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THE PROCESS CONTROLLER's GUIDE TO

IRON AND SULPHUR COMPOUNDS IN THE WATER AND WASTEWATER ENVIRONMENT

This is number 9 in the Process Controller Guide series of documents

Number 1	Pollution Control.
Number 2	Water Sources and Water Treatment**.**
Number 3	Wastewater Treatment
Number 4	Phosphorus Removal from Wastewater.
Number 5	Electricity and Electric Motors.
Number 6	Pumps, Blowers and their Operation.
Number 7	Mechanical Transmission of Power
Number 8	Flow Measurement
Number 9	**Iron and Sulphur compounds in the water and wastewater environment.**

This guide is intended to give Process Controllers an overview of the sources and impacts of iron and sulphur compounds in the water and wastewater environment.

It is intended that this document be a useful reference and training manual guide to all persons involved in the Water and Wastewater Industry.

These documents are dedicated to the thousands of men and women (both present and past) who are involved in the life critical profession of Water and Wastewater Treatment.

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THE PROCESS CONTROLLER's GUIDE TO

IRON AND SULPHUR COMPOUNDS IN THE WATER AND WASTEWATER ENVIRONMENT

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IRON AND SULPHUR COMPOUNDS IN THE WATER AND WASTEWATER ENVIRONMENT.

PART 1.

THE VARIOUS FORMS OF IRON IN THE ENVIRONMENT.

1.1 INTRODUCTION.

Iron is a chemical element with the symbol Fe and atomic number 12. The most common form (91.8%) has an atomic mass of 56. The weighted mean atomic mass is 55.845. By mass, it is the most common element on earth and the 4th most common in the earth's crust after Oxygen, Silicon and Aluminium.

Iron is not found on earth in the raw state as it is easily oxidised in the presence of moisture.

Iron is an important mineral in our bodies as it is found in haemoglobin, the protein that carries oxygen from our lungs throughout our bodies. It also helps our muscles store and use the oxygen. A 70kg person would have about 4 grams of iron in their body.

In plants, iron is essential for the synthesis of Chlorophyll that is vital for photosynthesis. This is the process whereby the plant converts carbon dioxide in the atmosphere into cellular material and releases oxygen into the atmosphere.

1.2 THE OXIDATION STATES OF IRON.

Iron can exist in a number of oxidation states of which two are of most interest in the water environment. There are the +2 state (Ferrous) and the +3 state (Ferric).

1.3 IRON IN THE ENVIRONMENT.

The various forms of the iron present in the earth's crust are shown in Table 1 below:

TABLE 1 – VARIOUS COMPOUNDS OF IRON FOUND IN THE EARTH's CRUST.

Chemical Name	Chemical Formula	Common Name
Ferrous Oxide	FeO	Wüstite
Ferric Oxide	Fe_2O_3	Hematite
FerroFerric Oxide	Fe_3O_4	Magnetite
hydrated Ferric Oxide	$FeO(OH).nH_2O$	Limonite
Ferrous Carbonate	$FeCO_3$	Siderite
Ferrous Sulphide	FeS	Iron Pyrites

The first 5 are the most important sources of iron for mining and extraction purposes. It is Ferrous Sulphide in the form of pyrites that is found with other minerals when mining; that is of greatest interest here.

It will be seen in part 2 how the mining industry can produce acid mine drainage water and its impact on the environment. Part 3 will show how the iron and sulphur content of a water source impact on the suitability and treatment of a water source.

PART 2

THE VARIOUS FORMS OF SULPHUR IN THE ENVIRONMENT.

2.1 INTRODUCTION.

Sulphur (also known as Sulfur) is a chemical element with the symbol S and atomic number 16. The most common form (95%) has an atomic mass of 32. It falls in the same group as Oxygen in the periodic table. It therefore shares some similar properties with oxygen but being about 60% larger than an oxygen atom, also shows several differences from oxygen.

Sulphur is the tenth most common element by mass in the universe, and the fifth most common on Earth. Though sometimes found in a soft bright yellow solid form; most sulphur on Earth usually occurs as sulphide and sulphate minerals. It burns with a blue flames and forms sulphur dioxide (SO_2).

Being abundant in native form, sulphur was known in ancient times, being mentioned for its uses in ancient India, ancient Greece, China, and Egypt. Historically and in literature, sulphur is also called brimstone which means "burning stone". Today, almost all elemental sulphur is produced as a by-product of removing sulphur-containing contaminants from natural gas and liquid fuels. Diesel fuel, for example, is available in South Africa in both a 500 ppm (parts per million) form and in a 50 ppm form. The reason for this will be covered later. Another source of sulphur is from the removal of sulphur from the discharge from the burning of coal and other sulphur containing materials.

The greatest commercial use of the element is the production of sulphuric acid for sulfate and phosphate fertilizers, and other chemical processes. Sulphur is used in matches, insecticides, and fungicides. Many sulphur compounds are odoriferous, and the smells of odorized natural gas, grapefruit, and garlic are due to organo-sulphur compounds. Hydrogen sulfide gives the characteristic odour to rotting eggs and other biological processes.

Sulphur is an essential element for all life, but almost always in the form of organo-sulphur compounds or metal sulphides. Three amino acids (cysteine, cystine, and methionine) and two vitamins (biotin and thiamine) are organo-sulphur compounds. Many cofactors also contain sulphur, including glutathione, thioredoxin, and iron–sulphur proteins.

The terms “thio” indicates the presence of sulphur in the compound. Disulphides through their S–S bonds, confer mechanical strength and insolubility of the protein keratin found in outer skin, hair, and feathers. Sulphur is one of the core chemical elements needed for biochemical functioning and is an elemental macronutrient for all living organisms – plant and animal.

Sulphur is the third most abundant mineral in our bodies following calcium and phosphorus.

In plants, sulphur is an essential element in forming proteins, enzymes, vitamins, and chlorophyll. It is crucial to the efficient fixation of nitrogen in legumes. Protein synthesis requires large amounts of sulphur, especially in the formation of oils within the seed.

2.2 THE OXIDATION STATES OF SULPHUR.

Sulphur can exist in a large number of oxidation states: from the most reduced to the most oxidised. These are given in the table 12below:

TABLE 2 – LISTING THE VARIOUS OXIDATION STATES OF SULPHUR

OXIDATION STATE								
Most reduced								Most oxidized
-2	-1	0	+1	+2	+3	+4	+5	+6
H_2S	H_2S_2	S	S_2Cl_2	$S_2O_3^=$	$S_2O_4^=$	SO_2	$S_2O_6^=$	SO_3
HS^-						H_2SO_3		H_2SO_4
$S^=$						$SO_3^=$		$SO_4^=$

In the water and wastewater; the most common states will be: -2; 0; +4; +6. This will be covered later.

TABLE 3 – LISTING THE NAMES OF THE MOST COMMON OXIDATION STATES OF SULPHUR

Oxidation state	-2	0	+4	+6
Common names	Hydrogen Sulphide	Sulphur	Sulphur Dioxide	Sulphur Trioxide
	Hydrosulphide ion		Sulphurous Acid	Sulphuric Acid
	Sulphide ion		Sulphite ion	Sulphate ion

2.3 SULPHUR IN THE ENVIRONMENT.

As mentioned above, most sulphur on earth in present as the sulphide or sulphate in minerals.

It was seen above that although sulphur may be found in an un-combined form as a powder; it is generally a reactive element. It readily undergoes oxidation or reduction reactions. These may be caused by chemical reactions or microbiological transformation. When rocks containing sulphur are weathered, they tend to be oxidised to sulphate ($SO_4^=$). This sulphate may be used or transformed by biological organisms including plants but ultimately is either removed in solution, lost to the atmosphere, or re-precipitated as sulphate or sulphide minerals elsewhere. This is all part of the sulphur cycle in the environment – remembering that sulphur cannot be destroyed; it is merely changed from one form to another during this cycle.

The above are natural inputs in the sulphur cycle. Industrialisation has modified the sulphur cycle significantly. The two most significant factors are:

1. combustion of sulphur containing fuels;

2. mining of sulphur containing minerals.

2.3.1 Combustion of Sulphur Containing Fuels.

These will include natural gas, petroleum based fuels (Petrol and diesel oil) and coal. As the combustion of these fuels uses oxygen from the atmosphere, the sulphur will mostly be converted to sulphur dioxide (SO_2). As this is a gas, it will travel into the atmosphere. It is very soluble in water and will form sulphurous acid (H_2SO_3) and sulphuric acid (H_2SO_4). This will become one of the components of what is known as “Acid Rain”. The other major component of acid rain will be acids formed from the oxidation of nitrogen.

The acid rain will speed up the leaching of minerals such as aluminium from rocks and soils that will drain into rivers and lakes and pass into the groundwater. Certain species such as fish are quite sensitive to the aluminium content of the water in which they live.

Acid rain will also damage buildings (especially those made from limestone, marble and other calcium containing materials) and metal fittings.

It was noted earlier that South Africa has two grades of diesel oil with sulphur content of 500 ppm and 50 ppm. The trend is to move to the higher grade (50 ppm) to reduce the air pollution effect of the fuel and to reduce the adverse impact on the engine itself.

In general, South African coal has a typical sulphur content of between 0.5 and 1.5%. Production of electricity using coal would therefore discharge sulphur dioxide into the atmosphere.

There are also natural discharges of sulphur containing gases into the atmosphere, such as from volcanos.

2.3.2 Mining of Minerals Containing Sulphur.

In certain gold and other mineral mines, there are large quantities of rocks containing sulphides, especially iron sulphide or Pyrites. When this rock is crushed to enable the extraction of the gold etc., the large surface area of the fine solids produced hastens the oxidation of the sulphide to sulphur dioxide. This will dissolve in the water to form sulphurous and sulphuric acid.

