

HYDROGEN SULFIDE IN SEWERS

by

Joel Amobi Johnson

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APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Quentin M. Mees
Quentin M. Mees
Professor of Civil Engineering

Sept. 8, 1967
Date

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ABSTRACT

Several factors relating to hydrogen sulfide generation in a sewer were investigated.

The Biochemical Oxygen Demand, velocity, dissolved sulfides and temperature were found to exert an important influence on H_2S concentrations. Diurnal peak times for H_2S concentrations coincided with those for BOD and velocity.

Effect of sewer sediments was studied. Data collected reveal that sulfide generation is directly related to sediment deposition.

Sewers of different designs were investigated. A comparison of several factors (sulfides, velocity, BOD and H_2S) is made.

It was found that hydrogen sulfide problems are minimized in well designed systems providing velocities appropriately related to the effective BOD.

CHAPTER I

INTRODUCTION

Statement Of Problem

The design of sanitary sewer systems for the purpose of minimizing the effects of hydrogen sulfide presents many conflicting and complex requirements which to date have not been absolutely resolved into mathematical expressions for the benefit of the designer.

Some of the more undesirable effects resulting from the presence of hydrogen sulfide are:

1. It is obnoxious and may be toxic to humans, animals and plants when in sufficient quantity. A 0.2% concentration is toxic to humans and the gas becomes potentially explosive at a concentration of 4.3% to 46% by volume in air.
2. The gas is destructive to various parts of the sanitary system. It is converted by aerobic bacteria in the presence of moisture and oxygen from the pipe atmosphere to sulfuric acid. The sulfuric acid then reacts with the lime in a concrete structure to form calcium sulfate or gypsum. The calcium sulfate in turn reacts with the calcium aluminates in the cement to form calcium sulfo-aluminate, a much larger molecule. The resulting crystal growth causes spalling of the surface of the concrete, thereby exposing underlying layers of concrete to further attack.

3. The gas attacks paints on sewer structures as well as that on other neighborhood structures and generally leads to depreciation of property values.

The many problems associated with hydrogen sulfide have been investigated as far back as 1881 by Rudolph Hering (14). Other investigations followed and have continued to the present, in attempts to resolve the problem.

Scope of Investigation

This thesis attempts to correlate some of the factors involved in the generation of sulfides and evolution of hydrogen sulfide.

Investigation was carried on through the months of June, July and August, 1967 representing the hottest time of the year.

The inter-relationships between sulfides, BOD, velocity and temperature are herein examined. Effect of sewer sediments on hydrogen sulfide generation was also studied by taking samples before and after the sewer was cleaned.

For purposes of this investigation a sewer line most likely to present the worst conditions was selected. A 12-inch line of the Pima County Sanitary District No., extending from Curtis road to Orange Grove road met the requirements. Other sewers of relatively good design were also investigated for comparison. These included lines on Roger road and Pantano Road within the city of Tucson. Figure 1 represents a profile of the Curtis-Orange Grove sewer line.

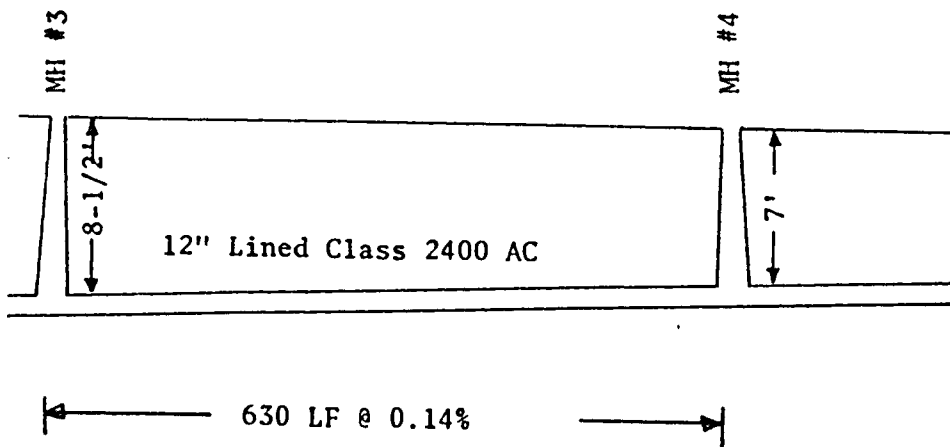


Figure 1. Profile of Sewer Line Tested

CHAPTER II

LITERATURE REVIEW AND PREVIOUS STUDY

The Ionization of Hydrogen Sulfide

Knowledge of the concentration of un-ionized hydrogen sulfide in sewage is highly important where sulfide nuisances are being encountered since the rate of escape of sulfides to the atmosphere is proportional to the H_2S concentration. Between 1899 and 1904 several authors made determinations of the primary ionization constant of H_2S at $18^\circ C$, using the conductivity method, with results shown in Table 1.

TABLE 1
IONIZATION CONSTANTS OF H_2S

Author	Constant	Reference
Walker and Cormack	0.57×10^{-7}	1
F. Auerbach	0.91×10^{-7}	2

In 1938 Epprecht (3) published a new determination of the constant yielding the value of 3.31×10^{-7} at $25^\circ C$.

Because of the wide discrepancy between the results of Epprecht and others, some data were collected at the laboratory of the Los Angeles County Sanitation Districts to resolve the differences (4). The apparent ionization constants were calculated by the formula:

$$\text{Log } K^1 = \text{log } [HS^-] - \text{log } [H_2S] - \text{pH}$$

in which $[HS^-]$ and $[H_2S]$ refer to concentrations.

If the effect of the ionic strength on the activities of ions be taken into account to secure the fundamental ionization constant, the equation takes the form:

$$\text{Log } K = \log [\text{HS}^-] - \log [\text{H}_2\text{S}] - \text{pH} - 0.5\sqrt{\mu}$$

where μ is the ionic strength.

By applying this correction to their values and those of other investigators and correcting to 25°C, the values shown in Table 2 were obtained (4).

TABLE 2
CORRECTED IONIZATION CONSTANTS OF H_2S

Author	Ionization Constant
Walker and Cormack	0.72×10^{-7}
Auerbach	1.15×10^{-7}
Epprecht	3.31×10^{-7}
Pomeroy	2.2×10^{-7}
Pomeroy	1.8×10^{-7}
Pomeroy	1.55×10^{-7}

For an ionic strength of 0.02 and a temperature of 25°C (conditions which may be considered typical for sewers where sulfide difficulties are observed) the apparent constant becomes 2.0×10^{-7} .

On this basis Table 3 was set up to give the factors by which the dissolved sulfide concentration must be multiplied to give the concentration of H_2S (calculated as S) in the liquid (4).

TABLE 3
 CONVERSION FACTORS FOR H₂S IN LIQUID

<u>pH</u>	<u>Factor</u>	<u>pH</u>	<u>Factor</u>	<u>pH</u>	<u>Factor</u>
5.0	0.98	6.7	0.50	7.9	0.059
5.2	0.97	6.8	0.44	8.0	0.048
5.4	0.95	6.9	0.39	8.2	0.031
5.6	0.93	7.0	0.33	8.4	0.020
5.8	0.89	7.1	0.28	8.6	0.012
6.0	0.83	7.2	0.24	8.8	0.0079
6.1	0.80	7.3	0.20	9.0	0.0050
6.2	0.76	7.4	0.17	9.2	0.0032
6.3	0.72	7.5	0.14	9.4	0.0020
6.4	0.67	7.6	0.11	9.6	0.0013
6.5	0.61	7.7	0.091	9.8	0.00079
6.6	0.56	7.8	0.073		

Concentration of H₂S in an atmosphere in equilibrium with a sulfide-containing liquid may then be found by multiplying the concentration in the liquid by a factor which varies with the temperature. Values of this factor for certain temperatures are shown in Table 4.

TABLE 4
CONVERSION FACTORS FOR H₂S IN AIR

<u>Temperature, °C</u>	<u>Factor to Determine Equilibrium of H₂S in Atmosphere in ppm by Volume.</u>
16	248
18	262
20	286
22	291
24	307
26	323
28	339
30	356

Influence of Velocity on Sulfide Generation in Sewers

In 1946 Pomeroy and Bowlus (5) discussed the influence of velocity on sulfide build-up in sewage. A tabulation was given of the velocities necessary to prevent the build-up of sulfides in flowing sewage corresponding to different values of the "effective BOD" of the sewage. The tabulated values agree with the relationship

$$V = 0.137 (\text{Effective B.O.D.})^{0.496} \quad (1)$$

in which "effective BOD" (EBOD) is defined as (measured B. O. D.) (1.07^{5-20}) , t being the temperature of the sewage in °C. Pomeroy and Bowlus do not however claim that the relationship given by them is rigidly true under all conditions, as the BOD alone is not an adequate measure of the influence of the sewage "strength" in the sulfide production process.

Accepting the theory that sulfides generated on the sewer wall are partly or wholly oxidized by oxygen absorbed at the sewage surface, W. J. Davy (6) formulated a relationship incorporating the factors connected with surface absorption of oxygen. The factors include those influencing the rate of absorption of oxygen at the sewage air interface and those determining the relative strengths of the sulfides and the other constituents of the sewage as competitors for this absorbed oxygen. The analysis of results obtained by such authors as Streeter, Wright and Kehr (7) from experiments on oxygen absorption into clean flowing water, indicate that the rate of gas absorption into or evolution from a flowing liquid can be expressed fairly accurately in terms of a power of the Reynolds number, N_{Re} , of the liquid flow.

