5.01\, f(x)\, S^{0.25}}{n^{0.5}\, r^{1.17}} \left[\frac{D_i}{D_{02}}\right]^{0.62} \tag{37}$$

in metric units and

$$K_L a_s^{20} = \frac{20.4\, f(x)\, S^{0.25}}{n^{0.5}\, r^{1.17}} \left[\frac{D_i}{D_{02}}\right]^{0.62} \tag{38}$$

if r given in feet.

Table 3 shows mass transfer rates for the four VSCs under investigation in a typical trunk sewer at 20°C as a function of water depth. Rates at temperatures other than 20°C can be estimated by calculating diffusivities as a function of temperature, which simplifies to the following equation:

$$K_L a_s^{T} = K_L a_s^{20} \left[\frac{D_i^T}{D_{02}^T}\right]^{0.62} \tag{39}$$

The prediction of the mass transfer rate in the previously developed equations is based on a sequence of models and estimates, each contributing to the overall uncertainty in the final result. In addition to the experimental errors in easily measurable quantities, such as T, r, and h, other sources for error or bias exist, and are summarized as follows:

1. The calculation of the molecular diffusivities, incorporates uncertainties in the estimate of V_b, as well as in the relation used to predict the diffusivity. The average error in V_b caused by the use of the methods of Schroeder and LeBas is reported as 4% (Reid, 1977). The overall errors of various methods for estimating D were calculated by Hayduk and Laudie. They report for the three methods used in this section, i.e. the two versions of Othmer-Thakar and the modified form of Wilke-Chang, average absolute errors of about 6% and maximum errors of 25%, when compared to the experimental observation for 89 compounds. These error estimates remained the same when V_b was estimated or actually measured. The relative uncertainty in D_{02} accordingly is estimated at 6% as well.

2. Contradictory statements were found about the accuracy of the exponent n. Roberts (1983) reports a 95% confidence interval of $0.61 < n < 0.63$, whereas Smith (1980) found 0.54 and 0.68 as lower and upper 95% confidence limits. This difference is likely to have been caused by varying experimental accuracy rather than reflecting a variation of n with turbulence, as both experiments covered about the same range of K_L. However, the close agreement of their values for n and the fact that other researchers have reported n-values of about 0.6, suggests that the value of n has a 95% confidence interval of 0.58 - 0.66 for conditions prevailing in wastewater collection systems. An exact assessment of the accuracy of n is not as crucial since the overall error in $(D_1/D_{ox})^n$ is dominated by the accuracy of the diffusivities. A good estimate for the average error made in calculating this expression would be, according to the above, $\pm$ 10%.

3. The largest uncertainty in the value of K_La is likely to be introduced by the use of the O'Connor-Dobbins equation. Brown (1974) reports that deviations of predicted reaeration rates from field observations obtained by Tsivoglou for various river reaches were unbiased and within a factor of 2. The accuracy of the model for sewers is likely to be even better, as is based upon the assumption of homogeneous cross section and velocity which seems more realistic for a concrete pipe than for a river. Mass transfer estimates in wastewater collection systems are restricted by the presence of substances that form films on the water surface. These considerations and the results presented by Rathbun (1974), showing mass transfer decreasing with addition of contaminants, suggest that applying the O'Connor-Dobbins equation to calculate absolute mass transfer rates for VSCs might lead to a systematic overestimation of volatilization rates in sewers. Its magnitude is likely to depend on the composition of the wastewater. Strong turbulence on the other hand, will tend to restrict the relative impact of contaminants on volatilization.

Whereas the errors discussed in 1. and 2. are more of a statistical nature and can be estimated, further experimental research will be required to quantify the bias introduced by the idealizations underlying the O'Connors-Dobbins model.

Summary

Results of the calculations presented in this section suggest the following conclusions:

1. Typical volatilization rates for the VSCs under study in sewers will be on the order of 4-10/day. The two most predominant compounds, i.e. H_2S and methylmercaptan show the highest mass transfer rates.

2. Higher temperatures and pipe flowing volume of less than 30% of capacity will tend to increase transfer rates strongly.