This is a multi-step process that is best illustrated in figure 1 below:

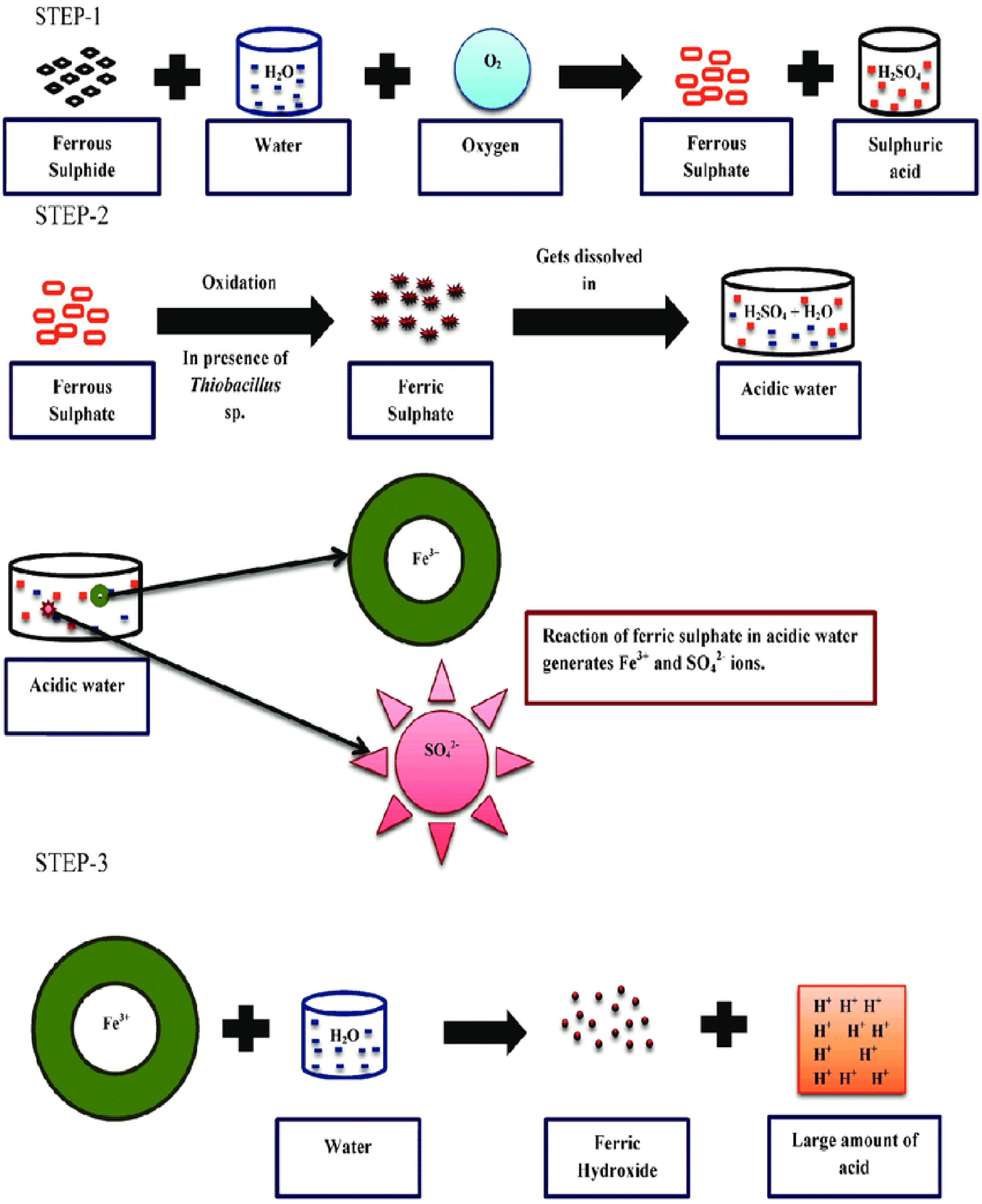

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Figure 1 – SHOWING THE VARIOUS STEPS IN THE PRODUCTION OF ACID MINE DRAINAGE

A bad case of acid mine drainage in shown in figure 2 below:

Infrastructure News

Figure 2 - SHOWING A BAD CASE OF ACID MINE DRAINAGE

The red colour is due to the iron content of the water. It is the iron, sulphur (as Sulphate) and the low pH of the discharge that is of greatest concern regarding its effect on the water resources.

In mining areas where there where the rocks, particularly those containing large amounts of calcite or dolomite, are able to neutralise the acid; the problem of acid mine drainage does not occur.

IRON AND SULPHUR COMPOUNDS IN THE WATER AND WASTEWATER ENVIRONMENT.

PART 3.

IRON AND SULPHUR IN RELATION TO WATER SOURCES AND TREATMENT

3.1 INTRODUCTION.

It has been seen earlier that both iron and sulphur are essential for plant and animal life. However, an excess of either or both, would be detrimental to the health and growth of both plant and animal life.

SANS 241 specifies limits for Iron and Sulphate (amongst others). These are summarized below in table 4.

TABLE 4 – SANS 241 LIMITS FOR IRON and SULPHATE.

Parameter	Aesthetic Limit	Health Limit
Iron as Fe	0.1 mg/L	2.0 mg/L
Sulphate as SO_4	250 mg/L	500 mg/L

3.2 TYPICAL IRON CONTENT OF RIVERS, LAKES AND GROUNDWATER.

A typical iron content of rivers and lakes, in the absence of obvious pollution, would appear to be in the range of 0.01 to 1.5 mg/L. This relatively low value in rivers and the upper layers of a lake would be due to the presence of dissolved oxygen, so that most of the iron would be present in the Ferric (Fe^{3+}) form. In the presence of carbonate and hydroxide from the alkalinity of the water, insoluble Ferric Carbonate [FeCO3] and hydrated Ferric Oxide [$FeO(OH).nH_2O$] would be formed. *[The letter "n" means that the number of molecules of water associated with each iron atom can vary*]. These are insoluble forms of iron and would therefore settle out.

Iron in groundwater can vary over a wide range. Iron content of up to 50 mg/L is possible. The iron may be dissolved from the rocks underground (such as "Koffie-klip") or from the downward movement of surface water. As seen in section 2.3.2, sources of iron such as acid mine drainage contain both iron and sulphuric acid. This will mean that at least some of the iron will be present as Ferric Sulphate. This is soluble in water and will move downward towards the water table. This will increase the iron content of the groundwater.

Acid rain will produce a similar effect although on a smaller scale.

As the surface water containing sulphates moves downwards, the dissolved oxygen content will decrease due to bacterial action and can become depleted. Sulphate reducing bacteria would then have an opportunity to start using the sulphate as their oxygen source and produce hydrogen sulphide as a waste product. The hydrogen sulphide together with the iron present in the groundwater can then reach a borehole or well point. This will give the characteristic rotten egg smell and the reddish-brown colouration of the water.

3.3 TYPICAL SULPHUR CONTENT OF RIVERS, LAKES AND GROUNDWATER.

A typical sulphate (as SO_4) content of rivers and lakes, in the absence of obvious pollution, would appear to be in the range of 3 – 30 mg/L. Where values significantly higher than these are found, this would lead one to believe that there is source of pollution that is adversely affecting these water bodies. Acid Mine Drainage (covered earlier), can have sulphate content in the thousands of milligrams per litre. Clearly it would not take much of the discharge to adversely affect a large body of water.

As surface water migrates down into the groundwater, it will dissolve minerals present in the soil. This will be worsened when the pH is lower such as in acid mine drainage or the effects of acid rain. The actual increase will depend only on the type of soil through which the water is passing. There will be a lower build-up of dissolved material when passing through a sandy soil when compared with a soil with a higher organic or mineral content. The sulphate content may increase to well over 100 mg/L.

As the water passes downwards, any initial dissolved oxygen will be used up by bacterial action leading to anoxic and even anaerobic conditions. As seen above, this can result in some conversion of sulphate to sulphide.

3.4 THE EXTRACTION OF GROUNDWATER CONTAINING IRON.

Groundwater usually has a very low dissolved oxygen content and is often zero. Also, there will usually be a significant carbon dioxide content and often, a noticeable hydrogen sulphide content. Depending on the length of time that the groundwater has been underground and the amount of bacterial activity some or all of the iron originally present in the Ferric (Fe^{3+}) form will be reduced to the Ferrous (Fe^{2+}) form. The Ferrous form tends to be more soluble.

Where the groundwater contains iron, with time the borehole may suffer from reduced yield due to blockage of the screen surrounding the borehole or the nearby sand, stone etc. The two main causes would be:

1. oxidation of the iron either at the screen or in the area extending outwards from the screen. This would be aggravated if the borehole was pumped down so low that air entered the area around the screen;

2. the development of iron bacteria that are microorganisms that use iron as an energy source or for other life functions. It is not unusual to find iron bacteria in boreholes in certain areas. Iron bacteria are not hazardous to health, but in some cases they cause troublesome borehole problems. Microorganisms from the genera Gallionella, Leptothrix and Crenothrix are some of the iron bacteria group.

   A major problem associated with iron bacteria and other naturally-occurring groundwater bacteria is slime or biofilm production. A reddish-brown slime is a metabolic by-product from the oxidation of iron and manganese by iron bacteria. Biofilm deposition can clog pump intakes, well screens, filters, and water pipes. Biofouling can occur in the aquifer near the borehole and can build up quickly in comparison to mineral incrustation. Iron bacteria can be a significant problem because of the effects on borehole yield.

   One could expect borehole fouling problems under the following conditions:

   a. pH is greater than 7.0;

   b. Calcium hardness is greater than 200 mg/L as $CaCO_3$;

   c. Iron is greater than 1.0 mg/L as Fe;

   d. Sulphates are greater than 50 mg/L as $SO_4^{=}$.

Fouling of screens may also occur in areas with a high calcium content when operation of the borehole causing dissolved carbon dioxide to escape resulting in calcium carbonate precipitation.

3.5 THE TREATMENT OF WATER CONTAINING IRON.

At the water treatment works, the Ferrous form can be converted to the Ferric form by oxidation. This may be by aeration or by chlorination. Aeration would have the advantage of reducing the dissolved carbon dioxide content. This will reduce the dose of pH adjusting chemical used to raise the pH to the optimum value for further treatment.

The subject of iron (and Manganese) removal was covered in Part 9 of Process Controllers Guide #2 on Water Sources and Water Treatment.