Davy therefore stated that the rate of oxygen absorption per unit area of sewage surface per hour per unit of oxygen partial pressure potential, K_G , may be expressed as

$$K_G = C_1 (N_{Re})^n \quad (2)$$

where C_1 is a constant depending on the system of units used and the concentration of oxygen in the atmosphere above the sewage.

For a sewage flow of surface width b perpendicular to the direction of flow and of cross sectional area A , the rate of oxygen absorption per unit length of sewer, O_T , expressed in p.p.m. of sewage per hour would be given by

$$O_T = C_2 \frac{b}{A} (N_{Re})^n \quad (3)$$

where C_2 is a constant depending on the system of units used. This absorbed oxygen would be divided between the sulfides and the other oxygen absorbing constituents of the sewage in proportion to their respective instantaneous rates of demand. Assuming the demand rates to be proportional to the amounts of sulfide S , and B.O.D. respectively, available for oxidation, and if the amount of oxygen absorbed by sulfides is small compared with that absorbed by other constituents of sewage, then

$$O_s = \frac{C_3 S}{C_4 (\text{BOD})} (O_T) \quad (4)$$

where O_s is the rate of oxygen absorbed by sulfides, and C_3 and C_4 are constants of proportionality.

Davy reasoned, that to prevent evolution of corrosive gas to the sewer atmosphere, it is necessary to keep a stream of sewage free of unoxidized sulfide. If rate of generation of the sulfides is equal to the rate of oxidation.

$$\text{Then } O_s = C_3 S$$

$$\text{and } C_4 (\text{B.O.D.}) = O_T = C_2 \frac{b}{A} (N_{Re})^n$$

$$\text{or } N_{Re} = \left(\frac{C_4 A}{C_2 b} (\text{B.O.D.}) \right)^{1/n} = C \left(\frac{A}{b} (\text{B.O.D.}) \right)^{\frac{1}{n}} \quad (5)$$

Assuming that the rate of generation of sulfides is proportional to $f(T)$, it follows that

$$S_{20} = \frac{S}{f(T)}$$

$$\text{where } f(T) = 1.07^{t-20}$$

and S_{20} is the amount of sulfide available at the standard temperature of 20°C.

$$\text{Hence } (O_s)_{20} = \frac{C_3 S_{20}}{C_4 (\text{B.O.D.}) f(T)} (O_T) \quad (6)$$

$$\text{and } (N_{Re})_{20} = C \left[\frac{A}{b} (\text{B.O.D.}) f(T) \right]^{\frac{1}{n}} \quad (7)$$

Davy plotted values of $\frac{A}{b} (\text{B.O.D.}) f(T)$ against values of N_{Re} or $\frac{VRe}{\mu}$ on a logarithmic scale.

V = velocity of flow

R = hydraulic radius = $\frac{A}{p}$

μ = viscosity

e = density of sewage.

He obtained a straight line of slope 0.89 or a value of 1.12 for n . His C value was 5700.

Hence, his equation for a marginal condition in respect to sulfide build-up is

$$N_{Re} = 5,700 \frac{A}{b} (\text{B.O.D.}) f(T)^{0.89} \quad (8)$$

Pomeroy (8) however postulated that there may be individual effects of velocity, radius and viscosity on the rate of solution of oxygen, not entirely encompassed by the assumption of a simple function of Reynold's number. On this basis he arrives at a different equation for the condition just marginal in respect to sulfide build up,

$$Z_m = \frac{EBOD}{S^{1/2} Q^{1/3} f(d/D)} \quad (9)$$

where EBOD is effective BOD, S is slope, Q is quantity of flow in cubic feet per second and $f(d/D)$ is a quantity depending upon the relative depth of flow in the sewer. It has a value of about 1.0 up to 1/3 depth, 0.85 at 1/2 depth, 0.65 at 2/3 depth and drops to zero for a full pipe.

A Z value of 7,500 he reports, is nominally the marginal value for build up. He warns against applying the formula to small flows generally below 0.1 m.g.d.

CHAPTER III

BASIC CONSIDERATIONS

Mechanism of H₂S Generation

In free flowing sewers, sulfides are produced by microbial slimes on the submerged surface of the sewer and by deposited sludge.

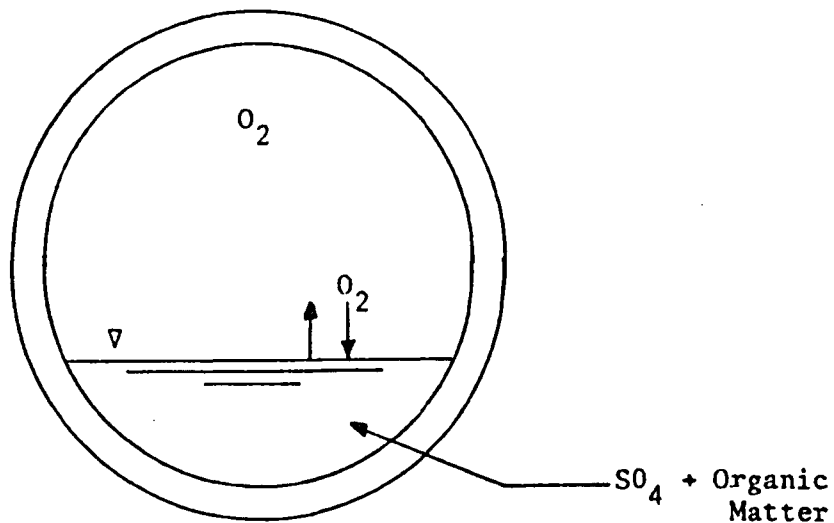


Figure 2. Flow of Relatively Fresh Sewage

Figure 2 represents flow of relatively fresh sewage at the upper end of a system. There is little or no slime development.

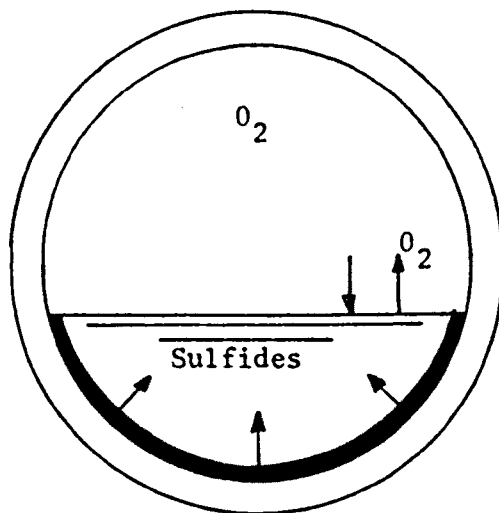
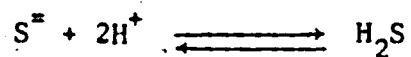


Figure 3. Slime Development Stage in Sewer

Figure 3 represents a situation which may occur farther down the collection system. With a lapse of time, slime develops providing a home for sulfur bacteria which reduce sulfates and proteins under anaerobic conditions to H_2S and other compounds.



Several species of organisms are capable of the reduction of sulfur compounds such as Desulfovibrio desulphurican, and Clostridium nigrificans.

After development in the slimes and sludges, the sulfides pass into the flowing material for accumulation and eventual release to the

sewer atmosphere through physical action, as shown in Figure 4.

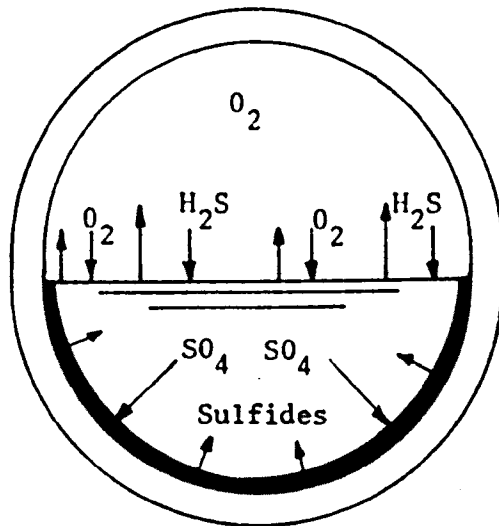
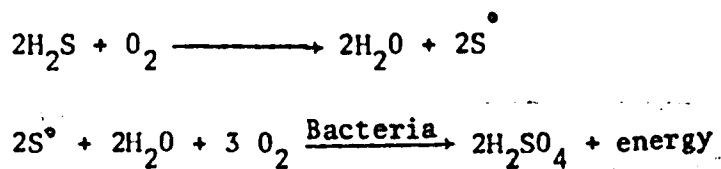


Figure 4. H_2S Release to Sewer Atmosphere

Figure 5 represents the final condition after the hydrogen sulfide is in the atmosphere. Here the H_2S combines with oxygen to form water and sulfur and may be condensed on the exposed surfaces of the system.



Under certain environmental conditions sulfur-oxidizing bacteria have been found to exist that belong to the genus Thiobacillus. These organisms in the presence of moisture can oxidize sulfur to sulfuric acid, which is the destructive agent of a sewer system. Certain filamentous sulfur bacteria namely Beggiatoa are also capable of oxidizing H_2S to sulfate with temporary storage of elemental sulfur as globules in the cells.