3. With the other parameters being constant, effects of changes in slope and roughness are not as pronounced as they have a less than linear impact on the transfer rates.

DESCRIPTION OF THE COMPUTER MODEL

As described previously, the contribution of any VSCs to concrete corrosion in sewers depends basically on five processes:

1. The rate of VSC production from precursors by a (bio-)chemical process

2. Losses from the wastewater by (bio-)chemical and physical processes, such as the formation of insoluable sulfide, sorption, and sedimentation

3. Mass transfer rate from wastewater to sewer gas

4. Removal from the headspace by processes such as condensation, and

5. Oxidation by microorganisms on the pipe walls.

The rate at which a particular VSC is produced in sewage will, as shown later, be crucial for its concentration and mass transfer.

To estimate the rate of stripping of VSCs a computer program was written that integrates the previously developed concepts. Since no information is yet available on the rate of VSC production, it was assumed to be a zero-order process described by a single rate constant, k_o. The following additional assumptions are required:

1. No losses of VSCs through sorption and biodegradation are assumed.

2. Environmental and flow conditions in the sewer are constant, in particular temperature, flow rate, the pipe's radius and slope, the sewage's velocity, and the resulting mass transfer rate.

3. Wastewater flow is turbulent which requires the use of the nonlinear relationship between $K_L a_s$ and the compounds diffusivity, as described by equation (37).

4. The removal of the VSCs from the sewer atmosphere is fast enough in order not to significantly reduce the driving force. This assumption is crucial and a more sophisticated model would require modeling the concentration in the pipe headspace as well, or some assumption about sewer gas concentration. However, the studies by Kangas and Kuster (1986) suggest the validity of the assumption.

Based on the above assumptions and the methods to estimate molecular diffusivities, and mass transfer rates of the VSCs described in the previous section, the program needs to predict the concentration of a VSCs in wastewater and their accumulated losses to the sewer gas as a function of time and distance from an origin. Fulfilling this task requires five steps. Each stage briefly described as follows:

Step 1: Calculation of flow velocity and water depth. The volatilization rates are expressed as functions of the flow velocity and the water depth in a section of sewer pipe. It is necessary to calculate these from the flow determining quantities, i.e. the flow rate Q, and the characteristics of the (circular) sewer, r (radius), S (slope), and n (roughness). Using nomenclature and results from the previous section, the flow rate is given by

$$Q = \frac{FR^{0.67}\, S^{0.5}}{n} \tag{40}$$

By substituting

$$x = (r-h)/r \tag{41}$$

the cross sectional flow area, F, and the wetted perimeter, w_p, can be expressed as a function of the pipe's radius and the relative depth of water, x, as follows

$$F = r^2\,(\mathrm{Arccos}(x) - x(1-x^2)^{0.5}) \tag{42}$$

$$wp = 2r\,\mathrm{Arccos}(x) \tag{43}$$

with the results of Arccos given in radians. Inserting equations (42) and (43) into (40) and rearranging yields

$$\frac{1.59\, Qn}{\tau^{2.67}\, S^{0.6}} = \frac{(\mathrm{Arccos}(x)-x(1-x^2)^{0.5})^{1.67}}{\mathrm{Arccos}(x))^{0.67}} \tag{41}$$

This equation probably does not have a convenient analytical solution for x. Instead, a simple numerical method was used in the program. The range of possible arguments x is limited by $-1 < x < 1$, with $x = -1$ corresponding to $h = 2r$ and $x = 1$ to $h = 0$. The right hand side of (41) is shown in Figure 4.2. For $x > -0.84$ it yields a monotonously declining function of relatively low curvature. Therefore its values were calculated for x ranging from -1 to 1 in steps of 0.02. After evaluating the left hand side of (41), the corresponding x, i.e. the relative water depth for a given set of Q, S, n and r can be calculated by interpolation. Using x, one can then calculate the flow cross section F, the wetted perimeter w_p, the water depth h, the hydraulic radius R, and finally, using the Manning equation, the flow velocity, v, with

$$V = \frac{R^{0.67} S^{0.5}}{n} \tag{42}$$

Step 2: Combining the O'Connor-Dobbins equation (24) and the Manning equation (42) yields the reaeration rate, K_2, of a homogeneous sewer reach as a function of n, S, and x, as given in equations (31) to (32).