If an iron compound is used as a coagulant, then it is important that the coagulant dosage, pH value and mixing be optimised. It is also important that all iron be fully converted into an insoluble Ferric form so that it can be settled out or removed by the sand filters. Any soluble iron present in the sand filter effluent could be converted into an insoluble form by final chlorination. This could result in turbidity forming in the distribution reservoir and pipework.

As indicated above, surface water will tend to have a fairly low iron content. The matters covered above would be applicable here as well.

3.6 THE TREATMENT OF WATER CONTAINING HIGH LEVELS OF SULPHATE.

Removal of sulphate alone from a water source would generally not be practical. Where the source water has a high dissolved solids content, then various processes such as demineralisation, reverse osmosis or ultra-filtration could be used. It is important to note that in these processes, the sulphate is not destroyed; it is concentrated into a waste stream that must be disposed of without causing additional pollution.

These processes were covered in Part 10 of Process Controllers Guide #2 on Water Sources and Water Treatment.

Acid mine drainage and industrial effluent can be treated to reduce the sulphate concentration before release to the sewer or the environment. Treatment of water with a high sulphate content using lime will generally leave a residual Calcium Sulphate concentration of about 2 000 mg/L. There are processes to reduce the sulphate content to a very low level.

One such process is the Barium Sulphide process. This process removes sulphates from the water by precipitating the sulphate as Barium Sulphate ($BaSO_4$) using Barium Sulphide (BaS). The Barium Sulphide is regenerated thermally by reducing the Barium Sulphate with coal at 1 000–1 100°C for about 15 minutes. The process produces elemental Sulphur as the by-product. There is a similar process using Barium Carbonate.

3.7 SULPHATE ADDITION DURING THE TREATMENT OF WATER.

Aluminium Sulphate and Ferrous or Ferric Sulphate are often used as coagulants in the treatment of water. All have the disadvantage of adding sulphate to the treated water. Depending on the characteristics of the water being treated, it may be possible to use a polyelectrolyte to reduce or even eliminate the use of sulphate and chloride based coagulants.

The solids produced from the use of Aluminium and Iron coagulants are very light and do not compact well. The use of polyelectrolytes offers the opportunity to produce a more compact and better settling sludge.

IRON AND SULPHUR COMPOUNDS IN THE WATER AND WASTEWATER ENVIRONMENT.

PART 4.

IRON AND SULPHUR IN RELATION TO WASTEWATER CONVEYANCE AND TREATMENT.

In most cases, the operation of the sewer system will fall outside the responsibility of the wastewater treatment works Process Controller. However, it is felt that it would be useful for the Process Controller to know what happens in the reticulation system discharging to the treatment works as this may have an influence on the operation of the wastewater treatment works.

Most of this part was written many years when the BOD_5 *test was in wide spread use. Its use has diminished somewhat in part due to the 5 day delay in obtaining results. This 5 day delay renders the test of virtually no use for process control.*

The test would be of use when there were sudden or significant changes in influent quality.

For all practical purposes and for use in this part – use 50% of the COD value (in place of the BOD_5*) for influent wastewater containing only or a large proportion of domestic wastewater.*

4.1 INTRODUCTION.

One characteristic by which wastewater, particularly domestic wastewater, is known to the public is its potential for creating odour nuisances. Sometimes, it is the odours escaping from sewer manholes that cause complaints. More commonly, the source is the wastewater treatment works particularly the overloaded or the poorly managed one.

Domestic wastewater contains organic sulphur and sulphates which under anaerobic conditions may be reduced by bacterial action to sulphides and other malodorous sulphur compounds. Of these compounds, the most notorious is hydrogen sulphide. It is a gas detectable in very low concentration. Hydrogen sulphide is also noted for its toxicity. The maximum safe concentration in air is only twice that of hydrogen cyanide. It has the dangerous side effect that the ability to sense it by smell is quickly lost. If a person ignores first notice of the gas, their senses will give them no further warning. If the concentration is high enough, unconsciousness will come suddenly, followed by death if there is not quick rescue. Deaths have occurred in sewers that can be attributed to hydrogen sulphide poisoning.

4.2 THE GENERATION OF SULPHIDES IN SEWERS.

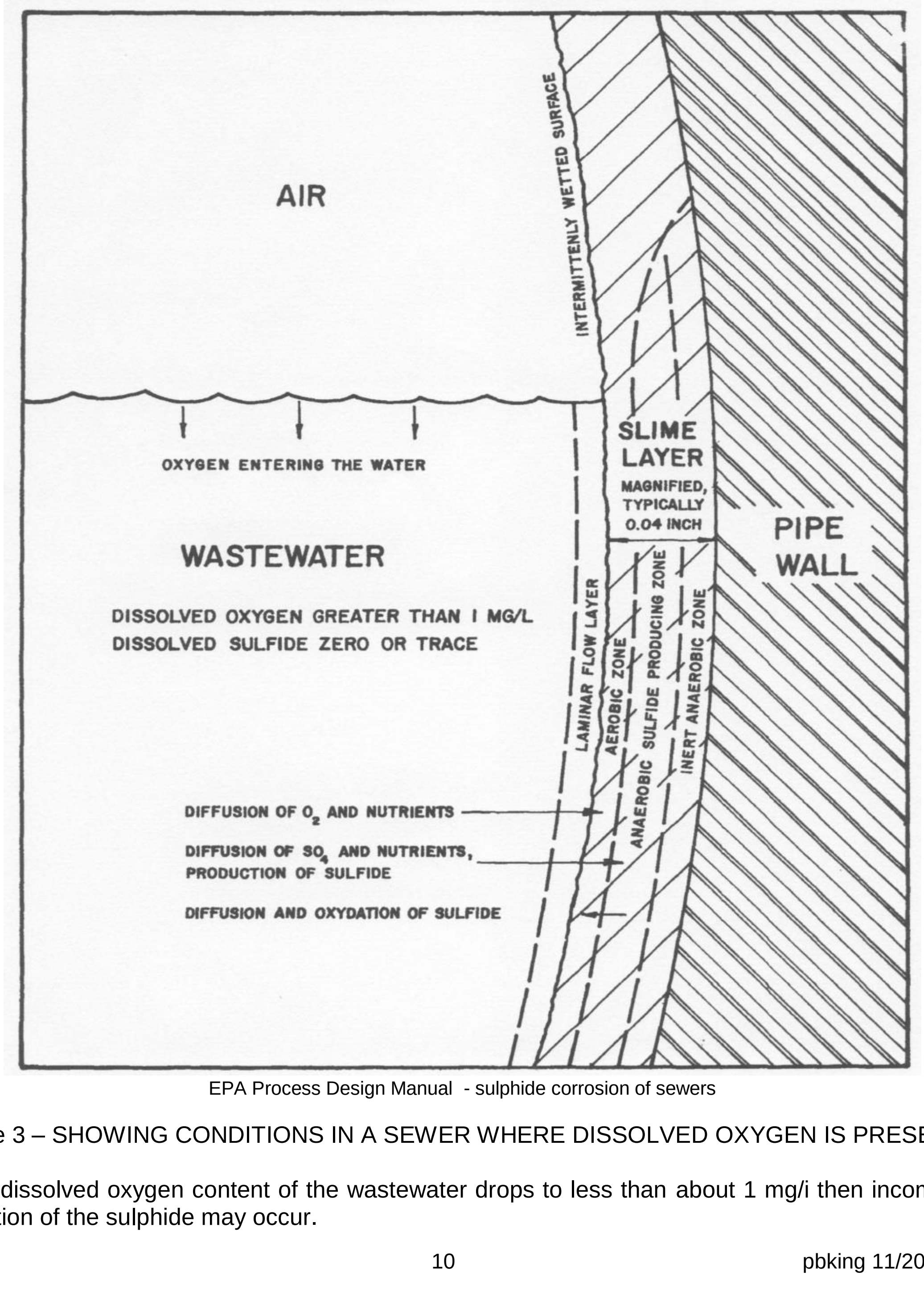
In domestic wastewaters, sulphur compounds are derived from human metabolism of foodstuffs, from household detergents both the detergent itself and from fillers used in the mixture. Also naturally occurring sulphates in the water and those added during the water treatment process eg. by using aluminium sulphate and ferrous or ferric sulphate. Typical total sulphate concentrations of 50 mg/L are found in domestic wastewater and up to 150 mg/L when certain industrial effluents are included. Certain industrial effluents contain sulphides. It is also possible that groundwater from “koffie-klip” areas may infiltrate sewers.

However, the commonest source of sulphides is biological activity in the sewer. The principle sulphur compound in wastewaters is the sulphate ion. Provided there is dissolved oxygen and/or nitrate present in the sewer, little change in sulphur compounds will take place. When organic material is present and both dissolved oxygen and nitrates are absent, then sulphate reducing bacteria will use the oxygen from the sulphate to oxidise organic matter.