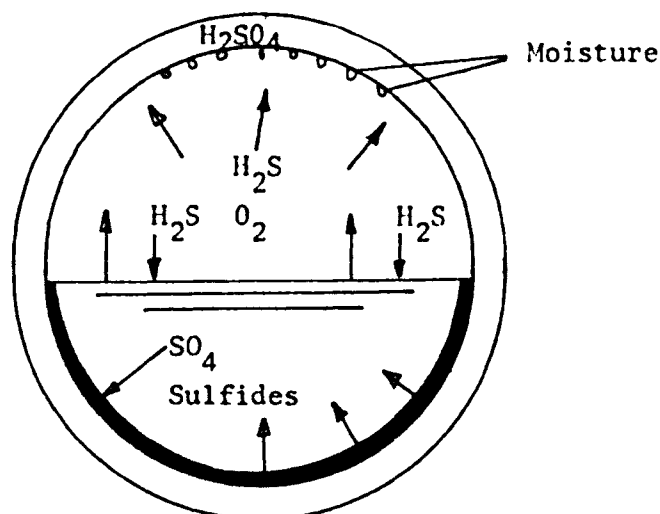


Figure 5. Final Stage Leading to H_2SO_4 Formation

Environmental Factors

The environmental factors relating to hydrogen sulfide generation fall into three basic areas of scientific study: chemical, physical and biological action. Within this framework, temperature, humidity, sewage strength, velocity, pH, surface area and other wastes apart from sewage become important parameters.

Effect of Temperature

Since the generation of sulfide is a biological process it is markedly affected by temperature. Baumgartner (10) measured rates of sulfide generation at four temperatures, using bottle experiments. Up to 30°C the rate of sulfide generation was found to increase about 7 percent per degree rise of temperature. At 30°C and 37°C the rates were similar indicating an optimum somewhere in between. At temperatures below 15°C , sulfides are virtually absent.

Effect of Humidity

Most sewers are relatively closed units and as a result humidity can build up to near saturation at times. High temperature and humidity provide an excellent environment in which microscopic organisms may flourish. Parker (11) demonstrated that the rate of acid production is much greater with increased temperature through the psychrophilic range and into the mesophilic range before the rate of production begins to decrease.

Effect of Sewage Strength

A high concentration of organic matter in waste water is an environmental factor which is very vital to the generation of hydrogen sulfide. A fair approximation of this concentration is afforded by the BOD. The higher the BOD, the higher would be the probable amount of sulfide generated. Pomeroy and Bowlus (5) found that the generation of sulfides generally ceases at about the BOD value of 80. Thus, there is a limiting value below which a build-up of sulfide will not occur, since aeration at the surface of the stream provides enough oxygen to oxidize the sulfides as fast as they are produced.

Effect of Sewer Velocity

Velocities less than 3 fps tend to provide conditions for slime development and at very low velocities, sludge deposits. At velocities in excess of 5 fps the greater turbulence can allow hydrogen sulfide to be more easily liberated.

However, in well designed systems the scouring effect associated with velocities anywhere from 3 to 5 fps keeps the system relatively free of slimes and sludge deposits.

Effect of pH

The greater the magnitude of hydrogen ion concentration the greater the possibility of hydrogen sulfide generation. Sulfide generation by bacteria is greatest at an optimum pH value of 8.0 to 7.5 and then declines with both increased and decreased pH values.

That portion of total sulfides that may be converted to hydrogen sulfide increases with decrease in pH value. Finally, the rate of generation of total sulfides in sewage, a vital factor, reaches maximum for a pH between 6.5 and 7.5.

Area of Biologically Active Surfaces

Since sulfides are not generated to any appreciable amounts in the body of the sewage, but by slimes and deposited sludge, it follows that the area of these active surfaces is a very important factor. An impressive illustration of the importance of surface area was afforded by the experience of the Santa Fe Springs Waste Water Disposal Company. In the skimming and settling tank where the company handled the given oil field and refinery waste, the increase in sulfides amounted to about 1.0 ppm. However when the waste was passed through sand filters with only a few minutes detention compared to the 6 hours in the settling, sulfide concentration of several parts per million were observed in the effluent.

Mees (15) Professor of Civil Engineering at the University of Arizona, Tucson, Arizona undertook a study to determine

1. How much area is provided by a given sediment deposit.
2. How much gas is generated per unit of surface area per unit of time.

He concluded from results obtained, Figures 6 and 7, that surface area is greatly increased by the presence of sediments (16).

Figure 7 also indicates an increase in the volume of gas produced with increase in sediment depth.

Also noted in this study was the effect of temperature on the activity of Desulfovibrio. The 1:10 dilutions of slime bacteria secured by washing the sediments and incubating at 30°C became positive in approximately one-third the time required for an identical dilution incubated at 20°C.

Effect of Other Wastes

One environmental factor that impinges on the sulfide generating potential is the effect of wastes other than domestic. The addition of sulfate, sulfide or sulfite wastes by industry compounds the natural problem. Sulfide production is generally increased with increased amounts of sulfate. Of course uncontrolled intrusion of industrial wastes is bound to complicate the problems associated with sewage treatment processes and facilities.

