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THE PROBLEM OF HYDROGEN SULPHIDE IN SEWERS

Dr. Richard D. Pomeroy PhD

2ND EDITION
Edited by A. G. Boon

Foreword

It is a pleasure and privilege to write a Foreword to this Booklet by Dr. Pomeroy, both because he is an acknowledged authority on the subject that he discusses in these pages, and also because of the esteem in which these Technical Publications by the Clay Pipe Development Association are held in this country. They represent an example to other industries of what can and should be done to inform their users.

The subject of Dr. Pomeroy's Paper is one which has not until recently attracted the attention it deserves in the U.K. There have been a number of incidents of corrosion or problems of smell in this country over the years which usually derived from unusual effluent conditions or exceptionally long retention times in pumped schemes. In 1966 one of the Stevenage "Notes on Water Pollution" dealt with the subject and indicated that Water Pollution Research Laboratory workers had found good correlation with Dr. Pomeroy's formulae for the accumulation of sulphide in sewage rising mains. However, the areas of the world where the problem has occupied the attention of engineers have been those hotter countries which have established sewerage systems, such as the United States, Australia and Southern Africa. Most of the research and clarification of the problems has come from engineers in those countries although as early as 1906 C.C. James described the condition in a book dealing with sewerage work in Egypt, India and the Far East. The only recent work in this country was undertaken at the Water Research Centre and related to oxygen injection into rising mains. With the current great expansion of the provision of sewerage systems in the Middle East it behoves engineers concerned with overseas sewerage projects to be well informed on the matter and this publication will undoubtedly help to achieve that.

The Booklet sets out the subject very clearly, starting with the production and effects of hydrogen sulphide, and dealing with its occurrence in sewage in a way which will illuminate the conditions inside a sewer pipe for the designer. Predictive methods for forecasting sulphide conditions and the rates of build-up are very thoroughly dealt with. All the equations developed for this are discussed including those for the full and the part full situations, and for rates of resulting corrosion. Examples of the use of these

equations make this section very useful for the designer.

Of course the Author recognises that accuracy in prediction of sulphide conditions in a sewer need not be relied upon if reliable materials capable of resisting corrosion are employed in the fabric of the sewer. In the section of his Paper dealing with this, the efficacy of vitrified clayware is rightly stressed. However, the means to prevent attack upon cementitious materials must be perfected and the characteristics of other pipe materials must be exploited since the present size limitations of 750mm bore on vitrified clay pipes with flexible joints means that they are not available to the engineer in all the sizes he needs.

In the nature of things of course the problems tend to be even more severe (and certainly more often noticed) in larger pipes. These are necessary in the larger sewerage systems as downstream trunk or outfall sewers and in existing systems large pipes may be essential as interceptors. In either case the retention time of the sewage is likely to be considerable before it reaches them and hence hydrogen sulphide production is very probable, particularly at high temperatures. Unfortunately, the newer materials which the engineer is forced to adopt for the larger sizes of pipe to counter likely corrosion, as a coating, a lining or the pipe body itself, do not have the track record extending over thousands of years that clay has! It is to be hoped that the engineering materials industry generally will continue to respond to the challenge of the hydrogen sulphide corrosion problem by development and improvement to provide the engineer with products whose long term dependability may be taken for granted.

There is no doubt that CPDA and Dr. Pomeroy have performed a very useful service at this particular juncture in publishing this booklet. It is to be hoped that all those concerned with sewerage will have the opportunity to read it.

Peter A. Banks
December 1976

John Taylor & Sons
Westminster, SW1P 1RY.

I am pleased that CPDA are re-issuing this valuable booklet and that it has been updated by Arthur Boon. New generations of designers need reminding of the old lessons and to be given the means of assessing the risks posed by hydrogen sulphide and the ability of their current materials to mitigate them.

In this latter respect vitrified clayware still stands supreme in its size range, now up to 1,000mm bore. Indeed the improvements both in pipe properties (notably strength) and adaptability of pipes to new user requirements have been substantial in the intervening years since the first edition. In the case of the other materials, necessary for the larger pipe sizes, coatings of cementitious pipes have been abandoned although linings continue to be reasonably effective. Plastics have made strides and experience has added much to the engineer's ability to specify the necessary characteristics.

However, in choosing materials, longevity is still the most important objective; "lay and forget" is the aim. Knowing all about the problem helps to ensure the choice is a correct one. This booklet serves admirably to ensure the engineer has that knowledge.

Peter A. Banks
June 1990

Acer John Taylor
Westminster, SW1H 0EX.

Dr. R. D. Pomeroy

Dr. Richard D. Pomeroy founded the firm of Pomeroy, Johnston and Bailey of California, U.S.A., specialists in water and waste technology.

Dr. Pomeroy is renowned throughout the world for his work in the field of hydrogen sulphide production and corrosion, and means for dealing with the problem. He has had numerous papers published over a thirty year period, culminating in writing the United States Environmental Protection Agency's "Process Design Manual for Sulfide Control in Sanitary Sewerage Systems", published in October, 1974. In the United States this document is recognised as the designers' guide for hydrogen sulphide problems.

In this booklet, written for the Clay Pipe Development Association, Dr. Pomeroy has further developed this subject and included published work from world-wide sources.

A. G. Boon

During the 32 years that Arthur Boon worked for WRC, he gained an international reputation for his research into, and knowledge of, waste water treatment processes and for the work he pioneered in the UK into the causes, consequences, and containment of sulphide corrosion of sewers. He co-operated with Dr. Richard Pomeroy and many other well-known experts to take part in the very successful IWPC seminar on "Septic Sewage: Problems and Solutions" held in 1979.

In September 1989, he joined Acer Consultants as a Director and has selected a team of experts to staff a new Process Design and Environmental Sciences office in Stevenage which is part of Acer Environmental. His expertise in these fields, together with the environmental aspects of water supply and sewage treatment, will continue to be of service to a wide range of national and international clients.

In editing this 2nd edition of Dr. Pomeroy's booklet, Arthur Boon has incorporated the results of research carried out since its first publication and brought in some additional detail.

Part 1

Production and effects

Hydrogen sulphide, H₂S, is a gas that is widespread in nature, and well-known because of its odour. It can arise from the decay of some kinds of organic matter, especially albumins. An example is the white of an egg, an albumin that can release large amounts of H₂S. The odour of H₂S is most commonly described as the odour of rotten eggs.

H₂S also occurs in many ground waters. Its presence in such waters is due not so much to breakdown of organic matter as to the bacterial reduction of sulphate. By this it is meant that certain bacteria are able to split oxygen from the sulphate ion, SO₄⁼, a common constituent of natural waters, and use it to oxidize organic matter. The sulphur is then left in the form of the sulphide ion, S⁼, which immediately changes by reaction with water to a mixture of H₂S and HS⁻ (read H S ion).

Physical-chemical properties of hydrogen sulphide

H₂S is a gas slightly heavier than air. It condenses to a liquid only at the low temperature of -62°C. It is fairly soluble in water. At 20°C, it can dissolve in pure water to the extent of 3850 milligrammes per litre (mg/l), or 2.7 litres of H₂S gas per litre of water. The solubility decreases about 2.5% for each degree increase of temperature. The stated solubility is the amount that will dissolve when the pure gas is brought into contact with pure water. From H₂S diluted with air, it will dissolve only in proportion to its concentration in the gas mixture. Thus, for example, air in which the concentration of H₂S is 0.1% (1000 parts per million, ppm) by volume of H₂S will, if brought to equilibrium with pure water at 20°C, produce a solution containing 3.85 mg/l. Stated differently, water containing 3.85 mg/l of H₂S can produce a concentration of 0.1%, or 1000 ppm, in air brought into contact with it. One mg/l in solution can produce a concentration of about 260 ppm by volume in the air if the temperature is 20°C, or 330ppm by volume if the temperature if 30°C.

When dissolved in water, hydrogen sulphide is partially ionized, so that it exists as a mixture of H₂S and HS⁻. The proportions depend principally upon the pH of the solution. In a typical natural water at a temperature of 20°C, and at pH 7.0, it is just 50% ionized; that is, half of it is present as HS⁻ and half as un-ionized H₂S. Table 1 shows the proportions ionized at other pH levels. Temperature and mineral

content of the water affect the degree of ionization, but only by a small amount. The sulphide ion, S⁼, also exists in water, but not in appreciable amounts except in solutions in which the pH is above 12. The solubility data given in the previous paragraph applies only to the equilibrium between the gas and the slightly acidic (low-pH) solution produced when it dissolves in pure water, or between the gas and the un-ionized H₂S in waters where the pH is not low.

TABLE 1
Proportions of H₂S and HS⁻ in Dissolved Sulphide

pH	Proportion of un-ionized H ₂ S (j factor)	Proportion of HS
5.0	0.99	0.01
6.0	0.91	0.09
6.2	0.86	0.14
6.4	0.80	0.20
6.6	0.72	0.28
6.8	0.61	0.39
7.0	0.50	0.50
7.2	0.39	0.61
7.4	0.28	0.72
7.6	0.20	0.80
7.8	0.14	0.86
8.0	0.09	0.91
8.2	0.059	0.941
8.4	0.039	0.961
8.6	0.025	0.975
8.8	0.016	0.986
9.0	0.010	0.99

Note: The proportion of un-ionised H₂S is referred to as the "j factor" when used in the predictive equations in Part 3 of this booklet

Toxicity of H₂S

Everyone is familiar with the odour of H₂S in its natural occurrences. Because of this familiarity there has been a lack of appreciation of its toxic character, and many deaths have resulted from carelessness in dealing with it. The threshold odour concentration of H₂S is very low - between 1 and 10 ng/l. It is potentially very dangerous because its smell is quickly lost as the concentration increases. In oil refineries, tanneries, viscose plants, and many other chemical industries, men have occasionally been exposed to H₂S in concentrations that have resulted in death, and there have been many deaths in sewers on this account. Even the H₂S from swamps and from natural hot springs can be deadly. Several lives have

been lost as a result of bathing in hot sulphurous spring waters in closed rooms. There is evidence that a concentration of 0.03% (300 parts per million) of H₂S in the air has caused death. It should be noted that this is the concentration that could arise from water containing 1 mg/l of un-ionized H₂S. Fortunately these hazards are now more widely recognised, and the frequency of fatal accidents has been greatly reduced.

Other forms of sulphide in waste waters

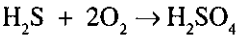
Up to this point the discussion has been about hydrogen sulphide and its ionized form, HS⁻. Sulphur combines with metals, too, producing compounds which are generally insoluble, such as zinc sulphide, ZnS, two copper sulphides, CuS and Cu₂S, several iron sulphides, etc. In all such combinations, as well as in H₂S and HS⁻, sulphur is in an electronegative state. In this state it is simply called sulphide.