Step 3: The molecular diffusivity of the respective VSCs in water is calculated using the methods of Schroeder and LeBas to calculate the molecular volume at the boiling point and the updated versions of Wilke-Chang and Othmer-Thakar to estimate the molecular diffusivities. In both cases the means of the values obtained from the two respective methods were used. The overall process of estimating diffusivities requires as input parameters the chemical structure of the compound and the viscosity of water only.

Step 4: Using the concept of tracing under turbulent conditions, the mass transfer rate, $K_L a_s$ for the VSCs can be estimated based on the knowledge of K_2, and the molecular diffusivities of oxygen and the VSC for a given temperature, respectively. The corresponding relations are given in equations (34) to (36).

Step 5: Using the simplifying assumptions described above, the concentrations of a particular VSC in sewage is given by

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial z} + k_o - \alpha K_L a_s C \tag{43}$$

where C is the concentration, k_o is its zero-order rate of formation, α is an empirical parameter that accounts for additional resistance to mass transfer, z = distance, and $K_L a_s$ is the loss rate of the VSCs to the (sewer) atmosphere. Assuming steady-state and that at $z = 0$ the concentration is zero, the solution for this differential equation is

$$C = C_o\,(1-e^{-\alpha K_L a_s z}) \tag{44}$$

where the equilibrium concentration C_o is given by

$$C_o = k_o/K_L a_s \tag{45}$$

The time of travel, tt, can be represented as z/v. The accumulated production of a VSC at a specific point in time, t, or space, z, is given by

$$P = k_o tt = k_o z/v \tag{46}$$

The accumulated losses of the compound to the sewer atmosphere, L, can then be expressed by

$$L = P-C \tag{47}$$

These equations show that both concentration of a particular VSC in wastewater and its accumulated losses are a linear function of its rate of production, while the mass transfer rate determines the equilibrium concentration, and the distance over which a steady value is created.

Summary

1. Mass transfer rates for the three VSCs likely to be most predominant in collection systems, i.e. H_2S, methylmercaptan, and dimethylsulfide are relatively similar. The volatilization rate for H_2S will be about 35% higher than for dimethylsulfide.

2. Volatilization rates increase significantly with decreasing pipe diameter, due to the large surface/volume ratio.

3. Typical effective volatilization rates, $\alpha K_L a_s$, for the four VSCs of concern will be on the order of 4-10/day.

4. Wastewater treatment systems operating at only a small fraction of their capacity have high rates of volatilization due to the high surface area to volume ratio.