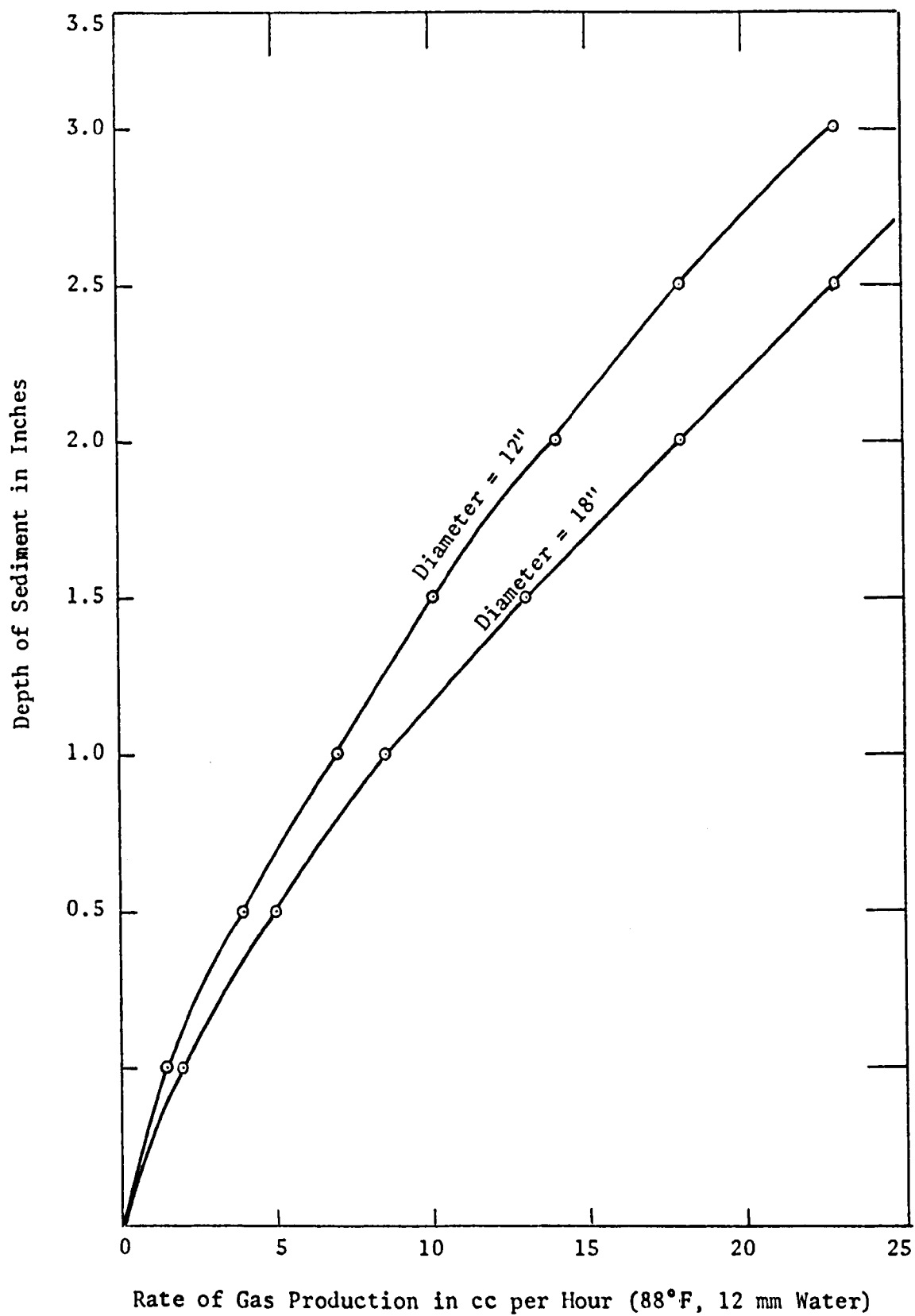


Figure 6. Rate of Gas Production Related to Sediment Depth

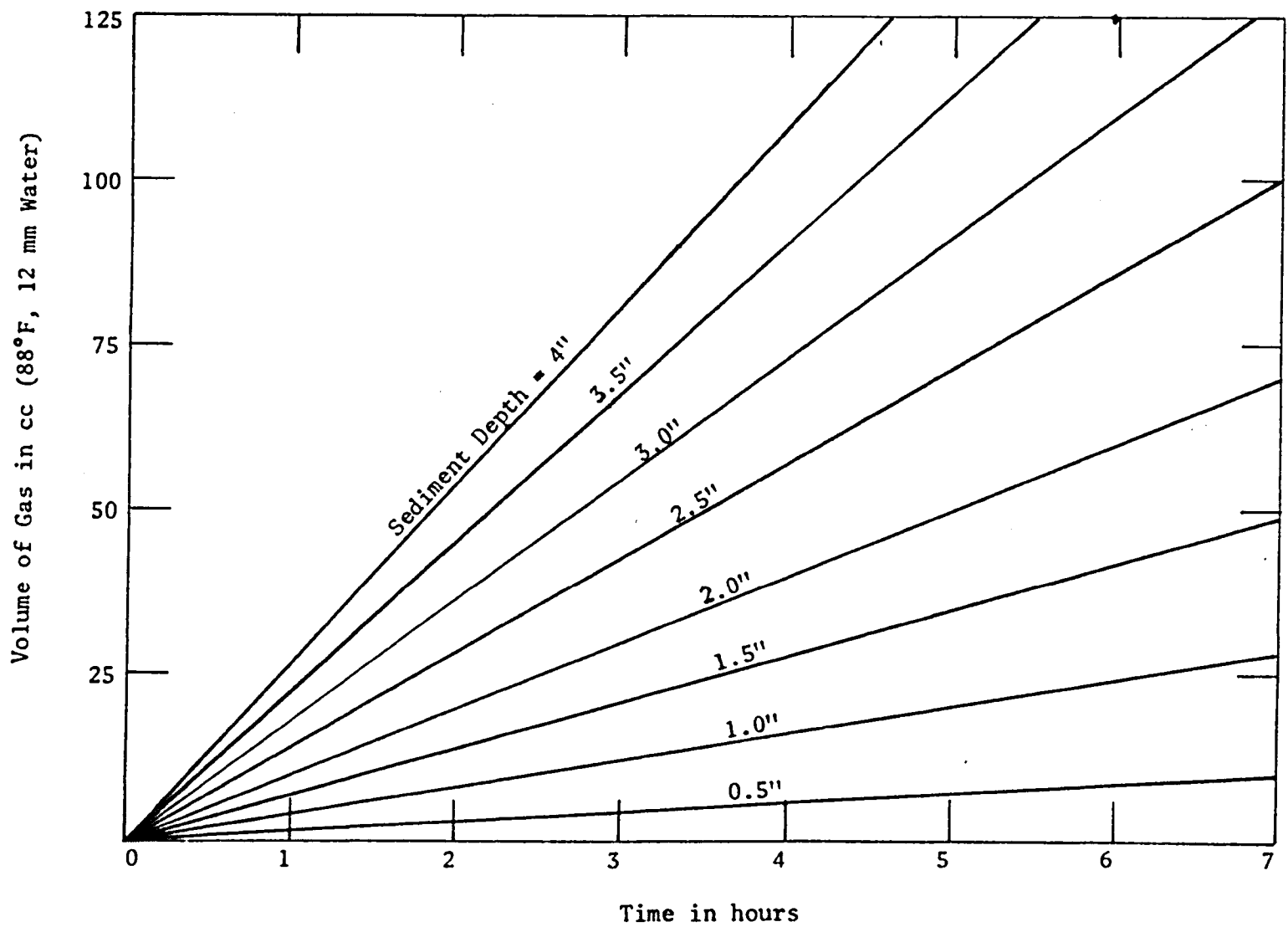


Figure 7. Gas Production Related to Sediment Depth

CHAPTER IV

EXPERIMENTAL METHOD AND PROCEDURE

Equipment and Apparatus

For the determination of H_2S in the sewer atmosphere, two types of equipment was employed. The first used, was the A.I.S.I. Hydrogen Sulfide Sampler shown in Figure 8. Its essential feature is a pump drawing air from the sewer atmosphere through a paper roll impregnated with lead acetate. The resulting blackness from the lead sulfide formed varies in intensity depending on the concentration of the hydrogen sulfide.

The second and final equipment used in the determination was the Mine Safety Appliances Monitor Sampler shown in Figure 9. Its essential feature is a pump drawing air from the sewer atmosphere through a colorimetric detector tube which changes in color from white to brown as hydrogen sulfide passes through. With the aid of a chart, the length of color change is converted to parts per million of hydrogen sulfide.

For the total and dissolved sulfide determinations, the Lamotte-Pomeroy Sulfide Testing Set was used. It is essentially a compact laboratory for field determination of sulfides. It conforms to the procedures set out in "Standard Methods" (12) for the colorimetric determination of sulfides.

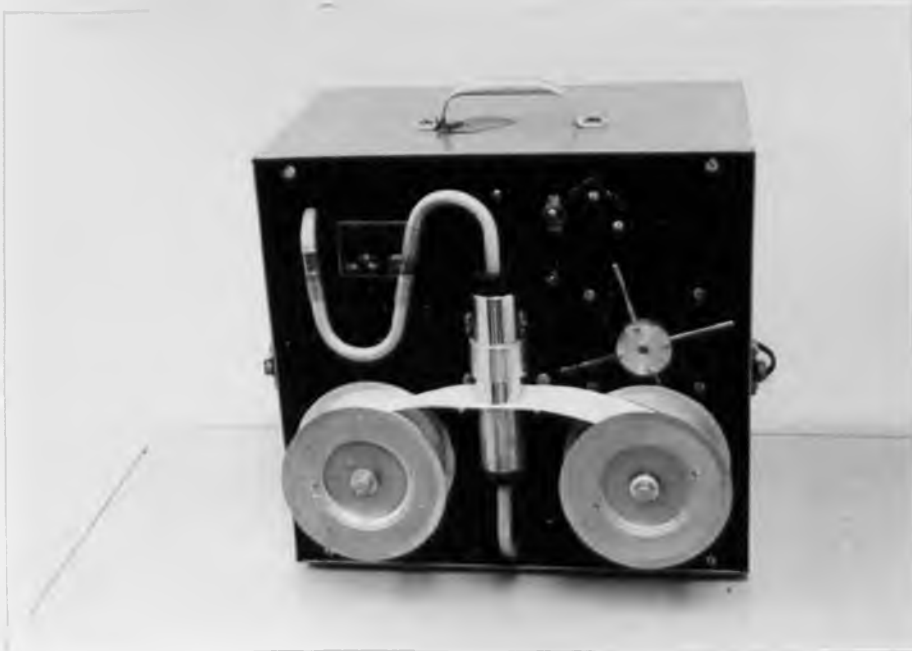


Figure 8. A.I.S.I. Sampler



Figure 9. Mine Safety Appliances H₂S Sampler Showing Pump and Vials Before and After Sampling.

(a) Vial Before Sampling (b) Vial After a Typical Run

Experimental Procedure

Two manholes were generally employed in the field investigations. The upstream manhole was employed for the hydrogen sulfide tests, while the adjacent down-stream manhole was used for the sulfide, BOD and depth measurements. For the hydrogen sulfide tests, air was sampled from the manhole through a plastic tube extending through a hole in the manhole cover to within six to twelve inches of the flow level. The temperature of the manhole was obtained by lowering an armored thermometer at the end of a line through a second hole.

Depth measurements at the sampling manhole were determined as the difference between the invert depth as measured from the lip of the manhole ring and the plumbob-weighted-tape distance to the free water surface measured from the same point.

Samples for the sulfide and BOD tests were obtained with a grab sampler. The temperature of the sewage was taken as soon as the grab sample was brought to the surface.

Portions of the samples for the BOD tests were refrigerated in a chest with crushed ice until brought to the laboratory. BOD determinations were then made in accordance with procedures outlined in "Standard Methods."

Velocity of flow at the end of each set of runs was determined by timing the travel of a ping pong ball between the two manholes. The velocity at any other given depth was then determined with the aid of a chart for hydraulic properties and relative depths (13).

Character of Tests

Tests were usually run at two hour intervals. The number of tests in any given day varied from three to six. Day and night runs were made to determine the 24 hour-variations.

The day run was usually between 8:00 A.M. to 6:00 P.M. while the night run in most cases lasted from 8:00 P.M. to 6:00 A.M.

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

Hydrogen Sulfide Measurement Techniques

An attempt was made to establish a curve, giving hydrogen sulfide concentration in the sewer atmosphere for any percent transmission reading obtained with the automatic A.I.S.I. haze and hydrogen sulfide sampler.

The field experimentation consisted in drawing the sewer gas at a rate of 5.75 liters per minute through the A.I.S.I. sampler. At the same time, a rate of 0.47 liters per minute was drawn through a Mine Safety Appliance hydrogen sulfide detector tube. Using the tube as a standard, a given percent transmission was associated with a hydrogen sulfide concentration.

A plot of transmission versus grains of hydrogen sulfide is shown in Figure 10. The erratic nature of the data, however, makes the plot of little use in determining actual concentration of hydrogen sulfide. A transmission of 20% for example, would give a concentration anywhere from 5×10^{-4} to 20×10^{-4} grains of H_2S . At lower transmissions, the band becomes very unreliable as possible number of H_2S values increase. The most reliable range of transmission is from 35% to 75%.