Letting “c” represent the carbon in an organic compound. the reaction may be written as:

$$SO_4^{=} + C + 2H_2O \longrightarrow 2\,HCO_3^{-} + H_2S.$$

Here carbon has been oxidised while sulphur has been reduced. For sulphate to be reduced to sulphide, it is required that the medium be completely devoid of free oxygen and of other active oxidizing agents such as nitrate and chlorine. The stream of fresh wastewater in a partially filled sewer is usually not completely anaerobic because it is exposed to the sewer atmosphere. Oxygen absorbed at the surface of the stream generally reacts quite rapidly, and in large sewers its concentration may be very low, yet enough is present to prevent sulphate reduction in the stream. If dissolved oxygen is present in the stream, it diffuses rapidly in to the slime layer, but the aerobic bacteria will use it so rapidly that the oxygen penetration is only about 0.25 mm. Further in than this, the slime layer is anaerobic and it is here where the reduction of sulphate to sulphide takes place. The sulphide generation layer is also only about 0.25 mm thick. At deeper levels, the slime layer is largely inactive because of the lack of a nutrient supply. As long as the surface of the slime layer is aerobic, sulphide diffusing out of the anaerobic zone will be oxidised. These processes are illustrated in Figure 3 below:

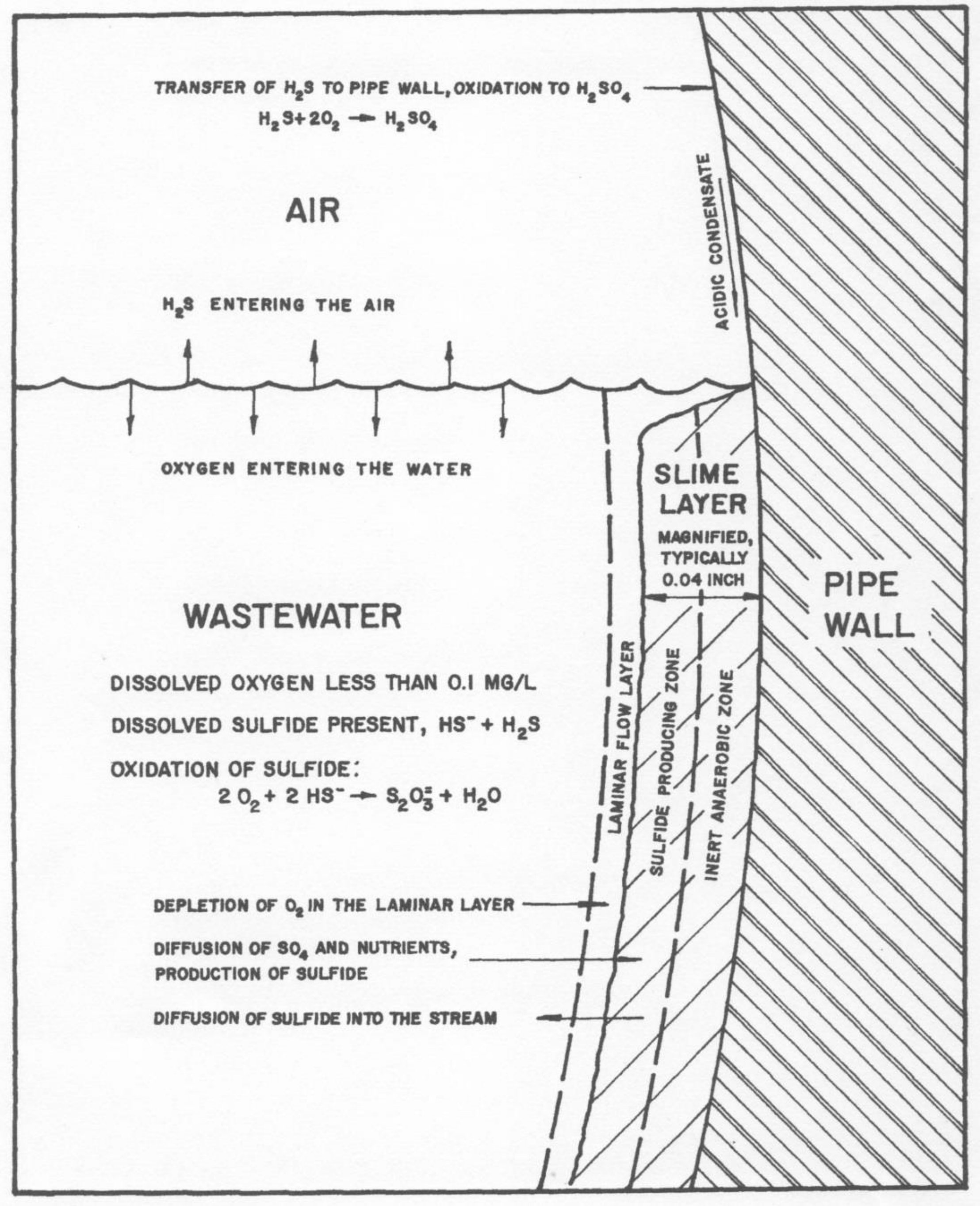


EPA Process Design Manual - sulphide corrosion of sewers

Figure 3 – SHOWING CONDITIONS IN A SEWER WHERE DISSOLVED OXYGEN IS PRESENT.

If the dissolved oxygen content of the wastewater drops to less than about 1 mg/i then incomplete oxidation of the sulphide may occur.

However completely anaerobic conditions must be reached before all the sulphide produced can pass into the stream. Figure 4 illustrates the process.



EPA Process Design Manual - sulphide corrosion of sewers

Figure 4 – SHOWING CONDITIONS IS A SEWER WHERE DISSOLVED OXYGEN IS ABSENT.

The rate at which sulphide can be produced by a slime layer is generally determined by the rate that the reactants i e. sulphate and organic nutrients can reach the sulphate reducing bacteria. When the slime contains a maximum population of these bacteria and when their metabolic rate is high because of favourable temperature and other conditions, the reactants do not have far to diffuse and the rate of sulphide generation reaches a maximum. By contract, if the population is sparse or the metabolic rate is lower, the reactants must diffuse further; as a result sulphide generation is at a slower rate. If the slime layer is thin, as for example in new pipes, the reactants may reach the pipe wall itself without being used up.

The sulphate reducers require sulphate and organic matter in the approximate ratio of 96 : 42. Usually the reactants do not reach the reactive zone in this ideal proportion. Either reactant will be rate limiting for the sulphide generation rate. It appears that the concentration at which sulphate will cease to be rate limiting in most wastewaters will be in the range 20 to 100 mg/L sulphate.

It has been assumed that the organic nutrients are proportional to the standard BOD in most wastewaters, and that the rate of production of sulphide by the slime layer is proportional to the BOD as the sulphate concentration is not rate limiting. With industrial wastewaters other considerations are necessary as they contain a different range of organic materials.

The effect of temperature on the rate of sulphide production by the slime layer is complex. The increased metabolic rate of the bacteria reduces the distance that the reactants need to diffuse and at the same time the diffusion coefficient increases. It appears that the overall effect is about 7% per degree Celsius.

An "effective BOD" or EBOD has been proposed as a convenient way to combine the temperature and BOD_5 effects. The relationship is:

$$[EBOD] = [BOD_5] * (1.07)^{(T-20)}$$

It has been seen above that the dissolved oxygen concentration is a critical factor in determining whether a slime layer will release sulphide into the wastewater.

The absorption of oxygen into the wastewater can take place at:

1. the surface of the wastewater;

2. points of high turbulence.

At the surface of the wastewater, the rate of oxygen transfer is proportional to the oxygen deficit, i.e. the difference between the actual concentration of oxygen in the wastewater and the saturated concentration of oxygen in the wastewater at the same conditions of temperature and pressure.

In addition to surface aeration, oxygen is added at junctions, drops, hydraulic jumps and other places of intensive turbulence that mixes air with water. If the wastewater is devoid of dissolved oxygen, so that the deficit is about 8 mg/L (at sea level); a drop of 300 mm would result in the dissolution of about 1 mg/L of dissolved oxygen. This may seem as a small amount but it could be enough to oxidize as much sulphide as would be produced in 1 500 m of flow.

The consumption of dissolved oxygen in the wastewater cannot be related to the standard BOD_5 or even to the 24 h BOD. The rates change with the age of the wastewater. The dissolved oxygen is used not only in the wastewater but also by the slime layer. In small sewers, particularly where the wastewater does not exhibit a rapid oxygen reaction rate and where dissolved oxygen contents are relatively high, a major part of the oxygen usage is at the slime layer. In larger flows, oxygen concentrations are very low, the gradient of the sewer is less then, the oxygen reactions at the surface of the slime layer are usually unimportant.

Sulphides may be lost in two ways:

1. by reaction of sulphide with oxygen:

2 by escape of hydrogen sulphide to the atmosphere.

Under the conditions usually found in partly filled sewers, a major part of the sulphide passing from the slime layer into the stream is subsequently destroyed by oxidation. This reaction may be either chemical or biochemical. In wastewaters that are biologically inactive because of toxic materials etc., the sulphide is oxidized chemically to sulphate by complex reactions. The reaction rates vary with sulphide and dissolved oxygen concentrations. The biological reaction is more rapid with Thiosulphate being the reaction product. This is shown in the following reaction equation:

$$2\,HS^{-} + 2O_2 \longrightarrow S_2O_3^{=} + H_2O$$

The rate of sulphide oxidation by this reaction varies with the biological activity of the wastewater. In fresh wastewater, the rate may be as low as 1 mg/L per h; but can increase to over 10 mg/L per h in wastewater that has flowed in the sewer for a few hours. The reaction rate is independent of dissolved oxygen and sulphide concentrations provided they are not less than about 1 mg/L. For sulphide to escape to the atmosphere, it must be in the form of a gas.

4.3 SULPHIDE SPECIES VARIATION WITH pH VALUE.

It has been seen in other Process Controller guides that chemicals such as Ammonia and the Carbonic species exist in different forms at different pH values. Sulphides show a similar property.

Sulphides exist in 3 forms – these were shown in part 2.2 Table 3. Summarised here, the three forms are:

1. H_2S Hydrogen Sulphide – a volatile gas;
2. HS^- Bisulphide Ion;
3. $S^=$ Sulphide Ion.

The fraction of each at various pH values is shown in figure 5 below:

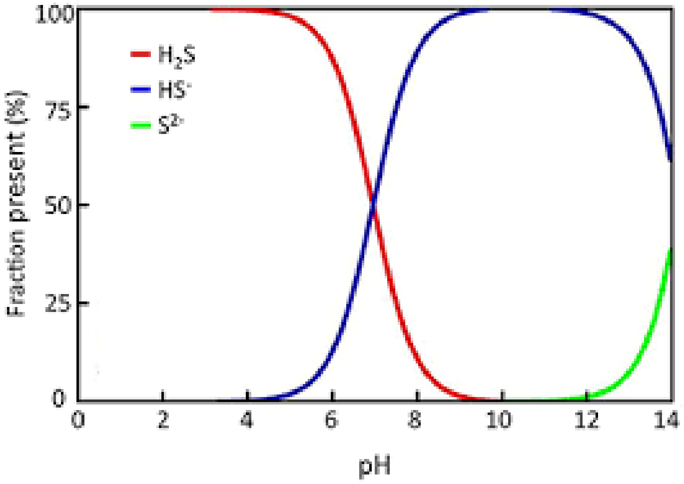


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Figure 5 – SHOWING THE VARIOUS FORMS OF SULPHIDE AT DIFFERENT pH VALUES.