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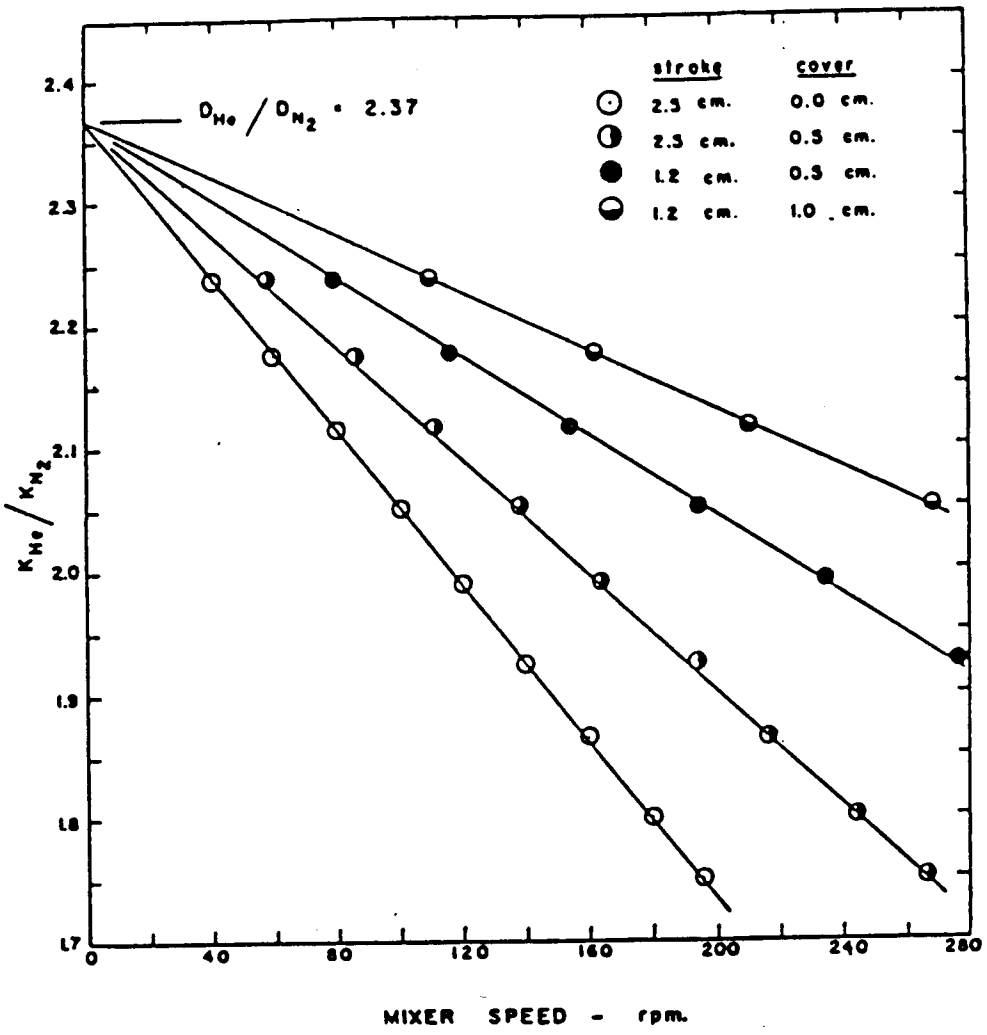


Figure 1. Ratio of K_L values as a function of mixer speed (after Dobbins, 1964).

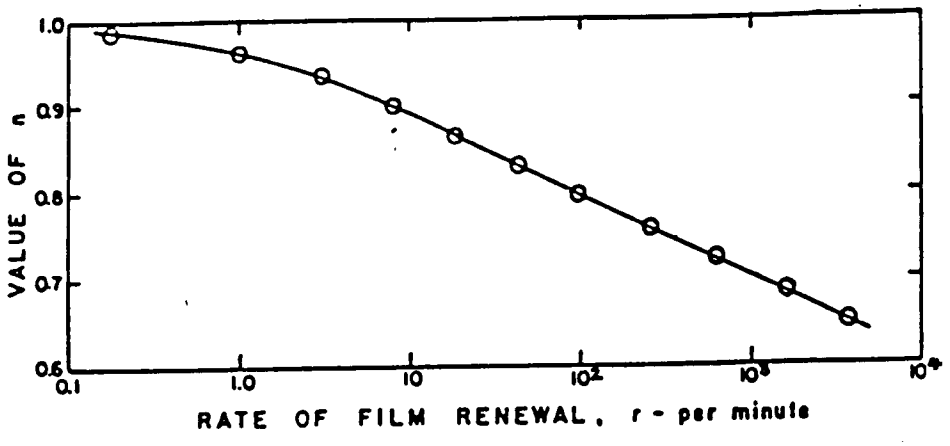


Figure 2. Relation between n and r (after Dobbins, 1964).

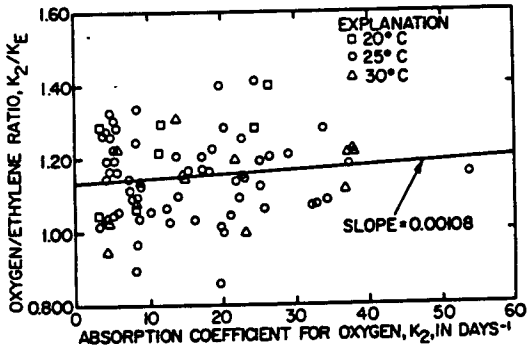


Figure 3. Ratio of oxygen to ethylene K_2 as a function of oxygen transfer (after Rathbun, 1978).