One obvious reason for the wide fluctuations in data obtained was the time element involved in making measurements. While it took an average of 30 minutes to have a suitable reading with the Mine Safety vial, it took from 30 seconds to 10 minutes for the A.I.S.I. sampler to

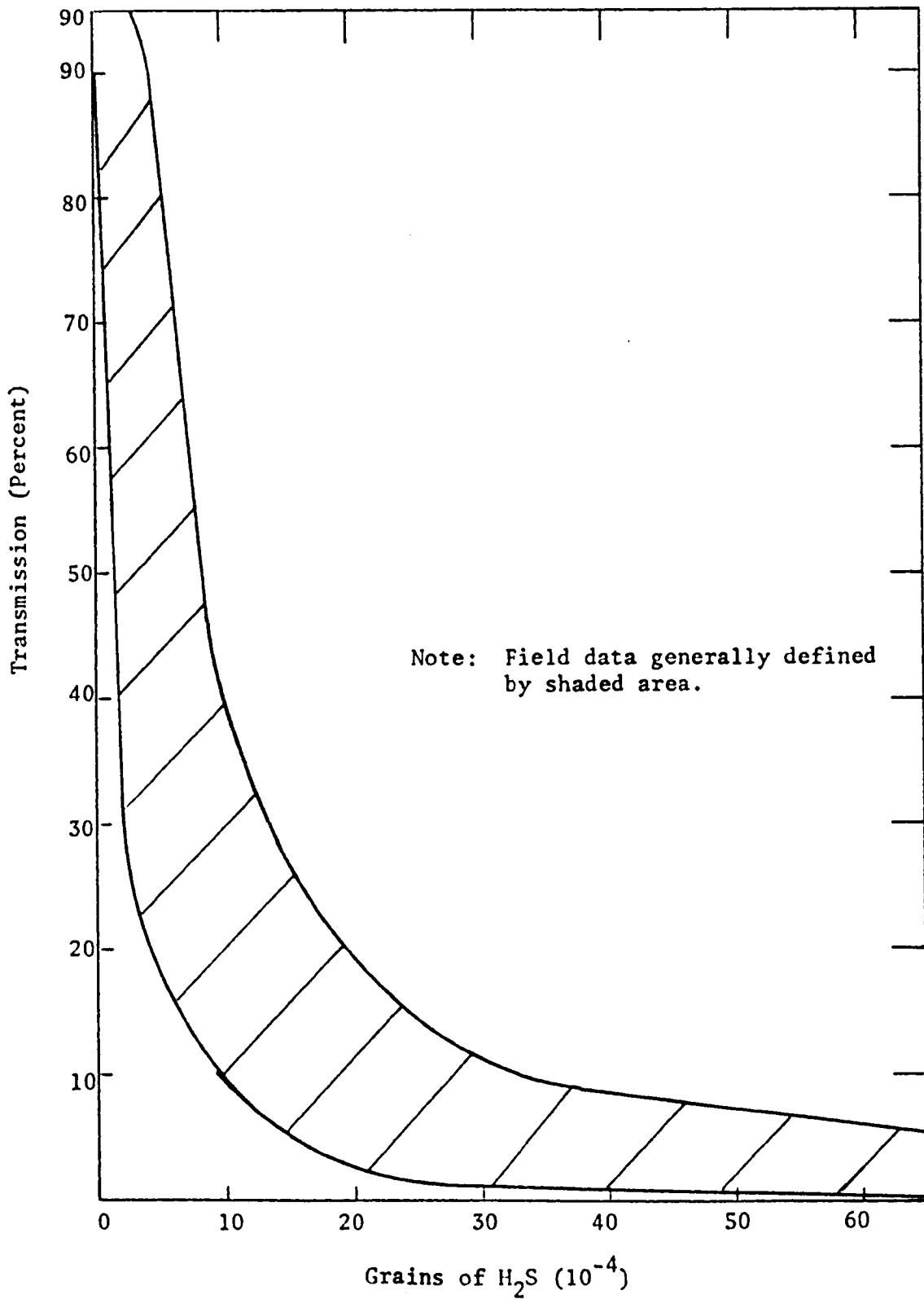


Figure 10. Grains of H₂S Versus Percent Transmission (A.I.S.I. Sampler)

register a reading. Hence the A.I.S.I. sampler reflects more of the intensity of H_2S evolution at any given time, while the vial does not. Another significant factor is the high H_2S concentration involved and the high flow rate of the A.I.S.I. sampler. The time allowed for the reaction might have been too short for a complete formation of lead sulfide on the indicator tape.

At this juncture, the A.I.S.I. sampler was abandoned in favor of the Mine Safety vials.

Relevant Factors in H_2S Generation

From the data collected, it was determined that the concentration of hydrogen sulfide was more a function of the total sulfides in the sewage than any of the other environmental factors. It is readily evident from Figure 11 representing a plot of total sulfides versus H_2S concentration, that the variates are proportional.

Using the method of least squares, the equation for the line of best fit was found to be

$$S_t = 0.82 + 0.022 H_2S \quad (10)$$

or
$$H_2S = 45.5 S_t - 37.3 \quad (11)$$

where S_t is total sulfides. Equations (10) and (11) however represent a particular solution and field condition.

An attempt at a more generalized relationship was made incorporating the relevant environmental factors. The effective BOD (EBOD) defined as $BOD (1.07)^{t-20}$ where t is temperature of sewage in degrees

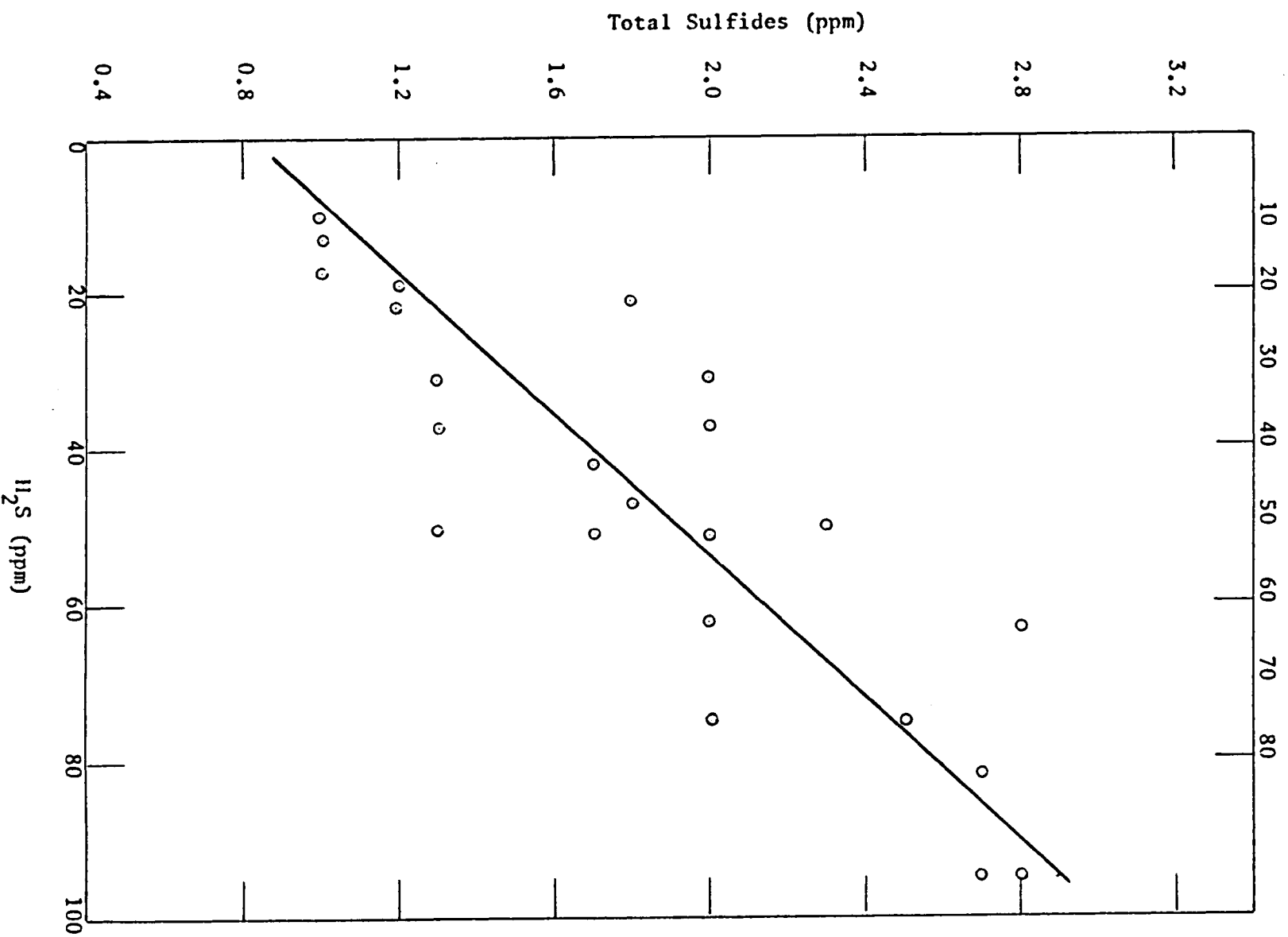


Figure 11. Total Sulfides Versus H_2S in Sewer Atmosphere

centigrade, dissolved sulfides S_D , velocity V and temperature of the manhole T_m in degrees centigrade were held to be the factors most likely to influence the generation of H_2S .