The effect of pH on the proportion of dissolved sulphide present as H_2S is seen to be dramatic. At pH values above about pH8 nearly all the dissolved sulphide is held as the HS^- ion which cannot be lost to the atmosphere. The significance of this will be seen later.

4.4 THE EFFECTS OF SULPHIDES IN WASTEWATER

Probably the most readily recognisable effect of sulphides in wastewater is the obnoxious odour of hydrogen sulphide escaping from manholes, pump stations and wastewater treatment works.

The generation of hydrogen sulphide in sewers and sumps makes it dangerous for workers to enter those areas while the gas is present. The incidence of fatal poisoning has been less in recent years due to greater attention to safety precautions, but a deadly atmosphere will always be a hazard to some degree. Sulphides do have an effect on wastewater treatment processes. One effect is the adverse reaction of the activated sludge process. The growth of Thiothrix, a filamentous organism is encouraged by the presence of sulphides - this results in a poorly settling sludge. This was most likely the cause of the failure of a treatment works when after a stoppage of lime treatment of the raw wastewater, sulphides of up to 15 mg/L in the influent were recorded. After shock treatment with lime and continual lime treatment, sulphides remained below 1 mg/L and the treatment works recovered.

Hydrogen sulphide acts directly on copper pipes and fittings as well as on silver and cadmium. The most corrosive effects are as a result of the oxidation of hydrogen sulphide to sulphuric acid. The overall reaction is:

$$H_2S + 2O_2 \longrightarrow H_2SO_4$$

Bacteria of the genus Thiobacillus are able to oxidise hydrogen sulphide to sulphuric acid. The most important of these are T. Thioxidans, T. Concretivorus and T.Thioparis. These bacteria are able to remain active in sulphuric acid up to 7% concentration. It is this sulphuric acid that has the disastrous effect on iron and on cement-bonded materials.

Briefly the sequence required for hydrogen sulphide initiated corrosion to take place is:

1. Sulphides must be present dissolved in the wastewater. The various sources of sulphides have been covered above;

2. significant amounts of hydrogen sulphide gas must escape from the wastewater into the air space above the wastewater;

3. some of this hydrogen sulphide must be transferred from the air to the surfaces above the wastewater level;

4. the sulphides, therefore reaching the surfaces not washed continuously by the wastewater, must next be oxidized with resultant formation of sulphuric acid;

5. The final stage is the chemical attack of the concrete or cement by the acid produced.

Each of these conditions and processes is an essential step in the sequence and consequently corrosion attributable to hydrogen sulphide can be minimized or prevented by controlling any one or combination of them. This will be covered in greater detail later.

The corrosion of sewer pipe made of cement-bonded materials is not uniform. The greatest corrosion is usually seen at the crown of the sewer. Because the wastewater is usually warmer than the pipe wall, the slightly warmer air rises from the centre of the stream surface to the cooler pipe wall above. As a result the maximum rate of transfer of hydrogen sulphide to the pipe wall is at the crown of the pipe. Uneven distribution of corrosion also results from the draining of acid-containing condensate down the pipe wall, particularly when there is a high rate of acid production. In the zone that is intermittently washed by the water, the pasty decomposition products are cleared away. As a result the pipe wall is laid bare to the attack of the acid when the water level is low. Deep penetration may therefore be observed in this zone. This is shown in figure 6 below:

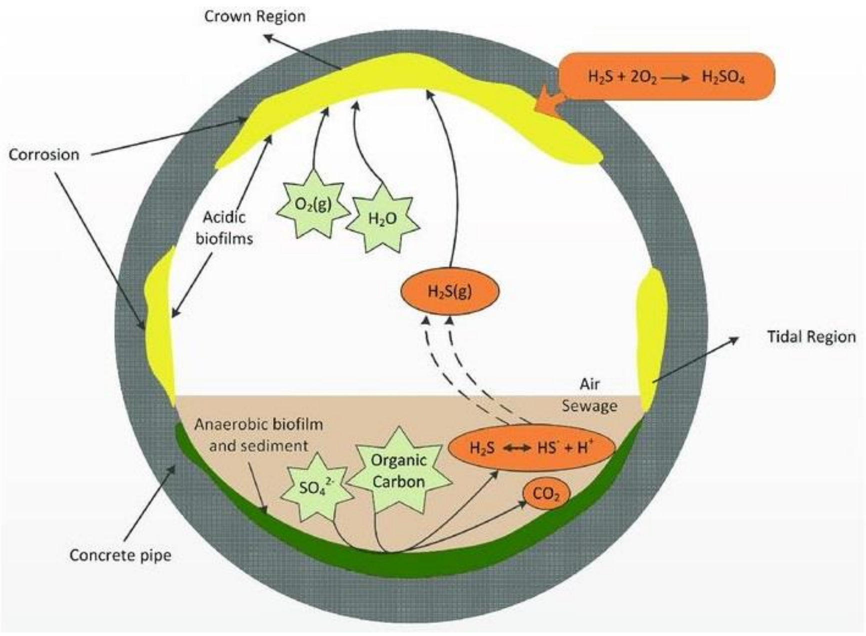

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Figure 6 – SHOWING ZONES OF CORROSION IN A SEWER.

Although the sewer shown in figure 6 s made of concrete, the same effect is seen in a fibre cement (AC) sewer.

The rate of corrosion of cement-bonded materials can be calculated from the quantity of reactive material in the pipe wall that will consume acid and the rate of acid production. The alkalinity or acid-reacting capacity of the pipe material can be determined by analysis or it can be estimated from the composition of the mix used in making the pipe. Typical alkalinities are shown in Table 5.

TABLE 25– MATERIAL ALKALINITY OF VARIOUS MIXES USED IN PIPE MANUFACTURE.

MATERIAL	**ALKALINITY As $CaCO_3$ % m/m**
Concrete with granite type stone	16 – 24
Fibre Cement (formerly Asbestos Cement)	50
Concrete with dolomitic type stone	Up to 90

Most concrete used in pipes can be regarded as comprising three primary ingredients – aggregate [stone and sand], cement and water. The last two combine chemically to form a gel-like mixture of complex hydrates which not only bind the aggregate particles together, but provided the concrete is reasonably well compacted, will provide a highly water impermeable product. This hardened cement paste is generally the vulnerable element in the concrete if exposed to aggressive environments. Cements, being compounds of calcium oxide, are chemically basic. They are thus sensitive to even weak acids, but generally resistant to neutral solutions and alkalis, with some important exceptions.

in the case of sulphuric acid corrosion of sewers, the constituents of Portland cement, both hydrated and unhydrated, are dissolved leaving mainly sulphates of calcium, aluminium, iron and free silica as a soft pasty mass in which any inert aggregate which has not dropped away, is embedded.

4.5 THE DEVELOPMENT OF CORROSION PROBLEMS IN SEWERS DUE TO SULPHIDES.

4.5.1 Conditions that Commonly Result in Higher Concentrations of Hydrogen Sulphide in Sewers.

There are a number of factors that increase the rate of corrosion problems in sewers. These include:

1. **a relatively high sulphate content of the wastewater.** The higher sulphate content of the wastewater; the higher the potential sulphide concentration that can be generated. The presence in the wastewater of a large proportion of industrial effluents with substantial sulphide or organic sulphur contents would aggravate this. This is why most Industrial Effluent By-Laws have a sulphide limit for discharge to the sewer;

2. **the pH value of the wastewater** - the lower the pH value of the wastewater is, the greater the proportion of molecular hydrogen sulphide. This is why most Industrial Effluent By-Laws have a lower pH value limit for discharge to the sewer;

3. **a strong wastewater**. This will have a higher rate of oxygen demand which rapidly uses up the available dissolved oxygen. Also strong wastewater usually contains more surface active material which reduces the surface rate of re-aeration. This is why most Industrial Effluent By-Laws have a Chemical Oxygen Demand limit for discharge to the sewer;

4. **a high wastewater temperature**. This accelerates biological activity so that oxygen is consumed more rapidly, likewise hydrogen sulphide generation starts sooner and then proceeds faster. Oxygen solubility and re-aeration rates are also lower. This is why most Industrial Effluent By-Laws have a temperature limit for discharge to the sewer;

5. **Long retention time in a sewer.** Here there is a much greater chance of the dissolved oxygen dropping to zero and anaerobic conditions developing This can occur in a large wet well, long gravity sewers with flat grades and in long rising mains;

6. **low wastewater velocity in the sewer.** This also favours oxygen depletion and hence sulphide generation commences earlier. The low velocity decreases the rate of oxygen absorption at the surface of the wastewater stream. This is likely to happen with a new sewer while the catchment area is still being developed. The outfall sewer would be designed for future flows but would have low flows and hence low flow velocity in the beginning. There is also a chance that the velocity could drop below the scouring velocity at times resulting in solids settling in the sewer.

4.5.2. Factors Tending to Increase the Emission of Hydrogen Sulphide from Wastewater.

1. **rate of emission of hydrogen sulphide.** The higher the concentration of molecular hydrogen sulphide in the wastewater, the higher the rate of emission;

2. **turbulence of wastewater**. A high wastewater velocity and shock turbulence will encourage emission;

3. **turbulence of airspace**. The higher the relative velocity and turbulence in the air way above the wastewater, the higher is the emission;

4. **characteristic of wastewater.** The cleaner the surface of the wastewater with respect to oil films, surface active agents etc., the higher the emission.

4.5.3. Factors Tending to Increase the Rate of Transfer of Hydrogen Sulphide From the Sewer Atmosphere to the Structural Surfaces Above the Wastewater Level.

1. **concentration of hydrogen sulphide above the wastewater.** The higher the concentration of hydrogen sulphide in the sewer air, the higher the rate of transfer;

2. **pH value of wall moisture**. A higher pH value of the wall moisture increases the transfer rate because the gas then is more soluble in the wall moisture. Sulphide may accumulate in this way before bacterial oxidation actually commences;

3. **turbulence in airspace**. An increased turbulence in the airway, due to high ventilating air velocity or wall roughness or projections, increases the rate of transfer.