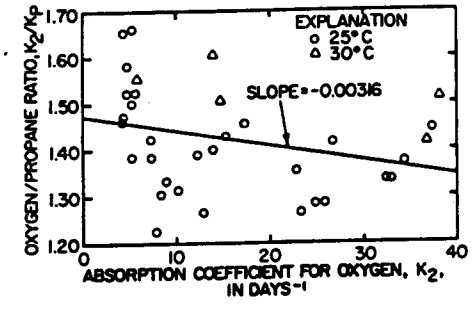


Figure 4. Ratio of oxygen to propane K_2 as a function of oxygen transfer (after Rathbun, 1978).

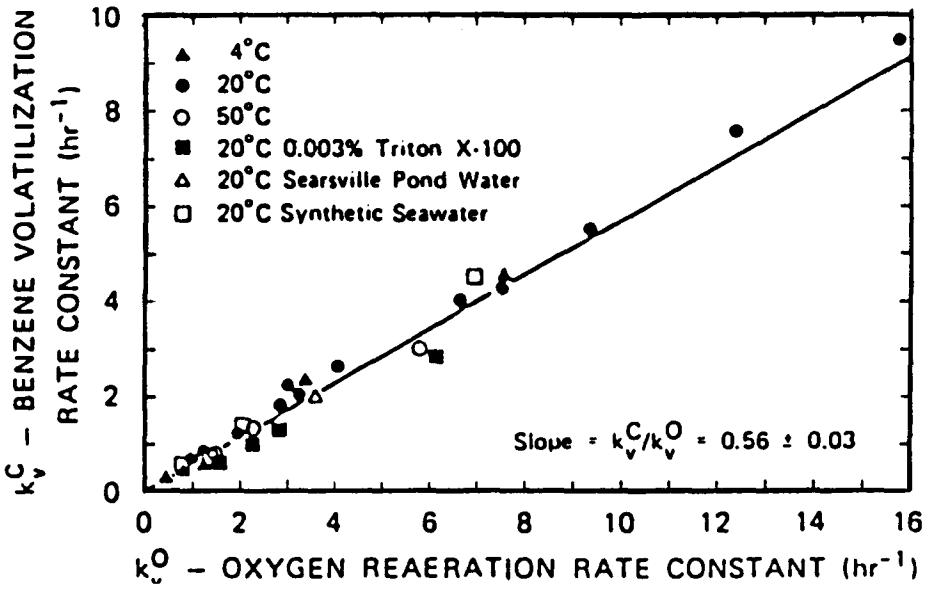


Figure 5. Correlation of benzene and oxygen reaeration rates (after Smith, 1980).