Hydrogen sulfide has been shown to be related to the EBOD of the sewage. The higher the BOD, the higher the sulfides generated. The availability of oxygen for oxidation of sulfides is proportional to the degree of turbulence or Reynold's number N_{Re} where

$$N_{Re} = \frac{VDe}{\mu}$$

But diameter D , coefficient of viscosity μ , and density of sewage are all constants.

$$\text{Therefore } N_{Re} \propto V$$

Since low velocities are associated with low turbulence and consequently low level of reaeration, it follows that more sulfides are generated and less oxidized. Chances of H_2S evolution are then increased.

$$\text{Hence } H_2S \propto \frac{1}{N_{Re}} \quad \text{or} \quad H_2S \propto \frac{1}{V}$$

The concentration of H_2S in the pipe is also a function of surrounding temperature.

Translating all concentrations to a common base of $20^\circ C$, it was assumed that the relationship between the factors is of the form

$$\left[H_2S (T_m - 20) \right]^A = \left(\frac{EBOD}{V} S_D \right)^B \quad (12)$$

$$A \log \left[H_2S (T_m - 20) \right] = B \log \left(\frac{EBOD}{V} S_D \right) \quad (13)$$

$$\log \left(H_2S (T_m - 20) \right) = B/A \log \left(\frac{EBOD}{V} S_D \right) \quad (14)$$

A logarithmic plot shown in Figure 12 yielded a straight line of slope

$$B/A = 1.11$$

$$\text{Hence } H_2S (T_m - 20) = \left(\frac{EBOD}{V} S_D \right)^{1.11} \quad (15)$$

Equation 15 applies for a definite field condition and a T_m range between 26°C and 30.7°C. The ratio B/A would vary with field condition.

Pattern of BOD, Velocity and H₂S Generation

One interesting aspect of H₂S generation is the cyclic nature of concentrations over a 24 hour period.

Figure 13 represents a plot of H₂S concentrations versus time of day for 2 sets of 24 hour runs. A peak generally occurs at 12:00 Noon during a day run and another peak is observed somewhere between 10:00 P.M. and 12:00 P.M. midnight for night runs. The BOD and velocity also follow a similar trend as is shown in Figure 14.

In an effort to determine H₂S generation along the sewer line, tests were conducted at two manholes 3500 feet apart. Table 5 shows the results obtained.