In waste waters of normal pH values (6.5 to 8), sulphide may be present partly in solution as a mixture of H₂S and HS⁻, and partly as insoluble metallic sulphides carried along as part of the suspended solids. In analyses of waste waters, a distinction is made between dissolved sulphide and insoluble sulphide. The sum of these forms is called total sulphide. The concentrations are normally expressed in terms of the sulphur content. The amount of insoluble metallic sulphide does not ordinarily exceed 0.2 to 0.3 mg/l if the sewage is of residential origin, but the amount may be larger in sewers containing trade wastes.

Sulphide in waste waters reacts with dissolved oxygen, mostly by biological processes. Under the conditions prevailing in sewers, the principal biological oxidation product is thiosulphate. If oxidizing bacteria are abundant in the waste water, and dissolved oxygen is also present, sulphide may be oxidized at a rate of 1 mg/l in five minutes, but in less active sewage, as for example fresh domestic sewage, the same reaction may take an hour. Sulphide can also react chemically with dissolved oxygen, that is, without the intervention of bacteria. This reaction is slow, producing a variety of products, including sulphur, thiosulphate, sulphite, sulphate, and others. The rate of reaction depends greatly on the presence of catalysts such as iron ions and the products produced are influenced by the pH value.

H₂S that escapes as a gas from solution in a sewer may be oxidized on exposed surfaces. If the surfaces are quite dry, free sulphur may be formed, but under

moist conditions a species of bacteria named *Thiobacillus concretivorus* oxidizes it to sulphuric acid by the reaction:



The acid causes corrosive damage to vulnerable materials.

The process of oxidation of hydrogen sulphide is a complex series of reactions involving many members of the species Thiobacilli, each with its own optimum growth rate at a given pH value. Some of the Thiobacilli can remain active in solutions containing up to 7% of H₂SO₄ (pH about 0.2).

The whole process of oxidation of hydrogen sulphide by bacteria and the factors which influence the bacterial corrosion of concrete in water are complex. Further reference may be made to the papers by Fjerdingstad (Ref. 1) and by Chen and Morris (Ref. 2) listed on page 24.

The occurrence of sulphide in sewage

Sewage contains bacteria, sulphate, and organic matter, so it has the elements required for sulphide generation. One further condition is necessary. The reduction of sulphate to sulphide can occur only under anaerobic conditions. In the absence of dissolved oxygen, nitrate can provide oxygen for bacteria and can thus prevent septic conditions developing. When all the "oxygen" provided by the nitrate anions, has been consumed by the facultative anaerobic bacteria, the conditions will be strictly anaerobic. This is a state that can develop in sewage, because many kinds of bacteria are present that rapidly consume dissolved oxygen and "oxygen" from nitrate. However, if the sewer is partly filled, the water surface exposed to the air absorbs oxygen. The rate of absorption is slow, and the bacterial action may deplete it to concentrations of a few tenths of a mg/l, or sometimes only a few hundredths. Still, where any dissolved oxygen or nitrate at all is present there can be no reduction of sulphate.

A layer of slime builds up on the submerged pipe wall in a sewer, very thin where the stream is swift, but a millimetre or more in thickness where it is slow. The slime layer is the site of intense micro-biological action, and it is here that anaerobic conditions develop, and that sulphate reduction and sulphide generation can take place.

There is frequently an aerobic (oxygen containing)

zone in the slime layer where it is in contact with the flowing stream. In a typical case the aerobic zone may extend into the slime layer to a depth of only 0.1mm, but it may be deeper if the stream carries several mg/l of dissolved oxygen. Sulphate and part of the organic nutrients diffuse through the aerobic zone and into deeper layers, thus supplying the requirements of bacteria that produce sulphide, and so it comes about that sulphide generation can occur even when the stream contains dissolved oxygen, but is unlikely to occur if nitrate were present as it will diffuse into the lower layers of the slime and provide a source of oxygen to prevent septicity. The zone where sulphide is produced is generally only a few tenths of a millimetre in thickness. The sulphate or the organic nutrients are used up in that distance and unless the slime layer is quite thin, there is a deeper layer that is relatively inactive.

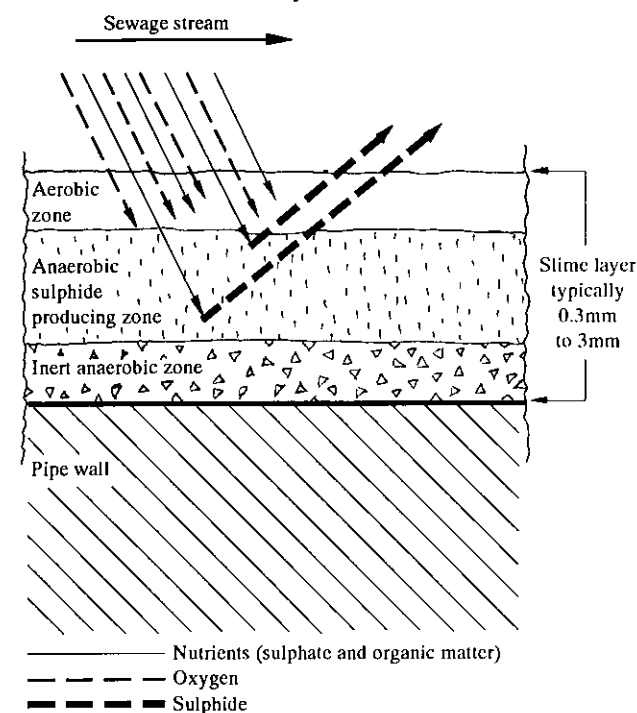
Sulphide diffusing out of the zone where it is produced is at least in part oxidized to thiosulphate in the aerobic zone. If much oxygen is present, the sulphide will all be oxidized there, but if the oxygen concentration is low, then part of the sulphide will escape from the slime layer into the stream. When this condition prevails, the sewer may show "sulphide build-up", meaning that the concentration in the stream will progressively increase as the sewage moves down the pipeline. However, oxidation occurs to some extent in the stream, and some H_2S escapes to the atmosphere, so the concentration tends to approach a steady state condition where the losses are equal to the rate that sulphide is produced.

Figure 1 shows a cross section view of the slime layer of a sewer, pictured on a magnified scale. Oxygen, organic nutrients and sulphate are seen to be diffusing into the slime layer. Oxygen and part of the organic nutrients are used up in the aerobic zone. Sulphate and the remainder of the organic nutrients are diffusing farther, reaching the anaerobic zone. The dense population of anaerobic bacteria found there, especially the species *Desulfovibrio desulfuricans*, are bringing about the reaction that produces sulphide, at a rate determined by the rate that the nutrients can diffuse into that zone. Sulphide is diffusing outward from the slime layer, part of it being oxidized in the aerobic zone and part escaping into the stream.

The concentration of oxygen necessary to prevent any sulphide build-up may vary widely, depending upon a number of conditions. The velocity of the stream is one factor. At low velocity the motion of the

water is not very efficient in carrying oxygen to the slime layer, and under these conditions a higher oxygen concentration is necessary if sulphide is to be barred from the stream than when the stream is swift. In a typical case it may require 0.5 mg/l of dissolved oxygen to prevent sulphide build-up, but under some conditions as much as 1.0 mg/l, or even more, may be required.

FIGURE 1
Cross section of slime layer



Note: The direction of diffusion of nutrients, oxygen, and sulphide in the slime layer is perpendicular to the pipe wall. The lines are shown as oblique to lessen confusion in the representation.

Forecasting sulphide build-up

A characteristic of the generation of sulphide in sewers is its sporadic occurrence. In the early decades of this century, this seemingly random appearance of sulphide in sewers was the subject of much speculation. Now that the mechanism of sulphide build-up is better understood, the reasons are clearer. It is evident that a major determining factor is the amount of oxygen (both dissolved and available from nitrate) in the sewage stream. If the oxygen concentration is high, there will be no sulphide build-up; if it is low, then sulphide build-up is expected.

The rate of sulphide production is influenced not only by oxygen concentration, but by other factors as

well. The rate increases with increase of temperature, and it depends in a complex way on the concentrations of organic nutrients and of sulphate. The rate of sulphide production can be limited by a scarcity of either sulphate or organic matter. Since both are consumed in the biological reactions that produce sulphide, they are required in a certain ratio. If there is an excess of organic nutrients, then the rate is limited by the amount of sulphate and if there is an excess of sulphate it is limited by the amount of organic nutrients.

The organic nutrients available for sulphide production in sewers have not been identified, but they must be in solution, since they must diffuse to the sulphide producing zone. It has been assumed that in typical municipal sewage the organic nutrients for sulphide generation are proportional to the biochemical oxygen demand or BOD (Pomeroy and Bowlus, 1946 - Ref. 3; Davy, 1950 - Ref. 4) or to the chemical oxygen demand or COD (Boon and Lister, 1975 - Ref. 5).

The effects of velocity on sulphide build-up are complex. At low velocity, solids may settle and move slowly and intermittently along the bottom. The loosely deposited solids quickly become depleted of oxygen, and sulphide generation proceeds until the depletion of sulphate or organic nutrients. If the solids are then disturbed by the motion of the water, sulphide is released into the stream in greater amount than would result from the process depicted in Figure 1. Higher velocities prevent this from happening, and also increase oxygen absorption into the stream, increase the rate of oxygen transfer to the slime layer, and shorten the time that the sewage spends in transit, all of which lead to lower sulphide concentrations. On the other hand, at low velocities, and especially if the sewage is intermittently stationary, as is usually the case in pressure mains from pumping stations, nutrients may become depleted in the water adjacent to the slime layer, thus retarding sulphide generation. An increase of velocity in a completely filled pipe will, up to a point, increase sulphide generation.

In the light of present knowledge, an equation could be written that would express the rate of sulphide build-up as a function of the various factors that influence generation by the slime layer and the losses by oxidation and escape to the air. Such an equation would not be very useful, because of the difficulty of securing the input information that would

be required. Most important would be the dissolved oxygen concentration. An accurate prediction of dissolved oxygen would require a detailed history of the sewage for an hour or so upstream from a point where a prediction of sulphide build-up would be attempted. Absorption of oxygen at the surface of the stream can be predicted if slope, pipe size and flow quantity are known, but extra oxygen will be added at junctions, drops, and other points of turbulence, and it is difficult to predict the rate at which oxygen will be consumed.