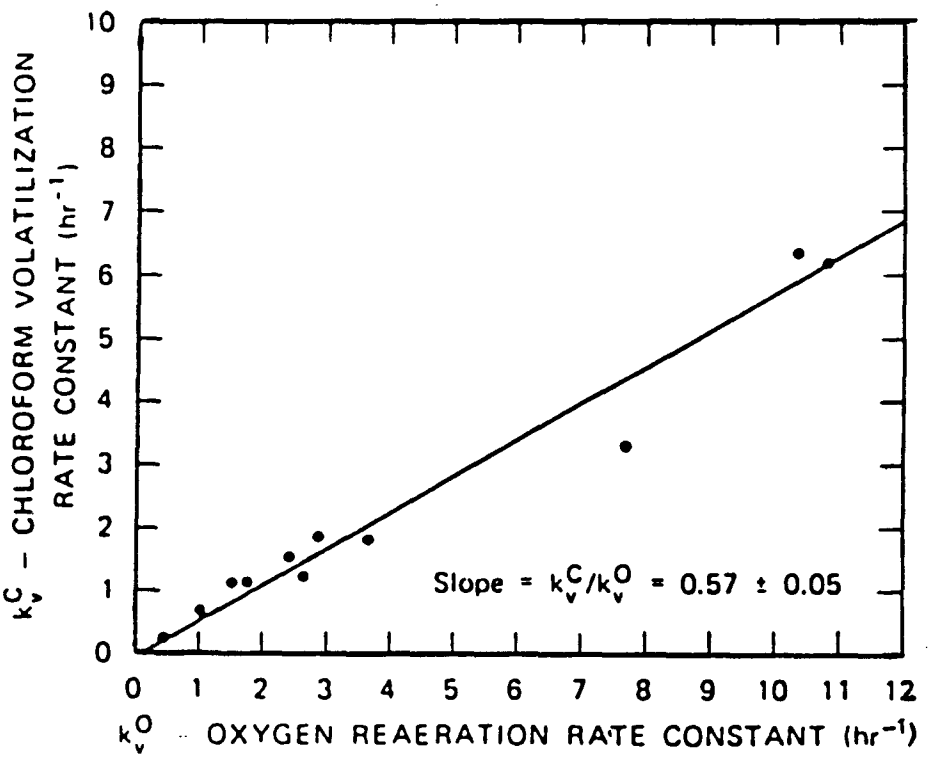


Figure 6. Correlation of chloroform and oxygen reaeration rates (after Smith, 1980).

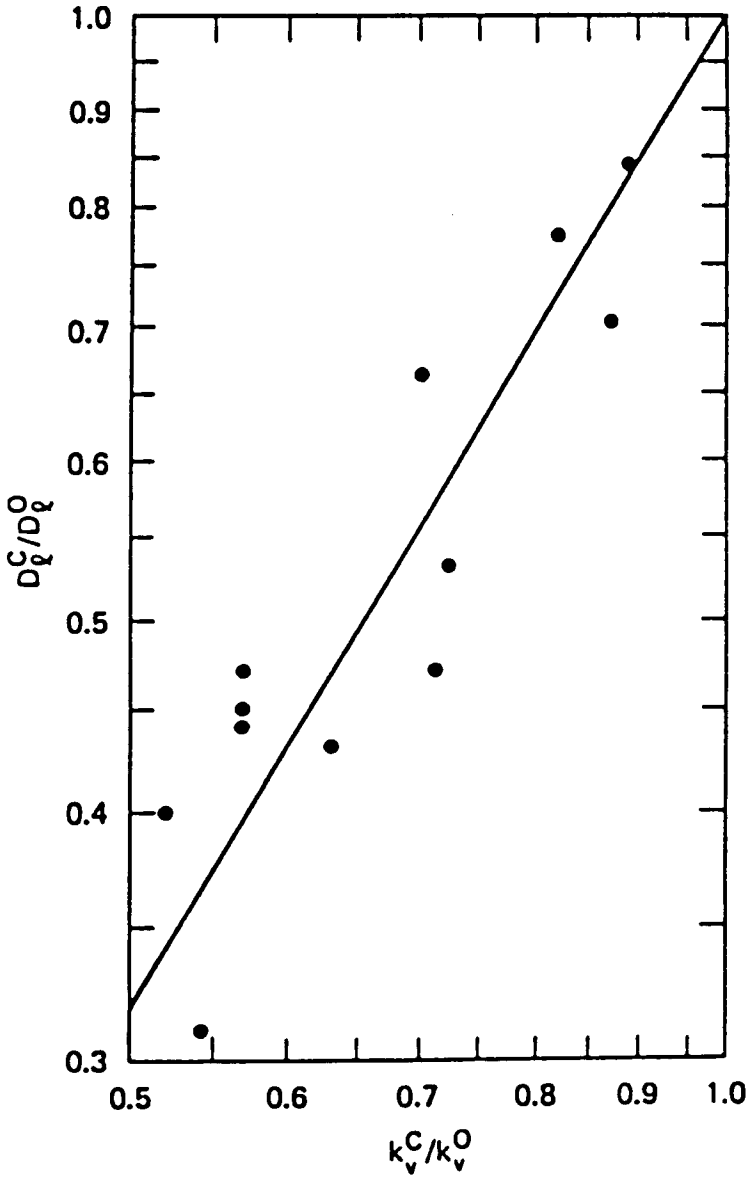


Figure 7. Correlation of Diffusivities and mass transfer coefficients (after Smith, 1980).