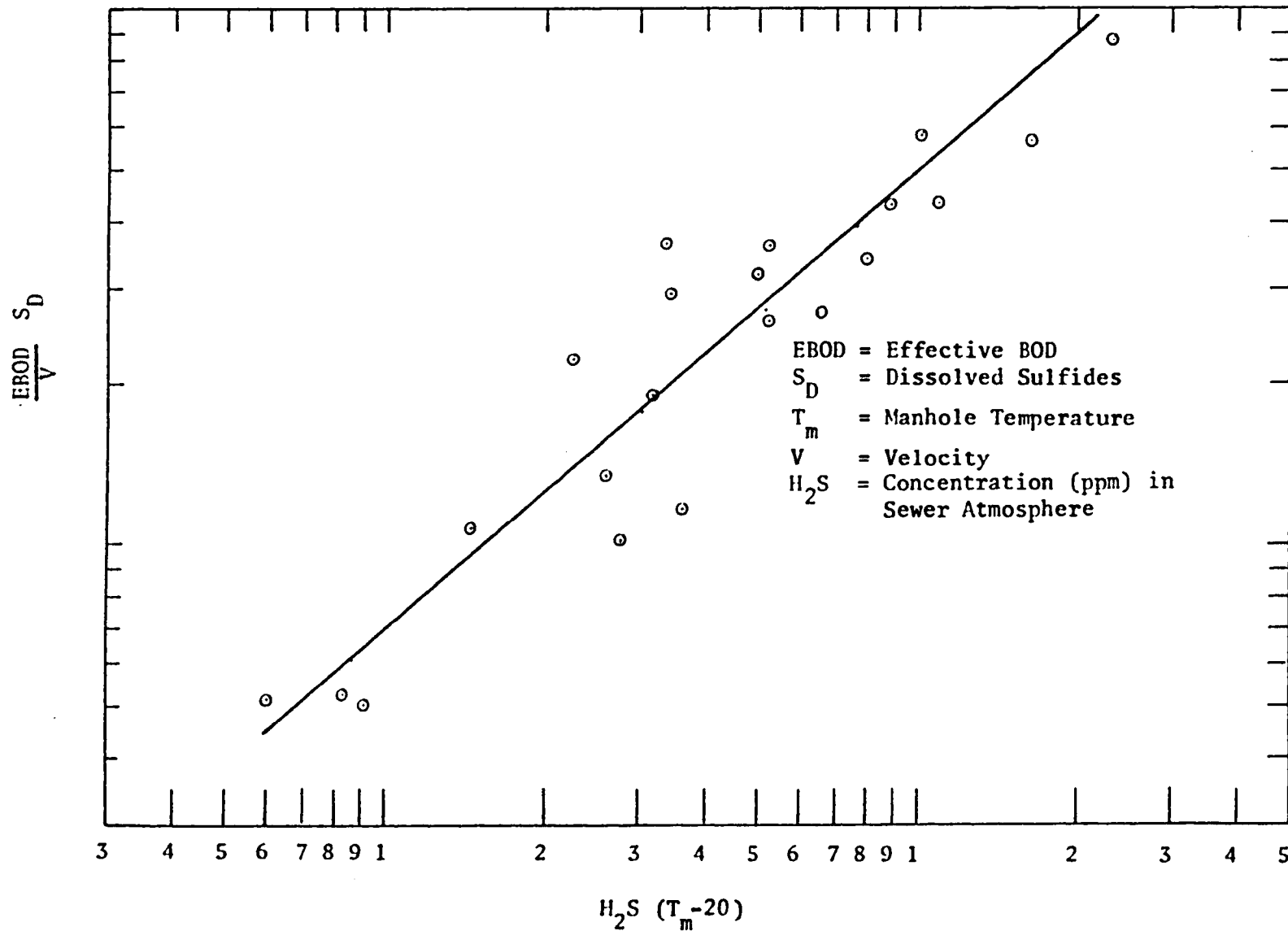


Figure 12. Relationship Between H_2S and EBOD, Velocity, S_D and T_m

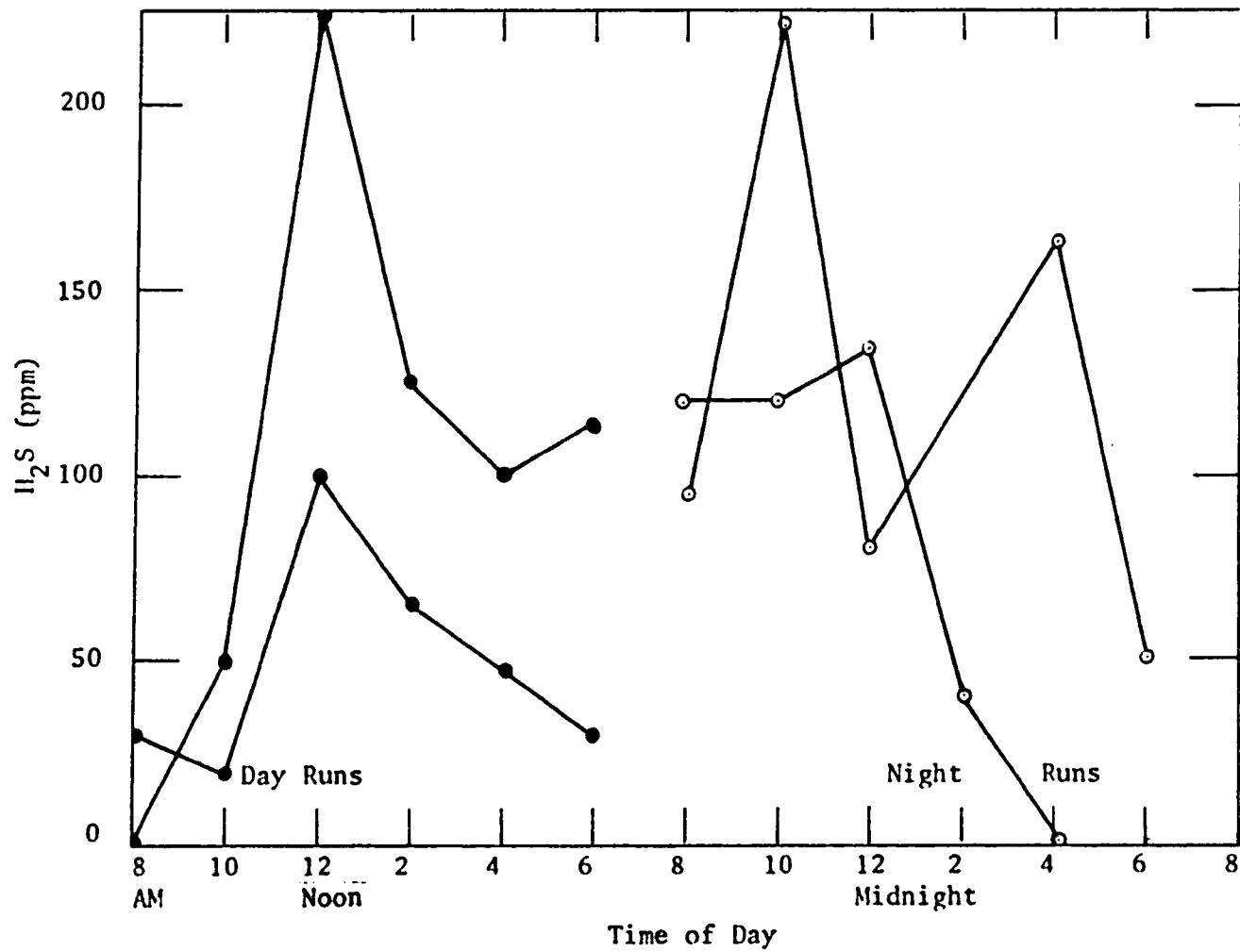


Figure 13. H₂S Concentrations Vs Time of Day

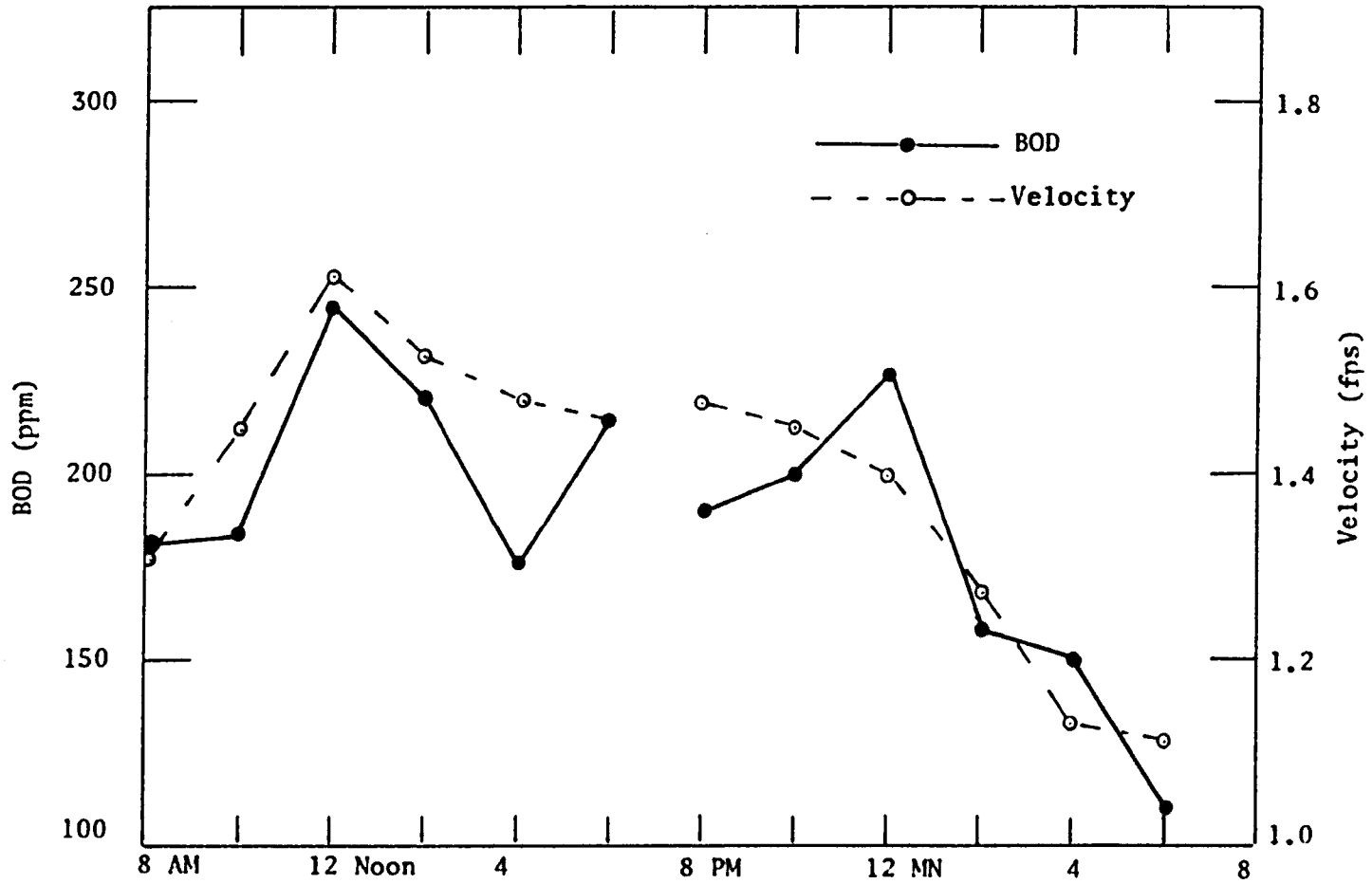


Figure 14. Diurnal BOD and Velocity Values

TABLE 5
H₂S CONCENTRATIONS

Time	Curtis Road	Sunset Road	Time
	H ₂ S (ppm)	H ₂ S	
8:00	-	-	8:30 A.M.
10:00	-	180	10:30 A.M.
11:30	75	115	12:00 Noon
2:15	58	25	2:00 P.M.
4:00	37	51	4:45 P.M.

The erratic nature of the results indicate a lack of concentration gradient with distance.

One factor that might be held responsible for the complexity of H₂S generation is the peculiar condition of the sewer line. The manhole covers are under a 4 inch depth of dirt, thus reducing aeration to the barest minimum. At peak velocities then, the higher turbulence without corresponding increase in re-aeration would lead to a more than normal release of H₂S to the sewer atmosphere. This is borne out by the fact that H₂S is highest at peak velocities around noon and lowest at low velocities usually from 2 A.M. to 6 A.M.

Sediment Analysis

In order to understand the effect of sediment deposits on sulfide and H₂S generation, tests were made before and after the sewer line was cleaned.

Tables 6 and 7 present a comparison before and after the cleaning for typical night and day runs.

TABLE 6

SULFIDE COMPARISON BEFORE AND AFTER CLEANING OF SEWER

Time	Before		After	
	Total Sulfides	T Sewage	T Sewage	Total Sulfides
8:00 P.M.	2.8 ppm	29.9°C	30.3°C	0.8 ppm
10:00 P.M.	4.0 ppm	29.9°C	30.3°C	0.8 ppm
12:00 M	2.7 ppm	29.7°C	30.3°C	0.7 ppm
2:00 A.M.	2.5 ppm	29.0°C	30.0°C	0.4 ppm
4:00 A.M.	2.8 ppm	28.9°C	29.5°C	0.1 ppm
6:00 A.M.	2.3 ppm	28.5°C	29.0°C	0.0 ppm
8:00 A.M.	2.0 ppm	29.0°C	29.5°C	0.0 ppm
10:00 A.M.	1.8 ppm	29.0°C	29.5°C	0.8 ppm
12:00 N	3.0 ppm	29.5°C	29.9°C	1.5 ppm
2.00 PM	2.8 ppm	29.8°C	30.0°C	0.7 ppm
4:00 P.M.	1.8 ppm	29.8°C	30.0°C	0.4 ppm
6:00 P.M.	1.5 ppm	30.0°C	30.0°C	0.3 ppm

TABLE 7
 H_2S COMPARISON BEFORE AND AFTER CLEANING SEWER

Time	Before		After	
	H_2S (ppm)	T Sewage ($^{\circ}C$)	T Sewage $^{\circ}C$	H_2S (ppm)
8:00 P.M.	95	29.9	30.3	120
10:00 P.M.	222	29.9	30.3	120
12:00 M	82	29.7	30.3	135
2:00 A.M.	29	29.0	30.0	41
4:00 A.M.	100	28.9	29.5	-
6:00 A.M.	50	28.5	29.0	-
8:00 A.M.	31	29.0	29.5	-
10:00 A.M.	21	29.0	29.5	50
12:00 N	100	29.5	29.9	269
2:00 P.M.	63	29.8	30.0	125
4:00 P.M.	47	29.8	30.0	50, 100
6:00 P.M.	31	30.0	30.0	115

Table 6 suggests that sediments contributed to a higher sulfide build up in the sewer tested.

The rate of gas production predicted by Mees (15) for 1 inch of sediment depth and 40 ft.² of surface area is 4.0 cc per hour. He postulated that H_2S production would range between 6% and 8% of this total. Hence 0.24 cc to 0.32 cc per hour of H_2S could be attributed to pipe sediment. As indicated in Table 8, surface area of sediment analyzed compares closely with his figure.

There seemed to be no marked change in the concentration of H_2S observed. Several factors might be considered as contributing to this seemingly unpredictable condition. One could be the higher sewage temperature approaching more closely the $30^\circ C$ incubation temperature of Desulforibrio. Another factor might be related to the fact that equilibrium conditions did not exist between the H_2S in the liquid and gas phases. This is borne out by computations derived from factors presented in Tables 3 and 4.

Using a pH value of 7 and a sewage temperature of $30^\circ C$ the predicted H_2S concentration in the sewer atmosphere can be computed as follows:

$$H_2S = 356 (0.33 S_D)$$

For S_D values of 2.3 and 0.8 ppm, H_2S concentrations are 270 and 94 ppm respectively. Values recorded in Tables 6 and 7 vary significantly from these.

TABLE 8
SURFACE AREA OF SEDIMENT BY SIEVE ANALYSIS

Sieve No.	Fraction Retained	Surface Area Constants (17)	Surface Area Fractions
200	0.018	120	2.16
100	0.056	60	3.36
50	0.092	30	2.76
30	0.174	16	2.78
16	0.347	8	2.78
8	0.138	4	0.55
4	0.074	2	0.15
3/8	0.100	1	0.1
TOTALS	0.999		14.64 ft ² /lb

Volume of sediment/linear ft. = 0.035 ft³

Depth of sediment in pipe = 1.0"

Density of sediment = 83.8 lb/ft³

Lbs. of sediment per ft. of pipe = 83.8x0.035 = 2.83

Surface area per linear ft. = 2.83 (14.64)ft² = 41.5 ft²

Influence of Contemporary Design on H₂S Generation

To determine the effect of design characteristics on the process of H₂S evolution, tests were conducted on sewer lines located on Roger and Pantano Roads within the city of Tucson. Test results from these more modern designs are compared with those of Curtis-Sunset Roads in Table 9.