The only practical approach to the problem of predictions is to limit such attempts to the restricted case that the unpredictable factors are favourable for build-up. That is to say, it will be assumed that sufficient sulphate is present so that it is not limiting, that oxygen concentration is low, that no nitrate is present either derived from the water supply or from industrial discharges, and that there is no toxic condition or other factor that inhibits the action of the slime layer.

The earliest attempts to predict sulphide build-up were limited to yes-or-no answers; there would or would not be build-up (Pomeroy and Bowlus, 1946 - Ref. 3; Davy, 1950 - Ref. 4). It was recognised, however, that quantitative forecasts might be possible for the restricted case of sewage in pressure mains and other completely filled pipes, where it is denied any contact with air. Sewage pumped into a pressure main often contains dissolved oxygen which may result from its fall into the wet well or from other causes, and on this account there may be no sulphide build-up initially, but after a time the dissolved oxygen and nitrate "oxygen" will be completely depleted and then the maximum sulphide producing capability of the slime layer will be displayed.

When the sewage becomes completely anaerobic, generation occurs not only at the pipe wall but also in the stream. The amount produced in the stream, however, is small in comparison with the output by the slime layer except in very large pipes.

In a small pipe of, say, 100mm diameter, troublesome sulphide concentrations may arise even where the retention time of the sewage in the main is as little as ten minutes. In larger mains the build-up rate is slower, but significant amounts are likely to be produced within 20 to 30 minutes in a pipe of one metre diameter.

Forecasting sulphide conditions

The equations which have been proposed for the forecasting of sulphide production in filled pipes and part-filled pipes, and for the prediction of rates of corrosion are set out and fully discussed in Part 3 of this booklet.

The formulae that have been proposed for predicting rates of sulphide build-up in gravity sewers are complicated, but attention may be given to a rather crude qualitative indicator that will aid in foreseeing future sulphide conditions (US EPA Sulfide Control Manual - Ref. 6). It is called the "Z formula", and is as follows:

Z = 3[EBOD] / (S^1/2 Q^1/3) * P / b

in which
EBOD = effective BOD, which is defined as the standard 5-day, 20°C biochemical oxygen demand multiplied by the temperature factor 1.07^(T-20)

where
T = Sewage temperature, °C
S = slope of the pipeline, m/100m
Q = sewage flow, litres/sec.
P/b = ratio of wetted perimeter (P) of the pipe wall to surface width (b) of the stream.

Before interpreting the meaning of the Z quantity, it is necessary to emphasize that neither the Z formula nor any other equation can, when applied only to a particular reach of sewer, provide an answer as to what the sulphide conditions will be in that reach, because upstream contributions cannot be ignored. Upstream conditions may include pressure mains in which sulphide build-up is probable, gravity sewers having flow conditions that allow build-up, or discharges of sulphide-bearing industrial wastes. What the equations do indicate is whether there is likely to be a tendency for build-up in the reach for which the calculations are made.

With these important warnings as to the limited application of the formula, it may be said that where a certain Z value is characteristic of conditions existing for two or three km upstream from a point of interest, and there is not an upstream sulphide source such as a pressure main, the following conditions may be reasonably expected.

TABLE 2
Z values and characteristic conditions

Z value	Conditions likely to be observed
below 5,000	Sulphide rarely present or only in very small concentrations
around 7,500	Peak concentrations of a few tenths of a mg/l of dissolved sulphide may be reached; slight corrosion of concrete and masonry in structures may occur. Substantial corrosion may sometimes be observed in the vicinity of points of turbulence.
around 10,000	Sulphide sometimes may develop in sufficient proportion materially to increase odours, and concrete and masonry structures may suffer substantial damage, especially near points of turbulence.
around 15,000	Odour of sewage will increase markedly at times. Rapid attack of concrete structures is to be expected at points of turbulence, with significant attack elsewhere. With concrete pipe of 25mm wall thickness, there is a strong possibility of failure within 25 years.
at or above 25,000	Dissolved sulphide will be present most of the time, and small concrete pipes possibly will fail in 5-10 years.

The Z formula is limited in its range of application. In large flows, generally above 2000 l/sec, there may be sulphide build-up even when Z is as low as 5000, but only at a very slow rate. On the other hand, with flows below 3 l/sec there may be no build-up even at relatively high Z values. In small sewers, the principal determining factor is the accumulation of debris in the bottom of the pipe. Such accumulations retard the flow until velocities are much lower than assumed in deriving the equations. The ability of the pipe to keep itself free from such accumulations must not be judged by the flow velocity that would prevail when the pipe flows half full, but by the peak velocities that will be reached at least once each day under the actual operating conditions.

A further complication in the application of predictive equations is the fact that the various quantities in the equation, with the exception of the slope of the pipe, are variable. In addition to random fluctuations, there are seasonal temperature changes and diurnal changes of flow and sewage strength. It is recommended that the average temperature for the warmest quarter of the year and the average sewage strength for the highest six hours of the day, with the corresponding flow, be used in developing a climatic Z value. If the formula then indicates that sulphide problems are likely, this should be taken as a warning that the system should be examined more carefully using the more complex equations for sulphide build-up rates, and judging the suitability of construction materials from the standpoint of corrosion resistance. In the size ranges for which corrosion resistant pipes are available, such pipes will generally be used if there is uncertainty about future sulphide conditions.

It may be noted that Z becomes infinity in a completely filled pipe. This is because filled pipes allow no exposure of the wastewater to oxygen, and sulphide build-up can proceed at a rate determined by the temperature and nutrient supply to the sulphide-producing bacteria. Even a relatively small pressure main can produce enough sulphide to cause damaging concentrations in a much larger flow to which it is a tributary, unless sulphide control measures are applied. Most of the very serious sulphide conditions that have been encountered in sewers have been due to sulphide produced in pressure mains.

Sulphide build-up rates in pressure mains

In pressure mains where detention times are longer than, say 10 minutes, there can be considerable sulphide build-up even in U.K. conditions, as strictly anaerobic conditions are most likely to prevail. This can sometimes also occur where unduly large wet wells retain sewage for long periods of time.

When the pump begins to operate, the heavy sulphide concentration is discharged, usually into gravity sewer, where serious corrosion can take place if acid susceptible materials are used for the pipeline. These sources of trouble are often disregarded by many engineers when designing pumping stations and pressure mains.

Three equations have been proposed for the forecasting of sulphide production in filled pipes, and are shown on page 18 and fully discussed thereafter.

Since the conditions in many pressure mains do not conform to the limitations under which the equations are applicable, many such mains produce less sulphide than the amount indicated by the equations. Where detention times are short, less than, say, 10 minutes, there is often little or no sulphide build-up, since a strictly anaerobic condition is not likely to be attained.

Forecasting sulphide build-up rates in partly filled pipes

The equations mentioned in the previous section yield fairly good predictions for sulphide build-up in filled pipes, provided dissolved oxygen and nitrate are entirely depleted, sulphate is present in adequate amounts, and the slime layer is in a fully developed and active state. The most practical forecast that can be made for a partly filled pipe must be similarly limited, and, in addition, it will be assumed that some oxygen will be present, but only in a deprivation range of less than 0.5 mg/l. Since many sewers contain more than enough dissolved oxygen to prevent sulphide generation, most gravity sewers will show less build-up than the amount forecast under the limiting assumption. There is little prospect that a practical equation can be devised that will do more than predict the largest concentration likely to be encountered, but this is the quantity that the engineer will need to consider unless there is good reason to believe that the sewage will be well enough aerated to suppress any build-up.

Aeration in partly filled pipes

The re-aeration rate of sewage flowing along a partially-filled channel can be calculated and is discussed by Boon (Ref. 7) as follows:-

Several formulae have been proposed and are listed below.

Pomeroy et al (Ref. 6) proposed the following:

Rf = 0.96 [1 + (0.17u^2) / (9.81d_m)] * 1.07^(T-20) * (M1u)^3/8 * d_m^-1 * (Cs - C) (1)

Meyer et al (Ref. 8) quoting Thistlethwayte (Ref. 9) suggested that:

Rf = 60 * 0.121 * alpha * (M2u)^0.408 * d_m^-1 * (Cs - C) (2)

where:
Rf = re-aeration rate of sewage (mg O2/l h)
u = velocity of sewage (m/s)

d_m = mean hydraulic depth (m), which is equal to unit volume divided by its surface area
 M_1 = slope of the energy line of the sewage (m/100m)
 M_2 = as above but with changed units (m/m)
 T = sewage temperature °C
 C_s = saturation concentration of dissolved oxygen in equilibrium with the atmosphere (mg/l)
 C = dissolved oxygen concentration in the sewage (mg/l)
 α = ratio of re-aeration rate in clean water to that in sewage.

An alternative to these equations would be to use one which was derived for streams and rivers and which was validated by WPRL in channels 13 cm wide and deep with a slope of 1 in 270 (i.e. similar in dimensions to a "standard" small sewer).

The equation proposed by Owens et al (Ref. 10) is as follows:

$$R_r = 0.22 \alpha u^{0.67} d_m^{-1.85} 1.024^{(T-20)} (C_s - C) \quad (3)$$

The value of α for Equation 2 was stated to be within the range 0.2 to 0.3 whereas studies under similar conditions to compare re-aeration rated in clean water and sewage by WPRL showed that α varied from 0.75 to 0.5 depending on the concentration of surface-active agent present within the range 0.1 to 10 mg/l respectively; for sewage it would be reasonable to assume that α was equal to 0.5.

Examination of these three equations shows that none has all the variables included that might be expected to affect re-aeration. Equation 1 takes into account most of the factors likely to affect re-aeration (including the Froude Number $u/(gd_m)^{1/2}$) except that the effect of "surfactants" is only included as an empirical coefficient of 0.96. Equation 2 takes no account of temperature effects which can be important particularly as the exchange (or mass-transfer) rate will increase with temperature by about 2% per °C (between 5 and 25°C) while C_s decreases by the same rate.

Equation 3 however makes no allowance for the effect of changes in slope and may only be applicable for large diameter sewers with shallow slopes.

In Table 3, the effects of using each equation to calculate values of re-aeration rates are given for typical gravity sewers (assuming that they are half-filled and cylindrical in shape so that $d_m = d/2.55$ where d is the pipe diameter (m)). The results indicate

that the rates are significantly affected by the values of α selected and that reasonable agreement would have been obtained if equations 1 and 2 had α values of 0.5 in place of 0.96 and 0.25 respectively and if Equation 2 had included a coefficient related to temperature corresponding to that used in Equation 1.