4.6 CONDITIONS TENDING TO PROMOTE THE CONVERSION OF HYDROGEN SULPHIDE TO SULPHURIC ACID.

1. **presence of nutrients**. The presence of sulphur or sulphide on the moist sewer surface and of carbon dioxide, oxygen, ammonia, phosphate etc., is necessary for the growth of the sulphuric acid forming bacteria;

2. **suitable environment**. A suitable environment is necessary for the sulphuric acid forming bacteria to commence their activities. In the cement-bonded materials, this may develop initially as a result of carbonation of the originally highly alkaline cement surface;

3. **adequate moisture**. Adequate moisture is required for the oxidation of hydrogen sulphide. This is usually present due to the high relative humidity of the airspace above the wastewater.

4.7 CONDITIONS TENDING TO PROMOTE ATTACK ON STRUCTURAL SURFACES.

1. **permeable or lean-mix cement and concrete.** A permeable and lean-mix (lower cement content) concrete is more susceptible to attack than dense concrete. More acid is required to cause disintegration of the same volume of rich-mix concrete than is needed with a leaner mix. A lean-mix cement or concrete has less structural strength and is more porous.

It is to be noted that sharp edges are subject to attack from two directions and more-over cause increased turbulence;

2. **condensed moisture on wall of sewer.** Condensed moisture running down sewer walls tends to concentrate acid conditions initially and cause the scouring of channels. Acid also tends to accumulate just above the wastewater level as shown in figure 6 above.

4.8 THE RESULTS OF THE DEVELOPMENT OF CORROSION DUE TO SULPHIDES.

The first signs of attack are whitish deposits on the surfaces exposed to the sewer gases. Gradually the cement is destroyed, a pasty layer in which the aggregates are embedded, is being formed. The paste is composed largely of finely divided calcium sulphate together with aluminium and iron sulphates and silica, it is strongly acid - the pH value usually lies in the range pH 1 to pH 3. There is generally a sharp line of demarcation between the destroyed and the unaffected concrete. In advanced stages of attack on pipes, the concrete may be only a thin shell, 6 mm thick or less. By this time the reinforcement, if any, will have already suffered severe corrosion.

Unless one undertakes a routine inspection of sewers, this first sign that one may get of serious corrosion of a sewer could be a blockage due to the crown of the sewer collapsing. If the reinforcing prevents the crown from collapsing, subsidence of the ground above the sewer may be first sign. This could be rather embarrassing if this happened under an important road.

In manholes, sumps and brick sewers, attack takes place on plaster finishes as well as on mortar, leading to softening, crumbling and general deterioration, and frequently also to expansion which may result in cracking of plaster and loosening of the bricks. Ceramic materials like bricks, glazed earthenware and tiles are not affected and such materials are often used, though suitable acid-resisting jointing material must then be used.

Metal components in manholes, sumps etc. are also affected by sulphuric acid. Particularly dangerous is the corrosion of manhole rungs. A rung may look safe, but break before one’s full weight is put on it. Besides the nuisance value in having to replace a sewer or a part of it because of severe corrosion, this could be very expensive to do; particularly in a heavily built-up area.

4.9 THE INCIDENCE OF CORROSION DUE TO SULPHIDES IN SEWER SYSTEMS.

It has been found that the incidence of corrosion due to sulphides in sewers is greatest at certain points, these include:-

1. the point where a rising main or a sewer flowing under pressure discharges into a gravity sewer,
2. the point where night soil or conservancy tank water or other high strength carbonaceous waste is discharged into the sewer;
3. the point where certain industrial effluents, especially those with a low pH value, are discharged into the sewer;
4. where main sewers are laid at such a flat grade that the velocity of the wastewater is less than the minimum required for scouring the sewer. This results in the slime accumulating on the sewer walls below the water level;
5. where the retention time in the system is long and the wastewater becomes septic in the lower reaches as a result of the complete utilization of the dissolved oxygen initially present in the wastewater.

4.10 AN INDICATION OF WHERE SULPHIDE CORROSION OF A SEWER IS LIKELY.

The above gives one an idea of where sulphide corrosion of a sewer is likely to happen. This is shown in an example in figure 7 below:

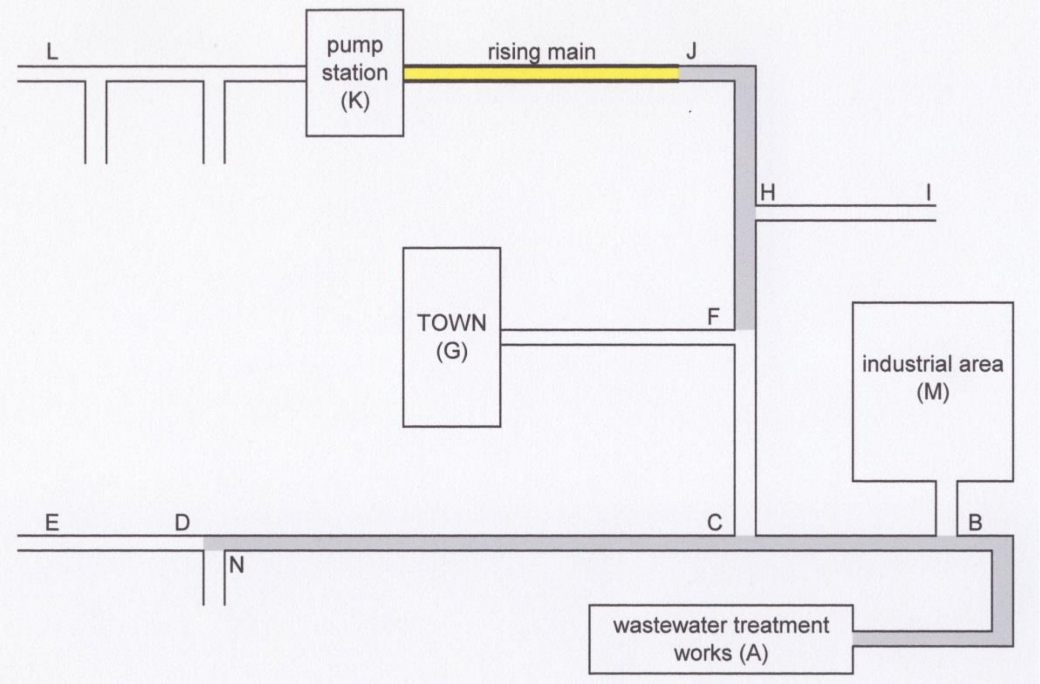

Figure 7 – SHOWING WHERE SULPHIDE CORROSION IS LIKELY IN A SEWER SYSTEM.

Key to Symbols:

A.	wastewater treatment works;
B.	wastewater from industrial area discharges to main collector sewer;
C.	major discharge point into main collector sewer;
D.	just above vacuum tanker discharge point;
E.	top end of sewer;
F.	wastewater from residential area discharges to main collector sewer;
G.	sewer reticulation in residential area;
H.	discharge of small rural sewer;
I.	top end of sewer;
J.	top of rising main [rising main is coloured yellow];
K.	pump station;
L.	top end of sewer;
M.	Industrial area;
N.	vacuum tanker discharge point.

4.10.1 Areas where Sulphide Corrosion is Less Likely to Occur.

No corrosion should take place in those areas where the wastewater would be fresh and no hydrogen sulphide would have developed - providing all sewers have been designed and laid properly. The last few lengths of pipe near to the junction to those in which sulphides are likely to be generated may need protection from gases travelling up the sewers.

These points are likely to be: E to D; G to F; I to H; L to K

4.10.2 Areas where Sulphide Corrosion is More Likely to Occur. (coloured grey in figure 7)

N to C: due to vacuum tanker contents being discharged. Vacuum tankers are used to empty conservancy tanks (storage of domestic wastewater) and the contents of septic tanks. In both cases, the wastewater will be anaerobic and contain sulphides;

J to H to F: due to the age of the wastewater in the sewers;

F to C: there could be dilution of the pumped flow with the gravity flow from the residential area. This would depend on the ratio of the flows, the age of the flow from the town etc;

C to A: due to the age of the wastewater in the sewers.

410.3 Real Life Situation.

There was a main collector sewer in a city that was laid on quite a flat grade. Due to growth in the catchment, this sewer became surcharged for several hours every day. This had the effect of washing away any acid formed by the bacterial oxidation of sulphide every day. The result was that the sewer remained in an excellent condition for more than 40 years.

Further down that sewer, there was a sudden drop in the sewer in order to accept flow from another sewer joining it. The result was extensive corrosion of the sewer at that point with the release of hydrogen sulphide as well.

4.11 THE PREDICTION OF SULPHIDE LEVELS IN A SEWER.

It would be useful to be able to predict sulphide formation in a sewer. This would give one an indication of where sulphide corrosion problems could occur. This would enable one to take pre-emptive action, such as choice of pipe material.

Some formulae have been developed to try to estimate the increase in sulphide concentration in a sewer. One of these is that of Pomeroy[1]. His theory was that the increase in concentration of sulphide during the passage of domestic wastewater through a rising main could be related to the BOD of the wastewater, the total period of retention in the main and the diameter of the main by the empirical equation:

$$Cs = k\ t\ L_{BOD}\ \frac{(1 + 0.004d)}{d}.\ 1.07^{(T-20)}$$

where:

Cs is the increase in sulphide concentration in mg/l;

K is a factor deduced from practical observations. It varies with retention time (t) as given in table 3 below:

Table 3 – VARIATION OF FACTOR k WITH RETENTION TIME (t).

Retention time in sewer (mins)	Factor k
0 – 10	0.0025
10 – 60	0.0050
60 - 300	0.0066

t is total period of retention in the rising main in minutes;

L_{BOD} is the average BOD of the wastewater in mg/L;

d is the diameter of the sewer in cm;

T is the temperature in Celsius.

The varying value for K probably corrects approximately for the fact that with increasing values of the retention time (t), the influence on the formation of sulphide of residual dissolved oxygen in the wastewater entering the main becomes less important. In deriving this equation, it was assumed that the concentration of sulphate available for reduction by microorganisms would not limit the formation of sulphide. In practice, however, the maximum concentration of sulphide that could be produced might be limited by the concentrations of organic sulphur and sulphate present in the wastewater.