TABLE 9
COMPARISON OF THREE SEWER LINES

Factors	Curtis-Sunset	Roger	Pantano
Slope, %	0.14	0.26	0.7
Diameter, inch	12	30	15
Velocity Range, fps	1.0-1.48	3.97-4.11	3.42-4.22
Temperature, °C	29.5	30.5	31.5
BOD, mg/l	147-265	120-225	144-200
Sulfide, ppm	1.0-4.0	0-0.2	0-0.2
H ₂ S, ppm	10-22	0-1.8	0-3.4

It is evident that design has an impact on sulfide generation and H₂S evolution. The major difference seems to stem from the low velocity in the Curtis-Sunset line, which makes for higher sediment deposition and low aeration.

From equation (9), the Z value for Curtis-Sunset Road was found to be 13,700, well in excess of the 7500 value given by Pomeroy (8) as the marginal condition for sulfide build-up. It is therefore not surprising that a high concentration of sulfides was detected.

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

Summary and Conclusions

An attempt was made to develop a relationship between H₂S concentrations and readings from the A.I.S.I. sampler.

Efforts were made to determine the inter-relationship between H₂S concentrations and several environmental factors. The factors investigated were:

- (a) Temperature
- (b) Velocity
- (c) Total and dissolved sulfides
- (d) BOD

Influence of sewer sediments on H₂S evolution was probed.

Finally several sewer lines were studied to find the effect of design on sulfide build up and H₂S generation.

The following conclusions may be drawn from the field experiment conducted.

1. Frequent fluctuations in hydrogen sulfide generation are such as to make any determination at best a crude approximation since most instruments require considerable time for measurement.
2. Considering all the shortcomings of an uncontrolled field experiment, it could be argued that diurnal hydrogen sulfide

concentrations bear a direct linear relationship to the total and dissolved sulfides levels.

3. For the test conditions, deposition of sediments leads to a higher sulfide build-up, but not necessarily a higher hydrogen sulfide concentration level.
4. Hydrogen sulfide problems are minimized in well designed systems providing velocities appropriately related to the effective BOD.
5. Sewer maintenance programs should provide for routine cleaning to minimize sulfide build up.

Suggestions for Further Studies

The following are recommended by the author for further study.

1. A control line should be constructed where any of the factors relevant to H_2S production could be manipulated. Of particular significance would be the provision for varying slope and sediment depth.
2. Washings from the sediment should be incubated to determine the hydrogen sulfide generation potential of sulfur bacteria.
3. Field studies should be initiated to evaluate the relationship of H_2S concentrations to pipe corrosion.

APPENDICES

APPENDIX A

DATA FROM CURTIS-SUNSET SEWER LINE

Date	Time	S _T (ppm)	S _D (ppm)	H ₂ S (ppm)	BOD (mg/l)	EBOD(mg/l)	V (fps)	T Sewage °C	T Manhole °C	T Shade °C
June 9, 1967	8:00 AM	1.0	0.3	10	147	220	1.27	26.0	26.7	22.0
	10:00 AM	1.0	0.4	13	126	144	1.48	26.4	27.2	27.5
	12:00 Noon	3.5	2.0	100	129	203	1.51	26.7	27.4	30.5
	2:00 PM	2.0	0.9	37	150	241	1.51	27.0	27.7	33.0
	4:00 PM	1.3	0.8	50	129	210	1.43	27.2	27.8	33.8
	6:00 PM	2.5	1.5	75	213	342	1.43	27.0	27.7	33.5
June 13th	8:00 AM	1.0	0.6	17	72	108	1.32	26.0	27.0	25.0
	10:00 AM	1.7	1.0	42	183	284	1.51	26.5	27.5	28.8
	12:00 Noon	2.0	1.4	62	265	423	1.51	26.9	27.5	30.0
	2:00 PM	1.3	0.7	37	134	215	1.48	27.0	27.5	32.0
	4:00 PM	1.2	0.9	19	106	173	1.45	27.3	27.7	32.9
July 8th	8:00 AM	2.0	1.4	31	180	331	1.31	29.0	30.7	27.7
	10:00 AM	1.8	1.0	21	182	335	1.51	29.0	30.7	32.0
	12:00 Noon	3.0	2.4	7100	245	465	1.61	29.5	30.8	34.0
	2:00 PM	2.8	2.0	63	211	410	1.53	29.8	31.0	35.5
	4:00 PM	1.8	1.2	47	176	342	1.48	29.8	31.0	37.0
	6:00 PM	1.5	1.0	31	216	426	1.45	30.0	31.0	37.0
July 13th	8:00 AM	2.8	2.3	95	190	371	1.48	29.9	30.5	32.0
	10:00 AM	4.0	3.2	222	200	391	1.45	29.9	30.5	29.8
	12:00 Noon	2.7	2.0	95	228	303	1.395	29.7	30.7	30.0
	2:00 PM	2.5	2.0	29	157	288	1.27	29.0	30.2	27.0
	4:00 PM	2.8	2.3	160	150	274	1.13	28.9	30.2	27.0
	6:00 PM	2.3	1.6	50	110	196	1.11	28.5	30.0	26.5
August 8th	8:00 AM	0.8	0.5	120	210	422	1.31	30.3	29.8	28.0
	10:00 AM	0.8	0.4	120	225	452	1.37	30.3	29.8	27.0
	12:00 Noon	0.7	0.3	135	215	433	1.345	30.3	29.3	26.8
	2:00 PM	0.4	0.2	41	180	354	1.17	30.0	29.3	25.0
	4:00 PM	0.1	-	-	115	219	1.02	29.5	29.5	24.5
	6:00 PM	-	-	-	200	368	1.0	29.0	29.5	24.0

SAMPLING ON ORANGE GROVE

Aug. 9, 66	Run	S _T	S _D	H ₂ S	B.O.D.	T _s	T _m	T sew	V (fps)
10:00	1	3.0	1.8	18.0	129	98.6	96.8	88.2	6.03
12:00	2	15.0	11.0	22.0	187	100.4	96.8	88.2	6.98
14:00	3	6.0	3.0	19.0	182	105.0	100.4	88.8	6.03
16:00	4	6.0	2.5	6.5	190	101.4	100.7	87.8	6.68

SAMPLING ON ROGER

Sept. 8th

10:00	1	0.1	0	0	158	91.4	88.7	85.5	4.11
12:00	2	0.1	0	1.8	164	93.2	89.3	86.0	4.25
14:00	3	0.2	0	1.0	120	95.0	88.7	87.0	4.03
16:00	4	0.1	0	1.0	148	96.0	87.8	87.0	3.97

SAMPLING ON PANTANO

Sept. 9th

10:00	1	0.2	0	3.4	198	92.3	87.8	88.7	4.22
12:00	2	0.2	0	2.6	180	96.3	88.7	88.7	3.92
14:00	3	0.1	0	2.6	144	96.0	87.8	88.7	3.57
16:00	4	0.2	0	2.6	190	96.0	88.7	88.7	3.42

SAMPLING ON CURTIS

July 29th

10:15	1	2.3		-	135	80.6	92.3	86.0	0.86
12:00	2	1.4		0.3	165	86.5	92.8	87.4	0.81
14:00	3	4.0		0.3	159	90.5	93.2	88.2	0.84
16:00	4	4.0		0.5	125	92.3	93.2	88.7	0.84

SAMPLING ON SUNSET

Aug. 4th

14:00	1	5.2			203	98.6		87.3	
16:00	2	5.0			142	99.0		86.9	

Aug. 10th

10:00	1	5.0		38.0	179	92.3	91.4	88.4	1.38
12:00	2	6.6	5.0	38.0	144	95.6	92.7	89.7	1.34
14:00	3	7.5		14.0	148	95.0	93.2	87.8	1.34
16:00	4	7.6		5.0	161	94.2	93.2	88.8	1.39

Sept. 10th

12:00	1	4.5	2.3		182			87.0	1.45
14:00	2	3.7	3.0		200			87.0	1.4
16:00	3		3.2		203			87.5	1.3

APPENDIX B

COMPUTATIONS RELATING H₂S TO EBOD, DISSOLVED
SULFIDES, VELOCITY AND TEMPERATURE

H ₂ S (ppm)	T _m (°C)	H ₂ S (Tm-20)	$\frac{EBOD}{V} S_D$
10	26.0	60.0	52.0
13	26.4	83.2	52.4
100	26.7	670.0	270.0
37	27.0	259.0	144.0
50	27.2	360.0	118.0
75	27.0	525.0	359.0
17	27.0	119.0	49.2
42	27.5	315.0	188.0
51	27.5	282.0	392.0
37	27.5	277.0	102.0
19	27.7	146.0	108.0
31	30.7	332.0	352.0
21	30.7	225.0	223.0
63	31.0	693.0	535.0
47	31.0	517.0	278.0
31	31.0	343.0	294.0
75	30.7	803.0	340.0
54	30.5	567.0	485.0
51	30.3	525.0	252.0
95	30.5	1000.0	576.0
222	30.5	2340.0	865.0
95	30.7	1015.0	435.0

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