TABLE 3
Examples of re-aeration rates of sewage in half-filled cylindrical gravity sewers calculated from Equations 1, 2 and 3 assuming a temperature of 15°C and a DO of 10% of saturation value

Pipe diameter (m)	Velocity (m/s)	Slope (m/100m)	Re-aeration rates (mg/l h)		
			Equation 1	Equation 2	Equation 3
			Pomeroy	Mayer/Thistlethwayte	Owens
0.25	{ 0.75 }	0.4	42	16	54
	{ 1.00 }		52	18	65
	{ 1.25 }		62	19	76
0.50	{ 0.75 }	0.4	21	8	15
	{ 1.00 }		24	9	18
	{ 1.25 }		27	10	21
0.75	{ 0.75 }	0.4	14	5	7
	{ 1.00 }		16	6	9
	{ 1.25 }		18	6	10
1.00	{ 0.75 }	0.4	10	4	4
	{ 1.00 }		12	4	5
	{ 1.25 }		13	5	6
0.25	{ 0.75 }	1.0	62	23	54
	{ 1.00 }		74	26	65
	{ 1.25 }		87	28	75
1.00	{ 0.75 }	0.25	9	3	4
	{ 1.00 }		10	4	5
	{ 1.25 }		11	4	6

For sulphide not to be formed, the re-aeration rate must exceed the demand rate. Studies in the UK (Ref. 11) and elsewhere (Ref. 6) have shown that the rate of uptake of dissolved oxygen by micro-organisms present in domestic sewage varies from about 2 mg/l h at 15°C and may increase to values about 20 mg/l h as the sewage "ages" within the sewerage system under aerobic conditions; the average rate would be about 14 mg/l h at 15°C. Where sewage contains a proportion of industrial waste waters or has a significantly lower BOD compared with domestic sewage (which may have a BOD about 400 mg/l) data from the U.K. have indicated the average uptake rate

to be about 6 mg/l h at 15°C. Respiration rates of slimes growing aerobically on submerged walls of sewers have been found to be about 700 mg/m² surface area per h at 15°C irrespective of the BOD of the sewage (within the range 90 to 780 mg/l). From these data it can be calculated that the total oxygen demand rate (in a half-filled sewer of cylindrical shape) of sewage at 15°C with an average respiration rate 6 mg/l h would be as follows:

TABLE 4
Respiration and oxygen demand rates

Pipe diameter (m)	Respiration rates (mg/l h)		Total DO demand rate (mg/l h)
	Slimes on surfaces	Sewage	
0.25	11.2	6	17
0.50	5.6	6	12
0.75	3.7	6	10
1.00	2.8	6	9

Comparison of the total demand rates for dissolved oxygen in Table 4 with the re-aeration rates given in Table 3, indicates that sewage should remain aerobic except for shallow slopes in large diameter sewers irrespective of which equation is used to make the calculation. However, there is clearly a need to collect more data to establish the correct equation that will provide the most accurate estimate of the re-aeration rates over a wide range of operational variables (including temperature and BOD of sewage).

Sulphide build-up in small sewers

Where the flow depth is less than about 50 millimetres, as in small collecting sewers, the sulphide build-up equations are not very useful. Even if the sewage is held motionless, there will be no sulphide build-up if the depth is less than 10 to 20mm, because there is a basic rate of oxygen absorption even in stationary water.

The flow can be highly variable in small diameter pipelines, alternately wetting and exposing surfaces where a well oxidized slime layer develops. Also, there are frequent connections along the way, adding aerated flows. Because of the combined effect of these factors, there may be no sulphide build-up even though the equations would predict a high rate of build-up.

Severe sulphide conditions are nevertheless sometimes observed in small sewers. The pipes, if corrodable, are damaged, and the sulphide produced there may also cause problems farther downstream.

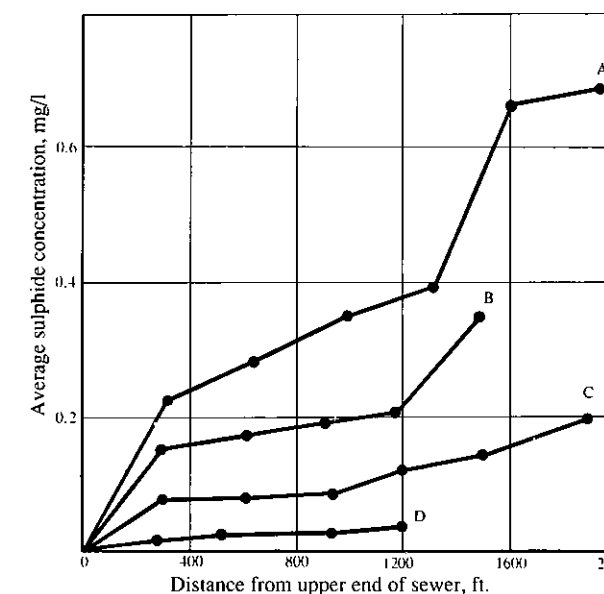
The determining factor seems to be the extent to which the pipeline becomes fouled with solids. If piles of paper and other debris build-up in the pipe, the sewage meanders through the mass, or passes through a series of semi-stagnant pools. The flow in small sewers is highly variable, however, and the surges of flow may move the solids intermittently down the pipe if the pipe slope exceeds some minimum value.

In a research project undertaken in California (USA), sulphide concentrations were measured in collecting sewers in residential areas, where the homes were mostly single-family dwellings (Ref. 6). The average over-all frequency of connected residential units was one per 10 m. Sulphide concentrations were measured at successive manholes as far downstream as there was a reasonably uniform slope and no junctions other than from service laterals. Usually two series of tests were made in each sewer.

The data were divided into slope classes and averaged. The results are shown graphically in Figure 2. It is evident that the laying of sewers at quite flat slopes, as is practiced in some areas, results in quite unsatisfactory conditions.

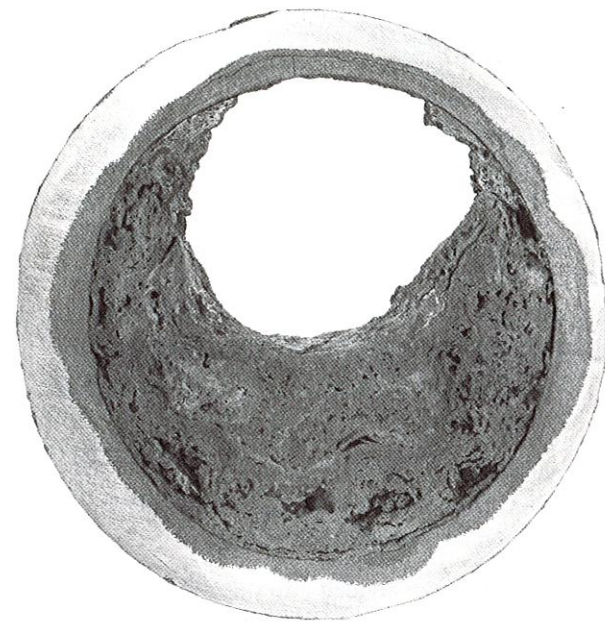
FIGURE 2
Sulphide Occurrence in Small Sewers

Line	Sewers %		Number of sewers	Average Results	
	Range	Avg.		B.O.D.	Temp. °C
A	0.20-0.25	0.23	18	253	24.7
B	0.32-0.46	0.40	22	212	24.4
C	0.52-0.64	0.57	16	178	24.7
D	0.72-1.20	0.90	8	184	24.3



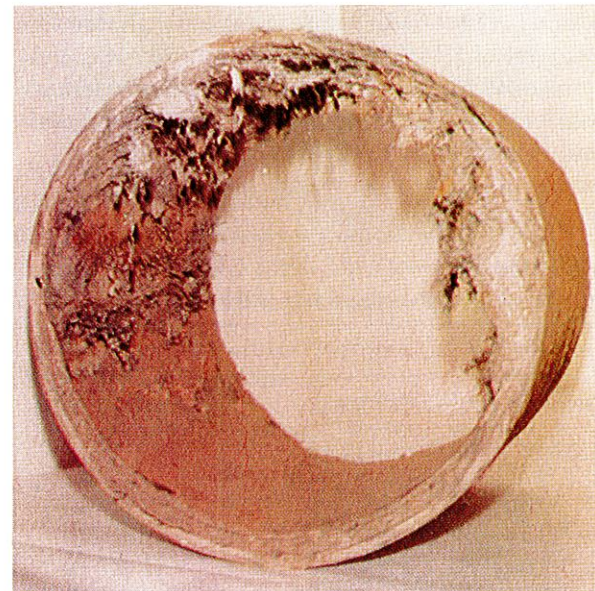
Reproduced from "Sulphide in Sanitary Sewerage Systems", by permission of U.S. Environmental Protection Agency.

FIGURE 3



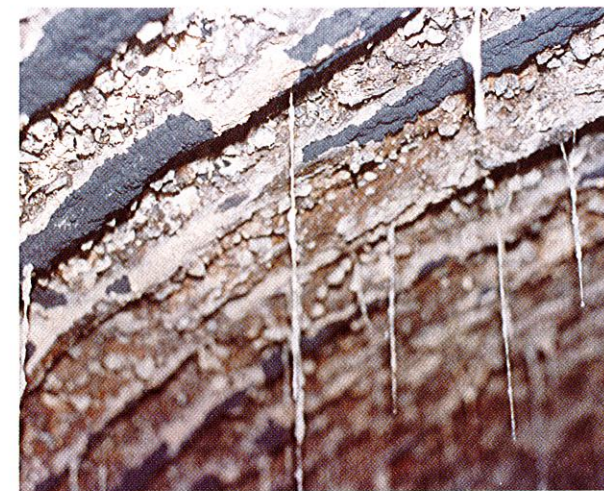
100 mm diameter cast iron pumping main after being in service for 25 years. The corrosion is due to graphitization.

FIGURE 5



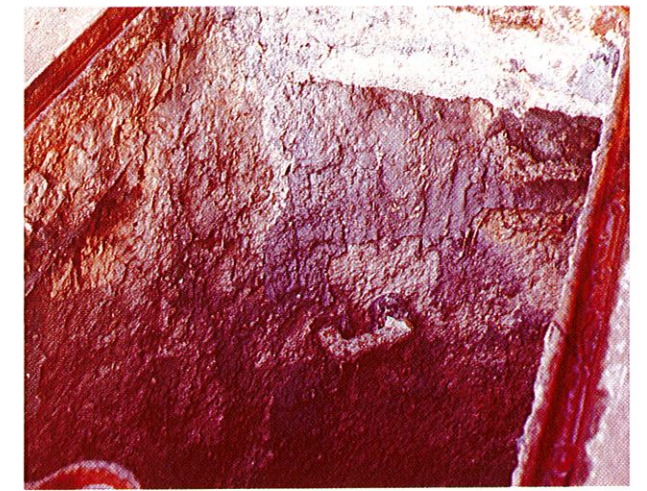
235 mm diameter asbestos cement pipe which was bitumen lined, showing the effects of 14 years of acid attack.