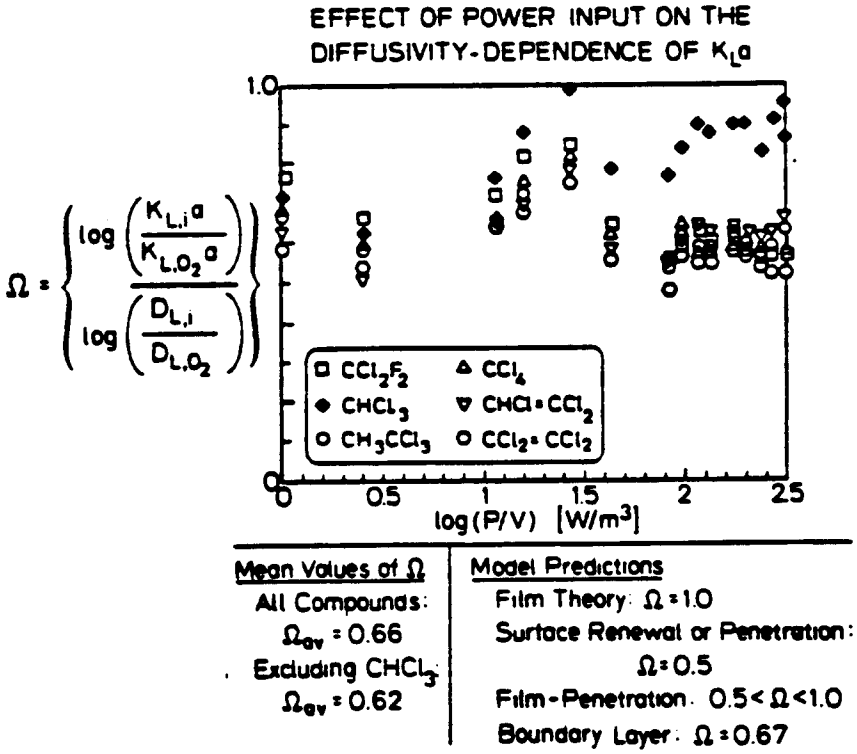
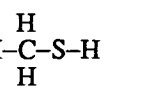
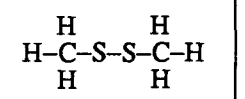


Figure 8. Diffusivity-Dependence exponents (after Roberts, 1983).

Table 1. VSC's found in sewer gas.

Name	Hydrogensulfide	Methylaercaptan	Disethylsulfide	Disarthyldisulfide
Chemical structure	H_2S			
Molecular weight	34.08	48.1	62.1	94.2
Melting point	-85.5°C	-123°C	-98°C	-98°C
Boiling point	-60.7°C	5.9°C	37.5°C	-
Vapor pressure (mbar)	5470 at -20°C 10330 at 0°C 17800 at 20°C	2 atm at 26.1°C	552 at 20°	-
Molar volume	34 cm^3/mol	55.6 cm^3/mol	77.2 cm^3/mol	100.5 cm^3/mol
Density (g/cm^3)	0.993 at -60°C	0.87 at 5°C	0.8 at 20°C	1.06 at 20°C
Solubility in water	3.93 g/l at 20°C	-	6.3 g/l	-
Henry's Law constant (atm. m^3/sol)	$8.7.10^{-3}$ at 20°C	-	$7.1.10^{-3}$	-
Molecular diffusivity in water at 20°C 10^5 $cm^{2/s}$	1.64	1.22	1.01	0.86
pK_{a1}/pK_{a2}	7.1/14	-	-	-
Concentrations in air (20°C)	1 ppbv = 1.5 $\mu g/m^3$	1 ppb = 2.2 $\mu g/m^3$	1 ppbv = 2.8 $\mu g/m^3$	1 ppbv = 4.2 $\mu g/m^3$

Average of values calculated using the methods of LeBas and Schroeder (Reid, 1977)
Average of values from the corrected Wilke-Chang and Othner-Thakar methods (Hayduk & Laudie, 1974)

Sources:
Kirk-Othner, 1979, *Encyclopedia of Chem. Techn.*, 3rd Ed.
Metcalf & Eddy, 1979, *Lovelock*, 1972, *Nature*, 237.
Stephenson, 1987.