An almost identical equation using COD in place of BOD has been developed:

$$Cs = 0.00152\, t\, L_{COD} \frac{(1 + 0.004d)}{d} .\ 1.07^{(T-20)}$$

Where L_{cod} = is the average COD of the wastewater in mg/L.

4.12 MANAGEMENT OF SEWER SYSTEMS TO MINIMISE SULPHIDE CORROSION.

These measures include changes both with the operating organization itself, and changes in respect of the usage of the sewers by industry. Proper operational measures can often do much to reduce the intensity of sulphide problems.

Some important measures that can be recommended are:-

4.12.1 Wastewater and Corrosion Surveys.

These surveys are necessary to show where operational and maintenance procedures should be altered or remedial measures taken to prevent or at least reduce to a minimum the corrosion and the other problems which have arisen from the presence of sulphides. As well as basic surveys, it may often be desirable to conduct a series of relatively localised tests to demonstrate the effectiveness of various alternative measures tried, in order to determine the best operational method of removing or reducing some local sulphide problem.

A corrosion survey is a special inspection of the systems above - water structures to determine the existing condition of the sewers, manholes, metalwork etc. Particular attention should be directed to places where softening or roughening of the concrete surface has started or where the aggregate is showing. It is essential that competent observers be used for these surveys and that results are recorded properly. Regular inspections are necessary, since although for some time a particular sewer has not shown any conspicuous signs of attack, a change of conditions may hasten attack so that significant corrosion could take place within a short period of time.

4.12.2. Control of Industrial Wastes.

As time progresses, the industrial waste fraction of municipal wastewaters appears to be increasing. Most Local Authorities have some legal powers with respect to the acceptance of industrial effluents into their sewers. In general, each industrial effluent discharge must be considered in relation to the composition and volume of the wastewater with which it will be mixed on entering the sewers. An alkaline waste will usually be beneficial by raising the pH of the wastewater and this will amongst others reduce sulphide emission by converting more of the sulphide into the non-volatile HS^- ion. An industrial effluent containing iron salts may help by precipitating some of the dissolved sulphide already present in the wastewater. Some effluents may have bacteriostatic effects. An effluent with a high COD is potentially harmful especially if its sulphur content is high. The addition of an acid effluent to a wastewater already containing sulphide may increase the sulphide emission rate significantly. Hot effluents, that raise the temperature of the wastewater significantly will increase the rate of biological activity and will also reduce the solubility of both oxygen and of hydrogen sulphide. These situations are unfavourable for sulphide control.

The volume as well as the strength of an industrial effluent must be taken into consideration when considering its acceptability. A small volume of a strong sulphide waste might be acceptable if the discharge was so regulated that as to be always small in proportion to the main flow with minimal resultant effect on the sulphide content further down the system.

The proper control of industrial effluents requires properly organised and constant supervision or control of the effluents actually being discharged into the sewers. Any harmful discharge conditions should be detected and warning given at once to the discharger, whereupon appropriate action for adequate control should be implemented.

4.13 THE PHYSICAL TREATMENT OF THE WASTEWATER IN A SEWER.

This consists of injection of either air or oxygen in to the sewer. Using air is one of the most successful methods applied to pumping systems. It has been used in many instances in the U.S.A. over about 50 years. Due to the higher pressure at the lower end of the rising main, an increased rate of oxygen absorption is reached. The injection of air reduces the concentration of sulphide in several ways. The dissolved oxygen destroys sulphide chemically and suppresses the sulphate reducing bacteria. If sufficient oxygen is in solution, aerobic and facultative bacteria will predominate and sulphate reducing bacteria will not multiply and become established. Also turbulence associated with the aeration will shear filamentous colonies of sulphide producers from the sewer wall.

In designing air injection systems, the following guidelines should be considered:-

1. The continuity of treatment. The rising main produces sulphide continuously whether the wastewater is moving or static. Air injection should therefore be continuous whether the pump is on or off;

2. The point of injection. For maximum utilization of the air, the point of injection should be at a low elevation. If there is a vertical riser from the pump, the air may be injected near the bottom of the riser, but it must necessarily be beyond the non-return valve, and in a location where the air cannot get back into the pump;

3. The manner of air injection. Air diffusers have sometimes been used. Since in a short distance, the air collects into large bubbles; it is usual practice to pipe the air straight into the rising main often via a standard type pressure tap;

4. The quantity of air needed.

Probably the most widely used formula to estimate the quantity of air needed is shown below as a sequence of calculation steps:

1. Initially allow 10 litres of air per minute per 10 mm of pipe diameter;

2. Where the average pressure at the injection point exceeds 15 m head of water, the air input may be reduced inversely to the absolute pressure;

3. If the length of the line is more than 1 500 m, increase the air input in proportion to the length;

4. If the oxygen input in kg/d is greater than the daily transmission of BOD_5 in kg/d, then no increase in respect of length is needed;

5 If the peak EBOD is greater than 400 mg/l, then increase the air input in proportion to the EBOD;

6. Size the blower or compressor to about 200% of the value obtained in Step 5 to allow for exceptional circumstances and fall-off in compressor efficiency etc.

In the interests of economy it is recommended that some provision for adjusting the air rate be made. Various methods may be used eg. starting and stopping the compressor or allowing it to idle. In a large installation, a cost-benefit analysis may show it to be economical to go to 2 speed motors or even to variable speed motors.

The measurement of air flow. Some kind of air measurement should be available so that the performance of the compressor can be observed.

4.13.1 The Use of Oxygen Instead of Air.

If the rising main is laid at a low grade, it may be difficult to dissolve enough oxygen by air injection to accomplish sulphide control. The use of commercial oxygen is a possible alternative to air since the rate of dissolution of oxygen is thereby increased. Where maximum BOD reductions are needed pure oxygen would be superior to air because the rate of reaction on the pipe wall is proportional to the dissolved oxygen concentration. A higher dissolved oxygen content can be carried in reserve in the wastewater leaving the end of the rising main. Wastewater containing the normal concentration of dissolved nitrogen can carry in addition 15 to 20 mg/L dissolved oxygen without bubble formation or significant loss if the water does not cascade. The use of air in a rising main can seldom produce a residual of more than 2 to 4 mg/L dissolved oxygen.

4.14 THE CHEMICAL TREATMENT OF THE WASTEWATER IN A SEWER.

Chemicals can serve to control sulphides in either of two ways:-

4.14.1 Oxidising the sulphide.

1. Chlorination.

Chlorination is usually performed using liquefied chlorine gas, but calcium and sodium hypochlorites may also be used although they are more expensive. Chlorine reacts with sulphide and also with organic sulphides, known as mercaptans - these are important odour components of wastewaters. The reaction with chlorine is immediate, whereas the biological deodorisation using air or oxygen is slow. In merely oxidizing the sulphide to sulphur, the chlorine consumption is 2.2 parts by mass per part of sulphide.

$$H_2S + Cl_2 \longrightarrow S + 2HCl$$

In order to oxidise to sulphate, theoretically 9 parts by mass are required.

$$H_2S + 4Cl_2 + 4H_2O \longrightarrow H_2SO_4 + 8HCl$$

In actual practice, about 12 parts by mass are required due to consumption of chlorine by side reactions. The uniform distribution of the chlorine in the sewer is difficult. A hydraulic jump just below the point of chlorination may help mixing. Chlorination into a rising main is more difficult. Any injector passing into the wastewater can catch rags and cause blockages.

Injectors cannot usually stick more than 0.1 pipe diameters into the stream and should be made of silver or another suitable material.

It might be necessary to have a second or third chlorination point if the sewer is long. Re-chlorination might be necessary about 3 km beyond the first point.

2. Hydrogen Peroxide.

This is usually used as a 30% solution in water. Theoretically it reacts with hydrogen sulphide in a 1 to 1 ratio, but in practice at 3 to I ratio is usually needed. The reaction is:

$$H_2O_2 + H_2S \longrightarrow S + 2H_2O$$

A cheap source of this chemical would be needed to make it economical.

3. Nitrates:

Nitrates are not commonly used because of their cost. Where there is a cheap source, such as secondary sedimentation or humus tank effluent, it may be worthwhile considering. Certain bacteria can oxidise organic matter by reducing the nitrates.. The nitrogen is converted to nitrogen gas. The addition of nitrate does not directly affect the oxygen balance as nitrate reduction will occur only in the absence of oxygen.

Sulphate reduction will not occur in the presence of nitrate if nitrate-reducing bacteria are present. A cheap source of nitrates is often found at a wastewater treatment works being the nitrified effluent from a secondary settling tank. Here nitrate contents of 5 to 20 mg/i as N may be found. If this water is run to the pump station at the bottom of the rising main, it may prove to be most effective in reducing the sulphaide problem. When excessive retention times occur in the rising main, this additional flow will help to reduce the retention time and by diluting the wastewater, will reduce its BOD concentration. This will have the nett effect of reducing the total oxygen consumption in the sewer.

See 4.14.3 below.

4.14.2 Converting the sulphide to a non-volatile form.

It was seen in 4.2.1 above; that above pH 8, more than 75% of the sulphide is present as the HS^- ion. This is non-volatile and therefore will remain in solution. This provides one method of reducing or preventing the sulphide corrosion of sewers.

Lime, ie. slaked lime or calcium hydroxide, may be used in two ways :

1. on a continuous basis;
2. in a “shock” load periodically.

By lining on a continuous basis, the pH of the wastewater is increased. By raising the pH to about 8,5 the emission of hydrogen sulphide is virtually stopped as about 97% of the sulphide is present as the non-vo1atile HS^- ion. The dosage of lime required is usually about 150 mg/L i.e. 150 kg per ML. This treatment does not reduce the total amount of sulphide present but merely holds it in the liquid phase. Raising the pH to 8.5 also appears to reduce the activity of the sulphate - reducing bacteria.

In shock dosing a sewer, the pH is raised to about 11. By doing this it is intended that the slime layer be inactivated. Sulphide generation can be stopped if the slime layer is inactivated, but this is only a temporary solution as sulphide generation can start within a few days and can be back to pre-treatment levels within a week. Higher pH values reached during dosing will generally have a more lasting effect, but economics plays a part, as well as the ability of the treatment works to handle the high pH slugs.