FIGURE 7



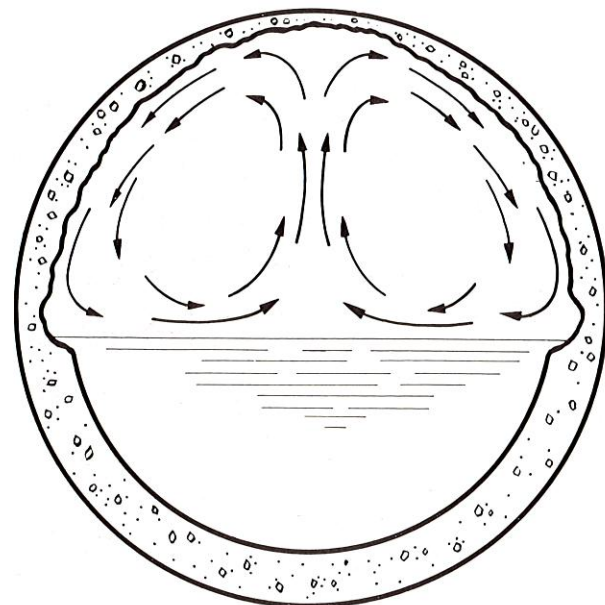
Exposed aggregate and reinforcement in a concrete pipe. The concrete was attacked by sulphuric acid oxidised from atmospheric hydrogen sulphide in the presence of moisture and the reinforcement attacked directly by atmospheric hydrogen sulphide.

FIGURE 9



Corrosion of a wet well where septic sewage was continually present, 5 years after construction. The rendering had been renewed and coated with a coal-tar paint only 2 years before this photograph was taken.

FIGURE 4



Unequal distribution of corrosion in a concrete sewer.

Reproduced from "Sulfide Control in Sanitary Sewage Systems", by permission of United States Environmental Protection Agency.

FIGURE 6



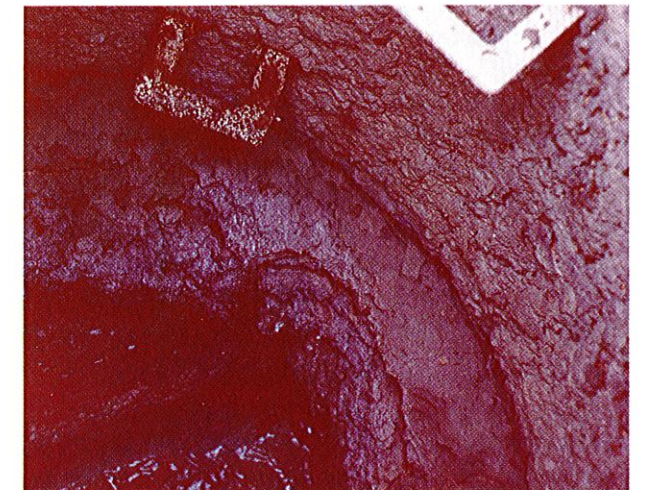
Remainder of bottom third of 225 mm O-G jointed concrete pipe from a sewer downstream of a pumping main discharge which had failed after less than 10 years service. The aggregate exposed after the cement had been attacked by sulphuric acid oxidised from atmospheric hydrogen sulphide in the presence of moisture is clearly visible.

FIGURE 8



Attack by sulphuric acid oxidised from atmospheric hydrogen sulphide in the presence of moisture at a pressure main outfall. Most of the mortar between the clay bricks has disappeared and the concrete benching has been severely attacked.

FIGURE 10



Corrosion of 200 mm concrete pipe, benching and manhole walls by sulphuric acid oxidised from atmospheric hydrogen sulphide in the presence of moisture, evident only 5 years after construction.

Corrosive effects of H_2S

It was mentioned in a previous section that H_2S can be oxidized biologically on moist surfaces to produce H_2SO_4 . Well ventilated structures may be kept dry enough to prevent this biological action from occurring, but the wall of a sewer is usually moist. The temperature of sewage is, on the average somewhat higher than the temperature of the surrounding earth. This is true at least at certain seasons in all sewers. Because of this temperature difference, water vapour escapes from the sewage stream and condenses on the exposed wall of the pipe. Where the sewage contains H_2S and the inside wall is moist, the Thiobacilli invariably appear and sulphuric acid is produced. Pipes made of cement bonded materials and of iron or steel, or any other material subject to attack by sulphuric acid, will be corroded.

There have been numerous cases of severe damage to concrete pipes on this account, where it has been necessary to replace the pipes before the expiration of the intended life. In extreme cases, concrete pipes have collapsed in as little as three years. Only the portion of the pipe exposed above the sewage is attacked.

It is not necessary for sulphide concentrations to be very high to cause corrosion. In the immediate vicinity of a point of high turbulence, as at a drop or a junction, an *average* dissolved sulphide concentration of 0.01 mg/l can cause serious corrosive damage. Under normal flow conditions in a large sewer an average of 0.1 mg/l of dissolved sulphide may be tolerable, or 0.03 to 0.05 mg/l in a small sewer. Because of the variability of sulphide concentrations, the peaks may be ten times as great as these averages. Tests carried out at the inlet to a sewage treatment works, where sewage (which contained 2 to 6 mg H_2S litre) cascaded 0.75m down into a wet well, resulted in 6% (v/v) sulphuric acid formation on the exposed walls when the temperature was 18°C.

The effect on cast iron is illustrated by Figure 3, a photograph of a pipe that served for 25 years as a pressure main from a pumping station. The inside diameter is 100mm and the wall thickness is 13mm. The pipe shown in the picture was near the end of the main in a location where it was only partly filled, this being a much more corrosive condition than where the pipe is completely filled. Corrosion has proceeded by

the process known as graphitization, in which the crystals of pure iron are dissolved out, leaving a weak, porous structure consisting principally of the carbides of iron. The zone of graphitization is easily seen. Despite the exceptionally thick wall, graphitization had penetrated all the way through the wall in some places necessitating replacement of the pipe.

The corrosion product is 42mm thick at the bottom, and occupies 70% of the cross-sectional area of the pipe. It is made up largely of iron sulphides. It occupies a volume of many times greater than the volume of metal that was dissolved. Despite its porous structure, the product is quite hard. Often a pipe like this is rendered useless because of the bulk of the accumulated iron sulphide.

The action of sulphuric acid on concrete converts it to a pasty mass consisting largely of calcium sulphate and the residual sand and gravel used in making the pipe. If the acid is formed very slowly, substantially all of it will react. However, if it is formed rapidly as a result of high H_2S concentrations, it can react only as fast as it can diffuse through the pasty layer. If there is much condensed moisture migrating down the pipe wall, a major part of the acid may make its way back into the stream, where it changes again to sulphate ions. (This cycling of the sulphur does not have any net effect on the pH of the sewage).

Where the sidewall is intermittently submerged, the pasty layer is washed away. Acid migrating down the wall can react rapidly with the bare concrete and thus there may be a deeply corroded zone between high and low water. Except for this waterline zone, the deepest penetration is normally observed at the crown of the pipe. This is believed to be due to the prevailing air currents caused by the temperature difference between the water and the pipe wall. Figure 4 shows the usual pattern of concrete pipe corrosion. Figure 6 illustrates the effect of the corrosion pattern drawn in Figure 4 with the remainder of part of a U.K. pipe. Figure 5 shows a corroded asbestos-cement pipe from the Middle East. Figure 7 illustrates corrosion to a reinforced concrete pipe from the U.S.A. Figures 8, 9 and 10 show various forms of attack on concrete, rendering and mortar in the U.K. Equations developed to forecast rates of corrosion are shown on pages 22 and 23.

Strategies for dealing with sulphide conditions in sewers

The amount of sulphide that can be produced is strongly influenced by choices that are made in respect to sewer routings, slopes, pipe sizes, pumping or not pumping, and other design features. Furthermore, the choice of materials of construction will determine whether or not there will be deterioration in those places where sulphide does appear.

A sewerage system using pipes which may be attacked by sulphuric acid should be essentially sulphide-free. Sometimes this can be achieved by increasing the dissolved oxygen content of the sewage. A condition of sulphide generation in a pressure main can often be remedied by the injection of compressed air. This is a practical method, provided that the pressure main has a continuous upward slope. Air applied at a low point will yield oxygen to the water as the bubbles pass up the pipe. If the pipe rises at a gentle slope of, say, 1%, the bubbles may pass without creating enough turbulence to supply dissolved oxygen as fast as the waste water requires it and the generation of sulphide may not be prevented. The amount of air that will be needed in any given case can be estimated by a formula that has been published. (United States EPA Sulfide Control Manual, page 5-8 - Ref. 6).

Instead of air, refined oxygen may be used, thus greatly increasing the rate of dissolving. However, even with pure oxygen injection, sulphide generation has been known to continue in a pressure main with very little slope. A favourable method for applying oxygen is to inject it on the delivery side of the pump at times when it is operating, taking advantage of the high velocity of the sewage and the maximum hydrostatic pressure. This method has been explored by the Water Research Centre, and several installations are in operation.

Addition of oxygen to the atmosphere of partly filled pipes has been suggested. There is little chance that this procedure will be fruitful. The exchange between the sewer air and the outside atmosphere is so great due to the rise and fall of the liquid level, and to the downstream draught, that a high proportion of the oxygen would be wasted. Even the presence of a pure oxygen atmosphere in the sewer would not prevent sulphide build-up in all cases.

Another method to increase the dissolved oxygen concentration is to add hydrogen peroxide, H_2O_2 . The peroxide does not react directly with sulphide at the

concentrations found in sewage, but it gradually decomposes in sewage to produce water and dissolved oxygen. The yield of oxygen is 47% of the weight of H_2O_2 applied. H_2O_2 is an expensive source of oxygen, but it is convenient to use and consequently is suitable where the amounts required are not large.

An alternative source of oxygen, to satisfy the respiration rate of the bacteria, is nitrate which could be added to the sewage as either the sodium or iron salts. The amount of "oxygen" available is equal to 2.8 times the nitrate nitrogen content and would be used at the respiration rates of the bacteria in the sewage and in the slime layers on the walls of the sewer. Its use is likely to be cheaper than H_2O_2 but more expensive than pure oxygen.

Various other chemicals are used, either to prevent sulphide generation or to destroy sulphide already present in the sewage stream.

One chemical sometimes used for this purpose is sodium hydroxide (caustic soda), which is periodically added to destroy the sulphide-producing bacteria in the slime layer. Generally, enough is added to raise the pH of the stream to about 12 for half an hour. The treatments needs to be repeated at intervals ranging from three days to a month depending upon the temperature and biological activity of the sewage. Sometimes lime (calcium hydroxide) is used in this way instead of sodium hydroxide but it can cause problems with scale formation.

Chlorine (including chlorine in the form of hypochlorite) is the most widely used chemical for sulphide control. It is often added to the sewage entering a treatment plant to remove any sulphide present in the stream. Applied at upstream locations, it may not only destroy any sulphide present but also prevent further generation for half an hour to an hour downstream or longer if a substantial excess is applied. To be completely effective, about 50 to 150mg chlorine per litre of sewage may be required depending on the BOD (or COD) of the sewage.

Various other chemicals have been tried, but any uses that they may have are limited to quite special conditions.

Where chemicals are to be relied upon to eliminate sulphide in a reticulation system, installation of a large number of application stations may be necessary, which often is not practical. Also a chemical method of control represents an ongoing expense which, while it may appear justified on economic grounds, is most

likely to be neglected. The amount of corrosion that may be suffered in any one year due to the presence of H_2S may be small and it may be neglected until the pipe is seriously damaged. Plans for continued use of compressed air, nitrate or oxygen may be reasonable, particularly when treatment of sewage can be advanced by this means, but it is dubious practice to plan a new sewerage system in a way that will make the durability of the pipe dependent upon continued chemical treatment (bactericides, lime, etc.) for sulphide control. The addition of hydrogen peroxide may only be considered as an emergency measure, because of its expense in relation to oxygen and nitrate.

Ventilation of sewers is sometimes resorted to in an attempt to reduce corrosion, but rarely can more than a minor part of the H_2S be exhausted before it has had time to react on the pipe wall. Insofar as ventilation is successful, it is likely to cause air pollution problems unless precautions are taken to clean the ventilated air by use of suitable scrubbing systems.

The choice of materials of construction

It cannot be said that there is any one kind of pipe material that should always be used for sewer, construction, but if there is a possibility that sulphide in significantly corrosive amounts may be present, a corrosion-resistant material should be chosen. Sulphide control methods will never provide equal assurance of a durable system, because of high capital and operating costs, and the need for continuous monitoring.

The most important structural element of a sewage collecting system is the pipe. The following kinds of pipe materials are available:

Vitrified Clay

This material is immune to attack by sulphuric acid and resistant to all chemicals found in sewage. A vitrified clay sewer properly laid and jointed will, if not disturbed by external forces, remain serviceable indefinitely.

In extremely rare cases of continuous discharge of undiluted trade waste containing a highly reactive chemical such as hydrofluoric acid, corrosion could occur in clay pipes, but as practical matter, chemical attack on such pipes in municipal sewer systems is unknown.

Where sulphide may be present, vitrified clay pipes should not be jointed with Portland cement mortar, as the cement will be attacked.

It may also be noted that vitrified clay pipes are not attacked by sulphates present in the ground.

Steel

If a steel pipe flows partly filled with waste water containing sulphide, corrosion may occur not only by the formation of sulphuric acid, but also by the corrosiveness of H_2S toward iron in the presence of air or dissolved oxygen, producing bulky accumulations of iron sulphide. In a pipe completely filled with waste water there is little or no corrosion even if sulphide is present, provided the pH is above 6.5 and the chloride content is less than 500 mg/l. Even where air is injected, corrosion due to dissolved oxygen is generally at a slow rate. However, if there are any high points or pockets, air may collect there and sulphuric acid may form. Serious corrosion has occurred in such locations.

Cast Iron

Cast iron pipes generally last longer than steel in all services because the pipe wall is thicker. Like steel pipes, they give good service when completely filled with waste water provided that the pH is 6.5 or higher and the chloride content is moderate. If the pipe is carrying sewage that contains sulphide and is flowing only partly filled, corrosion may be severe.

Asbestos-Cement

Asbestos-cement pipe is susceptible to attack by sulphuric acid, and it therefore is not safe to use for sewers except where it can be assured that sulphide concentrations will be very low. Because of the greater proportion of cement in the mix, it corrodes more slowly than concrete made with aggregates of an igneous type (granitic or basaltic) but this advantage is counteracted by the thinness of the wall.

Concrete

The corrosion of concrete sewers in the presence of H_2S has already been described on page 14.

Despite its vulnerability, concrete is an important sewer pipe material. For large trunk sewers the corrosion rates are generally lower than in small pipes because the slope, which influences the rate of release of H_2S from the water, is generally smaller. Large pipes have thick walls, so that with small sulphide

concentrations the pipe may serve for a long time before it is materially weakened.

Concrete may be used for smaller sewers, too, provided there is assurance that there will be very little sulphide.

Many attempts have been made to fortify concrete against attack by sulphuric acid. There are two approaches: altering the composition of the concrete and providing a protective lining.

The only property of portland cement concrete that will materially affect the rate of acid corrosion in sewers is its alkalinity. Pipes produced with a lean mix and granitic aggregate will have a low alkalinity and will corrode faster than where the mix contains more cement or where limestone aggregate is used. Some modifications of the concrete composition may influence the rate of reaction of a specimen in a vessel filled with dilute sulphuric acid, but on a sewer wall acid is formed so slowly that it can react almost as fast as it is formed despite variations of composition of the concrete.

Various linings for concrete pipes have been tried. The only one that has proved effective for protecting concrete sewer pipes from acid attack is a plasticized polyvinyl chloride sheet having projections that key it into the concrete when the pipe is cast. Hundreds of attempts have been made to apply coatings that merely adhere to the concrete, such as bitumen, coal tar epoxy,

and pure epoxy, but they have mostly failed when exposed to the sulphide conditions which exist in running sewers. To assure that there would nowhere be enough diffusion of acid through such lining, even after a long period of years, to loosen its adhesion to the pipe wall would require a degree of impermeability and perfection of application that so far appear unattainable.

Plastics

Pipes of polyvinyl chloride (PVC), acrylonitrile-butadiene-styrene (ABS), and polyethylene (PE) have been used for sewers in small sizes. The materials are all resistant to sulphuric acid attack.

The plastic and plastic composite materials are usually made into pipes with relatively thin walls because of the high cost of the materials. To prevent fracture or collapse of the pipes, they must be laid carefully to avoid unacceptable deflections under the backfill load.

A composite pipe is made by mixing polyester resin with sand and then providing a fibreglass reinforcement. The most vulnerable part of the composite is the glass, because water has the ability to creep along the fibres. The pipe must be manufactured so that this cannot happen. Under some conditions pipes of this kind have deteriorated when sulphuric acid was present and the pipes were under load.

Part 3

Predictive equations

The equations developed to predict the production of sulphide in filled and part-filled sewers and the rates of corrosion to be expected are presented in the following pages.

Some parameters within the equations, such as sewage temperature, pH, alkalinity of concrete, may vary widely according to the location of the system. If these are wrongly chosen, the predictions may be seriously in error. Some *typical* ranges for temperature and pH are given in table 5 below.

TABLE 5
Temperature and pH ranges

Area	Sewage Temperature (°C)		Typical pH value
	Summer	Winter	
U.K.	19°	14°	6.7-8.2
Middle East	24°-32°	15°-24°	7.0
America (California)	26°	20°	7.0-8.0

A basic decision must be made as to whether the "most conservative" or "average" equations should be used, and also care must be taken not to use mutually exclusive equations within the same calculation, e.g. equation (j) for sulphide production in a sewer running almost full, and then a low proportional depth to estimate the corrosion rate in equations (q) and (r).

It must be remembered that velocity, depth of flow, and strength of the sewage will vary diurnally, and there will be an annual temperature cycle. For these reasons, sulphide concentrations are highly variable. Estimations of sulphide concentrations and rates of corrosion may be made for various combinations of conditions that will prevail in a sewer. Alternatively, the calculation can be made for an average annual condition, which will give a somewhat different result, but generally close enough in view of the approximations that are already inherent in the forecasts.

(a) Equations for full pipes

Three equations have been proposed for the forecasting of sulphide production in filled pipes. The most fundamental quantity appearing explicitly or implicitly in these equations is the sulphide flux from the slime layer into the stream, expressed as grammes of sulphide per square metre-hour (g/m²-hr) and

designated ϕ_{sc} . Extracting this quantity from the proposed equations, we have the following:

$$\phi_{sc} = M_a [\text{BOD}](1.07)^{(T-20)} \quad (\text{a})$$

Pomeroy, 1959 (Ref. 12) & 1974 (Ref. 6)

$$\phi_{sc} = M_b [\text{COD}](1.07)^{(T-20)} \quad (\text{b})$$

Boon and Lister, 1975 (Ref. 5)

$$\phi_{sc} = M_c u [\text{BOD}]^{0.8} [\text{SO}_4]^{0.4} (1.14)^{(T-20)} \quad (\text{c})$$

Thistlethwayte, 1972 (Ref. 9)

The values of the coefficients under conditions favourable for build-up are:

$$\begin{aligned} M_a &\approx 1.0 \times 10^{-3} \\ M_b &= 0.228 \times 10^{-3} \\ M_c &= 0.5 \times 10^{-3} \end{aligned}$$

and:

[BOD] = concentration of standard biochemical oxygen demand, mg/l.

[COD] = concentration of standard chemical oxygen demand, mg/l.

[SO₄] = concentration of sulphate, mg/l.

u = velocity, m/sec

T = sewage temperature, °C

The BOD of sewage is generally a third to a half as great as the COD. Equation (a) predicts the maximum rate of formation of sulphide by slimes, and equation (b) predicts the average rate.

Equation (c) is the only one that attempts to take into account the effects of velocity and sulphate concentration. When the velocity is slow there may be impoverishment of nutrients near the slime layer. The effect is most pronounced where the average velocity is low because of long intervals of no water movement, as is often the case in pressure mains from pumping stations. It appears, however, that a relatively slow velocity suffices to maintain the nutrient supply, and an increase of velocity above this minimum does not cause any further increase of the build-up rate. Similarly, the sulphide build-up rate does not increase indefinitely with increase of sulphate concentration. From the limited information available it does not appear that sulphate is a limiting factor if it is present in amounts exceeding a value somewhere between 10% and 25% of the BOD, or between 4% and 10% of the COD. Consequently, equation (c) is likely to give predictions that are too high if the stream is very swift or the sulphate concentration is very high. On the other hand,

equations (a) and (b) will give results that are too high if the sewage is stationary much of the time or if the sulphate concentration is very low.

The complete equations from which equations (a) and (b) for sulphide flux were extracted included a term for sulphide generation in the stream. In effect, build-up in the stream, in mg/l-hr, was assumed to be $0.0015[\text{BOD}](1.07)^{(T-20)}$ or $0.00067[\text{COD}](1.07)^{(T-20)}$. Reduced to comparable forms, the full equations from sources (a), (b) and (c) are:

$$\frac{d[S]}{dt} = 1.0 \times 10^{-3} [\text{BOD}](1.07)^{(T-20)} r^{-1} (1+0.37D) \quad (\text{d})$$

$$\frac{d[S]}{dt} = 0.228 \times 10^{-3} [\text{COD}](1.07)^{(T-20)} r^{-1} (1+0.37D) \quad (\text{e})$$

$$\frac{d[S]}{dt} = 0.50 \times 10^{-3} u [\text{BOD}]^{0.8} [\text{SO}_4]^{0.4} (1.14)^{(T-20)} r^{-1} \quad (\text{f})$$

in which

$\frac{d[S]}{dt}$ = the rate of change of sulphide concentrations, mg/l-hr.

r = hydraulic radius ($\frac{1}{4}D$ in the filled pipe), m

D = pipe diameter, m

(b) Equations for part-full pipes

As a result of extensive researches in the system of the Los Angeles County Sanitation Districts (USA), an equation has been developed that provides serviceable forecasts within the limitations mentioned on page 9 (Parkhurst and Pomeroy, 1976). It has one term representing the rate that sulphide is added to the stream by the slime layer and another term that represents the losses. In its general form the equation is:

$$\frac{d[S]}{dt} = M' [\text{BOD}](1.07)^{(T-20)} r^{-1} - N(\text{su})^{3/8} [S] d^{-1} \quad (\text{g})$$

in which:

[S] and [BOD] are the concentrations of sulphide and of standard BOD, mg/l.

M' and N are empirical, and in part elective, coefficients

$\frac{d[S]}{dt}$ = the rate of change of sulphide concentrations, mg/l-hr.

T = sewage temperature, °C

r = the hydraulic radius (cross-section area of the stream divided by the wetted perimeter), m

s = slope of the energy line of the sewage in the pipe (which is approximately the slope of the pipe), m/100m

u = velocity of the stream, m/sec

d = mean hydraulic depth (cross-section area of the stream divided by the surface width), m

A depth of flow must be determined at which u, r and d are to be measured, because sulphide production varies with the exposed wetted area, which itself varies with diurnal changes in depth of flow.

Values of M' and N for the equation can be chosen to meet various objectives. It would not be fruitful to try to choose these coefficients so as to predict the average performance of all sewers. If those carrying well aerated sewage are averaged with all of the sulphide producers to derive a predictive equation, there would be very poor correlation between predicted and observed results. The other extreme would be to choose coefficients that would forecast build-up rates that would in no case be less than the observed rates. More practical is an equation that forecasts rates that in reality are exceeded in only a minor proportion of the cases, and then not by any large amount.

Two sets of coefficients are provisionally offered as useful for design purposes representing different degrees of conservatism:

A - median prediction for those sewers that actually do show sulphide build-up:

$$M' = 0.32 \times 10^{-3}, N = 0.96.$$

B - conservative prediction; rarely will build-up exceed these predictions by any substantial amount:

$$M' = 0.32 \times 10^{-3}, N = 0.64.$$

These equations should be considered applicable to sewers up to a metre in diameter. Quantitative sulphide build-up information in larger sewers is meagre, but it seems desirable to use $M' = 0.50 \times 10^{-3}$ for sewers one to two metres in diameter if the flow depth is more than half of the pipe diameter.

It may be noted that M' corresponds to M_a in equation (a), the sulphide flux equation given earlier for filled pipes. M' is less than M_a because of dissolved oxygen in the stream.

If COD is used instead of BOD, the coefficient corresponding to M' would presumably be about 0.073×10^{-3} .

To summarize, the predictive equations, including alternate forms using COD instead of BOD, are shown below.

Synopsis of equations for forecasting sulphide build-up rates

Forecasts for filled pipes.

$$\frac{d[S]}{dt} = 1.0 \times 10^{-3} [BOD] (1.07)^{(T-20)} r^{-1} (1+0.37D) \quad (d)$$

or,

$$\frac{d[S]}{dt} = 0.228 \times 10^{-3} [COD] (1.07)^{(T-20)} r^{-1} (1+0.37D) \quad (e)$$

or,

$$\frac{d[S]}{dt} = 0.50 \times 10^{-3} u [BOD]^{0.8} [SO_4]^{0.4} (1.14)^{(T-20)} r^{-1} \quad (f)$$

Forecasts for partly filled pipes - reasonable expectation in sulphide-producing sewers.

$$\frac{d[S]}{dt} = 0.32 \times 10^{-3} [BOD] (1.07)^{(T-20)} r^{-1} - 0.96 (su)^{3/8} d^{-1} [S] \quad (h)$$

or,

$$\frac{d[S]}{dt} = 0.073 \times 10^{-3} [COD] (1.07)^{(T-20)} r^{-1} - 0.96 (su)^{3/8} d^{-1} [S] \quad (i)$$

Forecasts for partly filled pipes-conservative.

$$\frac{d[S]}{dt} = 0.32 \times 10^{-3} [BOD] (1.07)^{(T-20)} r^{-1} - 0.64 (su)^{3/8} d^{-1} [S] \quad (j)$$

or,

$$\frac{d[S]}{dt} = 0.073 \times 10^{-3} [COD] (1.07)^{(T-20)} r^{-1} - 0.64 (su)^{3/8} d^{-1} [S] \quad (k)$$

The symbols used are these :

$\frac{d[S]}{dt}$ = sulphide build-up rate, mg/l-hr.

[BOD] = biochemical oxygen demand concentration, mg/l

[COD] = chemical oxygen demand concentration, mg/l

[SO₄] = sulphate concentration, mg/l

T = sewage temperature, °C

D = pipe diameter, m

s = slope of the energy line of the sewage in the pipe, m/100m

u = velocity of the stream, m/sec

d = mean hydraulic depth (cross-section area of the stream divided by the surface width), m

r = the hydraulic radius (cross-section area of the stream divided by the wetted perimeter), m

The sulphide build-up curve in partly filled sewers

According to these equations, the sulphide concentrations in a partly filled sewer will approach a limiting level, designated [S]_{lim}, where the losses equal the additions. Accordingly,

$$\frac{M'[BOD](1.07)^{(T-20)}}{r} = \frac{N(su)^{3/8}[S]_{lim}}{d} \quad (l)$$

(Parkhurst and Pomeroy, 1976 - Ref. 13)

Using the conservative values shown in equation (j), that is, 0.32 x 10⁻³ for M' and 0.64 for N, and noting that d/r = P/b, in which P is the wetted perimeter and b is the surface width of the stream, we may write,

$$[S]_{lim} = \frac{0.5 \times 10^{-3} [BOD] (1.07)^{(T-20)} \times P}{(su)^{3/8} b} \quad (m)$$

For the less conservative equation (h) the numerical coefficient would be 0.33 x 10⁻³.

If COD is used instead of BOD, the coefficient would probably be about 0.2 x 10⁻³ instead of 0.5 x 10⁻³ and about 0.13 x 10⁻³ instead of 0.33 x 10⁻³.

The approach to [S]_{lim} will follow what is called a first-order curve. Knowing [S]_{lim}, the curve can be drawn if there is also a parameter for the time scale. For convenience, use may be made of the half-life, that is, the time in which the process approaches half way to the limiting state. The half-life, designated t_{1/2} and expressed in hours, is calculated by the following equation:

$$t_{1/2} = \frac{0.69d}{N(su)^{3/8}} \quad (n)$$

For the conservative equation, with N = 0.64, this becomes

$$t_{1/2} = \frac{1.07d}{(su)^{3/8}} \quad (o)$$

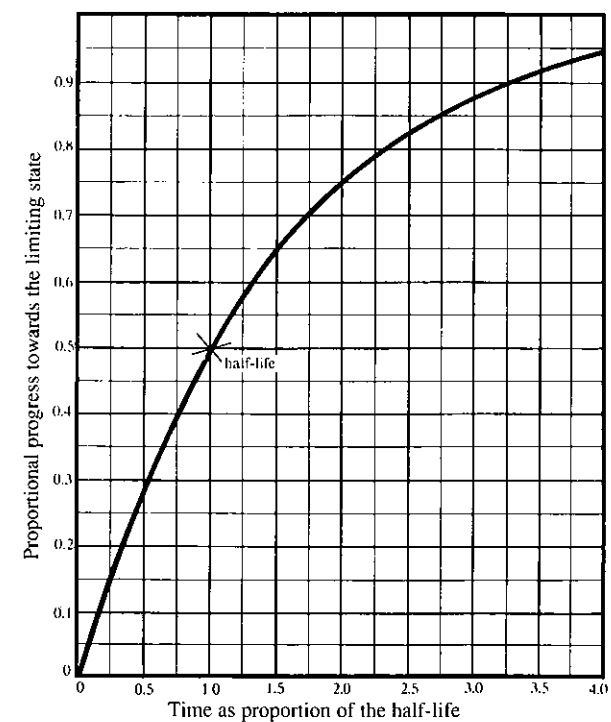
Table 6 is presented as an aid in obtaining geometric and hydraulic functions that will be useful in the application of these equations.

TABLE 6
Geometric and hydraulic functions

Proportional depth	Surface width(b) ÷ D	Wetted perimeter (p) ÷ πD	Section area(a) ÷ ¼ πD ²	Hydraulic radius (r) ÷ ¼ D	Mean depth(d) ÷ D
0.05	0.436	0.144	0.019	0.130	0.034
0.10	0.600	0.205	0.052	0.254	0.068
0.15	0.714	0.253	0.094	0.371	0.103
0.20	0.800	0.295	0.142	0.482	0.140
0.25	0.866	0.333	0.196	0.587	0.177
0.30	0.917	0.369	0.252	0.684	0.216
0.35	0.954	0.403	0.312	0.774	0.257
0.40	0.980	0.436	0.373	0.857	0.299
0.45	0.995	0.468	0.436	0.932	0.345
0.50	1.000	0.500	0.500	1.000	0.393
0.55	0.995	0.532	0.564	1.059	0.445
0.60	0.980	0.564	0.625	1.111	0.502
0.65	0.954	0.597	0.688	1.153	0.567
0.70	0.917	0.631	0.748	1.185	0.641
0.75	0.866	0.667	0.805	1.207	0.730
0.80	0.800	0.705	0.858	1.217	0.842
0.85	0.714	0.747	0.906	1.213	0.996
0.90	0.600	0.795	0.948	1.192	1.241
0.95	0.436	0.856	0.981	1.146	1.768
1.00	0	1.000	1.000	1.000	∞

The above table is reproduced from Hydraulics Research Paper No. 4 H.M.S.O.

FIGURE 11
Dimensionless Data for the First-Order Curve



Worked example (1)

A sewer 0.45m in diameter laid at a gradient of 1 in 667 (0.0015) is expected to flow half full at a velocity of 0.60 m/sec. The sewage temperature will be 22°C and the BOD will be 350 mg/l. Using predictive equation (j), calculate the following:

1. Initial sulphide build-up rate starting with zero sulphide.
2. Limiting sulphide concentration that will be approached.
3. The half-life of the process.
4. The sulphide build-up curve.
5. At what distance would be sulphide concentration reach 1.0 mg/l?

Preliminary calculations:

Calculate first the following quantities:

$$[BOD] \times (1.07)^{(T-20)} = 350 \times 1.145 = 401$$

$$(su)^{3/8} = (0.0015 \times 0.60)^{3/8} = 0.0721$$

$$d = 0.393 \times 0.45 = 0.177 \text{ (}\pi D/8 \text{ in a half-filled pipe)}$$

$$P/b = 1.57 \text{ (}\pi/2 \text{ in a half-filled pipe)}$$

$$r = 0.25 \times 0.45 = 0.1125 \text{ m (D/4 in a half-filled pipe)}$$

Answers sought:

1. Initial rate of sulphide build-up

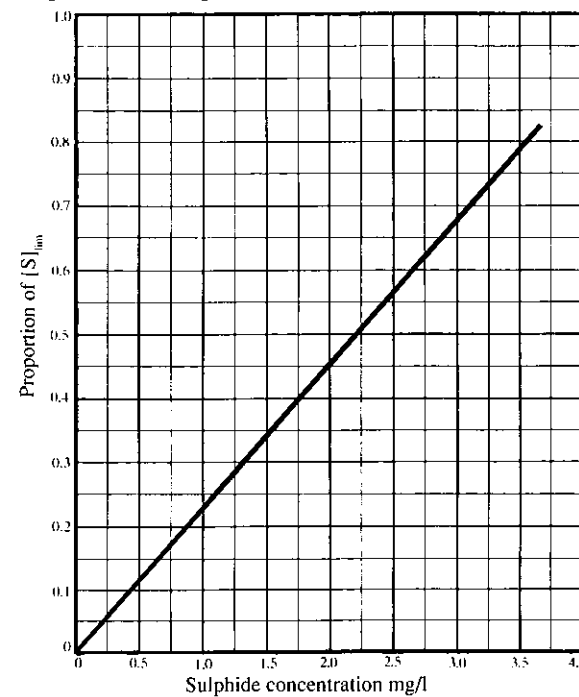
$$= \frac{0.00032 \times 401}{0.1125} = 1.14 \text{ mg/l-hr}$$
2. $[S]_{lim} = \frac{0.0005 \times 401 \times 1.57}{0.0721} = 4.37 \text{ mg/l}$
3. $t_{1/2} = \frac{1.07 \times 0.177}{0.072} = 2.63 \text{ hours}$

TABLE 7
Application of the general first-order curve

Time (half-life = 2.6 hours)		Sulphide Concentration ([S] _{lim} = 4.37 mg/l)	
Proportion of half-life	Hours	Proportion [S] _{lim}	mg/l
0.2	0.5	0.13	0.57
0.4	1.1	0.24	1.05
0.6	1.6	0.34	1.49
0.8	2.1	0.43	1.88
1.0	2.6 ← Life →	0.50	2.19
1.2	3.2	0.57	2.49
1.6	4.2	0.67	2.93
2.0	5.3	0.75	3.28
2.5	6.6	0.82	3.58

A plot of these results is shown below

FIGURE 12
Sulphide build-up curve



5. According to the calculation, the concentration of 1.0 mg/l would be reached in about 1.0 hours, which, at a flow velocity of 0.6m/sec, or 2160 m/hr, would be at a distance of 2.2 km.

Where the initial sulphide concentration is not zero, build-up will follow the same curve from whatever point represents the initial concentration. If the concentration is greater than $[S]_{lim}$, it will decline toward $[S]_{lim}$ along a curve that is the mirror image of the build-up curve.

Very few sewers run for long distances with uniform flow conditions. If the sewer has changing slopes or increments of flow, curves can be drawn for the different flow conditions, and the theoretical changes of sulphide concentrations can be forecast by stepping from one curve to another. It must be remembered, however, that in real situations there are likely to be jumps in the dissolved oxygen levels as a result of the aeration that occurs at junctions or drops. In very large sewers most of the dissolved oxygen supplied to the stream comes from these point sources. If the point sources of oxygen input along the way are exceptionally large, the actual sulphide concentrations may be much less than shown by the calculations.

Forecasting rates of concrete corrosion

The rate of corrosion of a concrete sewer can be calculated from the rate of production of sulphuric acid on the pipe wall, which is in turn dependent upon the rate that H_2S is released from the surface of the sewage stream.

The transfer of H_2S across the air-water interface is a two-way process since H_2S molecules in the air can go back into solution. This reverse process is minor, since the H_2S concentration in the sewer atmosphere is small compared to the equilibrium concentration. The effect has been considered in developing equation (p). The rate of release or the flux of H_2S from the stream surface, as here used, means the net rate of transfer across the interface.

The following equation has been developed for the flux of H_2S into the air under typical conditions:

$$\phi_{sf} = 0.7 (su)^{3/8} j [DS] \quad (\text{U.S. EPA, 1974}) \quad (p)$$

in which

ϕ_{sf} = the flux of sulphide at the sewage/air interface, g/m²-hr

s = the slope of sewer, m/100m

u = stream velocity, m/sec

j = pH-dependent factor for proportion of H_2S (Table 1)

[DS] = dissolved sulphide concentration, mg/l

The equation applies under ordinary flow conditions except that it gives results substantially too low for small, high-velocity streams with Froude numbers greater than 2.

Under most conditions, very little of the H_2S escapes entirely from the sewer. The film of moisture on the pipe wall, teeming with Thiobacilli, is very efficient in converting to sulphuric acid all of the H_2S that reaches it. The average flux of H_2S to the exposed pipe wall is equal to the flux from the stream into the air multiplied by the ratio of the surface area of the stream to the area of the exposed pipe wall, which is the same as the ratio of the width of the stream surface to the perimeter of the exposed wall. The average flux of H_2S to the wall is therefore calculated as follows:

$$\phi_{sw} = 0.7 (su)^{3/8} j [DS] (b/P') \quad (q)$$

in which

ϕ_{sw} = average flux of H_2S (expressed as sulphide) at the air/wall interface, g/m²-hr

[DS] = dissolved sulphide concentration, mg/l

b = surface width of the stream, m

P' = exposed perimeter, $(\pi - P/D) D$, m

Values of the ratio b/P' at different relative depths of flow may be calculated from Table 6.

If the pipe is made of a cement-bonded material, or any acid-susceptible substance, the acid may partly or entirely react. Insofar as it does react, it will penetrate the wall at a rate inversely proportional to the acid-consuming capability of the wall material. The proportion of acid that reacts is variable, ranging from 100% when the acid formation is slow, to perhaps 30% to 40% when it is formed rapidly or there is a high rate of condensation. A factor should be included in the equation to express the proportion of the acid that reacts. When this is done, the equation for the rate of corrosion is as follows:

$$c = 11.5 k \phi_{sw} (1/A) \quad (r)$$

in which

c = the average rate of corrosion of the material, mm/yr

k = factor representing the proportion of acid reacting, to be given a value selected by the judgement of the engineer.

ϕ_{sw} = average flux of H_2S (as S) to the pipe wall, g/m²-hr

A = acid-consuming capability, or alkalinity, of the pipe material, expressed as the proportion of equivalent calcium carbonate.

Stutterheim and Van Aardt (Ref. 14) pointed out that the use of calcareous aggregate (limestone or dolomite) will increase the alkalinity of concrete and thus prolong the life of structures subject to damage by sulphide conditions. The alkalinity of concrete made with granitic or other acid resistant aggregate may range from about 0.16 up to 0.3. When calcareous aggregate is specified for sewer construction, it is usually required that the alkalinity of the product be equal to 80% or 90% $CaCO_3$.

Manholes, as well as sewer pipes, may be affected by the acid produced from H_2S , but if normal flow prevails through a manhole the damage will be inconsequential, since the wall area is large relative to the water surface.

Manholes are sometimes the site of high turbulence. Under these conditions the damage is likely to be severe if the sewage contains sulphide.

Worked example (2)

A sewer 0.45 m in diameter laid at a slope of 0.0015 is flowing half full at a velocity of 0.60 m/sec. The pH of the sewage is 7.2, and the dissolved sulphide concentration is 1.0 mg/l. If the pipe is made of concrete having an alkalinity equal to 0.20 of calcium carbonate, what will be the average rate of corrosion?

Solution

$$\phi_{sw} = 0.7 (su)^{3/8} j [DS] (b/P') \quad (\text{Equation q})$$

$$(su)^{3/8} = (0.0015 \times 0.60)^{3/8} = 0.072$$

$$j = 0.39$$

$$b/P' = 0.64 \quad (\text{Table 1})$$

$$\phi_{sw} = 0.7 \times 0.072 \times 0.39 \times 1.0 \times 0.64 = 0.0126 \text{ g/m}^2\text{-hr}$$

$$c = 11.5 k \phi_{sw} (1/A) \quad (\text{Equation r})$$

The rate of acid formation is relatively slow. There is not yet a firm basis for estimating k but it seems likely that for these conditions it might be between 0.7 and 0.9. Use 0.8,

$$\begin{aligned} c &= 11.5 \times 0.8 \times 0.0126 \times (1/A) \\ &= 0.116 (1/0.2) \\ &= 0.58 \text{ mm per year} \end{aligned}$$

The maximum rate of penetration, which will be at the crown or near the water line, may be 50% greater than the average. It must also be remembered that corrosion rates will be much greater, often ten times as fast, in the vicinity of points of much turbulence.

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