4.14.3 Real Life Situation.

The use of lime on a continual basis at a dosage of 150 mg/L has proved to be successful at a certain pump station. The station was designed to pump approximately 55 ML/day up a 5 000 m rising main but for a long time was pumping only about 15 ML/day. Only one of the two 800 mm mains was being used. During an interruption to the liming procedure, sulphides of up to 15 mg/L as S were recorded at the wastewater treatment works at the end of the main. After shock dosing with 500 kg of lime to pH 11.5, normal liming at 150 mg/L was resumed. Sulphides remain below 1 mg/l and often remain below 0.5 mg/L.

Initially when the daily volume pumped was less than 10 Ml/d, there was a very long retention time in the sewer. In the off-peak period, secondary sedimentation tank effluent was pumped to the upper end of the second rising main and drained into the wet well of the pump station via a scour-valve. This together with the lime dosing described above was very effective in reducing the hydrogen sulphide content of the wastewater as received at the wastewater treatment works.

4.15 A BRIEF GUIDE TO DESIGNING TO AVOID SULPHIDE PROBLEMS.

Severe sulphide problems occur in sewer systems where flows are sluggish or the wastewater is contained for some time in filled pipes out of contact of air. One of the most important points here is the consumption of the available dissolved oxygen. Only once the dissolved oxygen has been used up will sulphate reduction take place. With all other factors being equal,;the shorter the retention time in the rising main, the less the oxygen consumption and the less the chance of sulphide problems occurring.

It has been shown that there appears to be a relationship between the effective BOD and the minimum velocity required in the sewer to prevent sulphide build-up. One such relationship is:-

$$Vmin = 0,137\ (EBOD)^{0.5}$$

$$\text{where } EBOD = BOD_{5\,(}1.07)^{T-20}$$

Thus a wastewater with an EBOD of 500 to 600 mg/L, would require a minimum velocity of 1.0 to 1.2 m/sec. Turbulence at the end of the rising main must be avoided.

If the pipe size is decreased, slope and flow remaining the same, the velocity is virtually unchanged, but the mean hydraulic depth is increased and hence reaeration of the stream is diminished. The effect is not large when the pipe is running less than half full. When the pipe is nearly full, the mean hydraulic depth increases rapidly, seriously diminishing the oxygen supply. For the same quantity of wastewater and the same slope, the largest practical pipe size is the best if sulphide generation is determined to be a problem. The possibility of acid conditions resulting from the oxidation of hydrogen sulphide is one of the factors influencing the choice of pipe material for sewers. Other factors are finance and the availability of alternative materials.

4.15.1 Choice of Pipe Material.

A cost benefit analysis would permit a choice to be made on the principle of lowest present worth of all present and future costs. Some of the various types of pipe used are listed together with a brief mention of their characteristics affecting their suitability.

1. Vitrified Clay Pipes

   This is a very old pipe material having been used for more than 4 000 years. This material is immune to alteration by sulphuric acid. However, the use of cement mortar joints is not satisfactory because the action of sulphuric acid on the mortar causes expansion and this can break the joint in the pipe. An improvement, is a plastic seal between the pipes. The use of Vitrified Clay Pipes seems to be decreasing these days;

2. Steel or Ductile Iron Pipes

   If the pipe is used filled, then at pH values above 6.5 and chloride contents of less than 500 mg/L little corrosion will occur even in the presence of sulphides. If the pipe is used partially filled then both sulphuric acid and hydrogen sulphide will cause corrosion;

3. Cast Iron Pipes

   Similar to steel, but because the pipe wall is thicker, they usually last longer than steel;

4. Concrete Pipes

   These may be made with a siliceous aggregate or with a dolomitic aggregate. The concrete with the dolomitic aggregate has greater acid neutralising capacity, but is more expensive. It is recommended, that where the possibility of sulphide corrosion exists, that dolomitic aggregate pipes be used;

5. Fibre Cement Pipes (previously known as Asbestos Cement or AC Pipes).

   These consist of about 85% cement and 15% asbestos fibres. The asbestos fibres are insoluble while the cement is soluble in the dilute sulphuric acid. The asbestos cement thus neutralises acid in the same way as dolomitic aggregate concrete. Compared with them on a mass by mass basis, the asbestos cement pipe has a longer life. This is due to their lower permeability, better compaction and to the fact that they corrode more evenly;

6. Plastic Lined Concrete Pipes

Problems have been experienced with these types of pipes. One problem has been the satisfactory bonding of the liner to the pipe. If the pipe is laid below the ground water level, infiltration of water under the liner may lift it off the concrete. Pinholes in the plastic can allow serious corrosion to occur behind the liner.

The most satisfactory method of construction is to have anchors on the plastic lining that are an integral part of the pipe. An example is shown in figure 8 below:

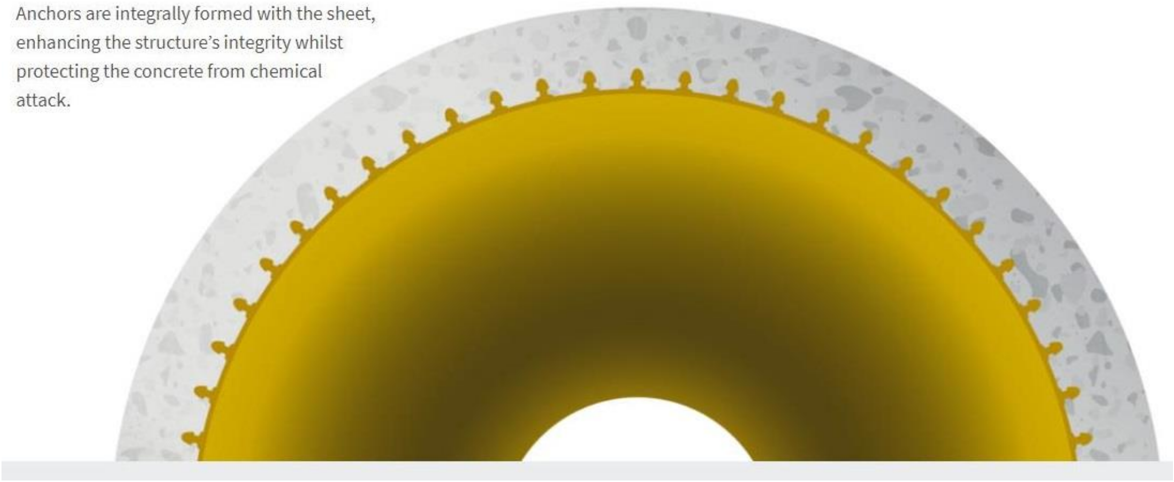

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Figure 8 – AN EXAMPLE OF WHERE THE LINING IS AN INTEGRAL PART OF THE PIPE STRUCTURE.

7. <u>Plastic Pipes.</u>

These may be made of uPVC (unplasticised Polyvinyl chloride) or HDPE (High density Polyethylene).

They are immune to attack by sulphides. They also have a lower friction factor resulting in less resistance to flow.

4.16 REPLACEMENT OF SEWERS.

The traditional method of replacing a sewer damaged by sulphide corrosion (or other causes); was to dig a trench, take out the old pipe and lay a new one. This would cause major disruptions to roads and other services. The modern techniques are trenchless as they involve pulling a new pipe inside the old pipe.

1. slip lining – here a slightly smaller diameter pipe in pulled inside the old pipe. The slight reduction on pipe size is usually compensated by the lower friction of the new plastic lining resulting in little or no loss in capacity. This technique is shown in figure 9 below.
2. pipe cracking and replacement – here the old pipe is cracked open and a new same sized or even larger diameter pipe is pulled through. An example is shown in figure 10 below:

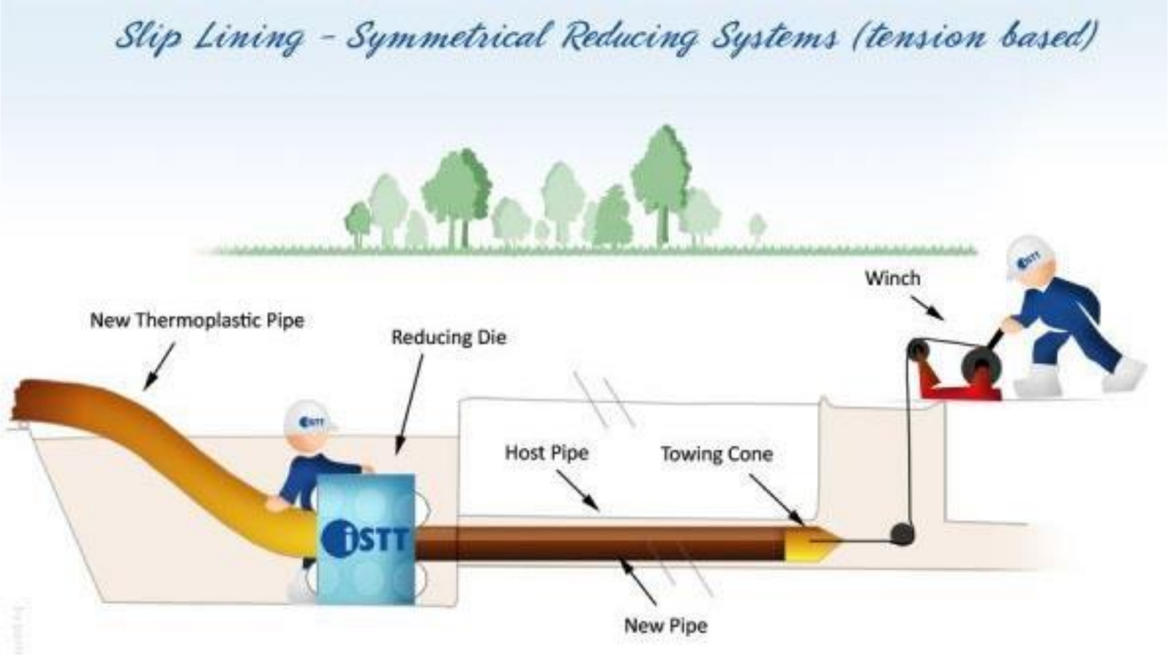

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Figure 9 – SHOWING SLIP LINING OF A PIPE.

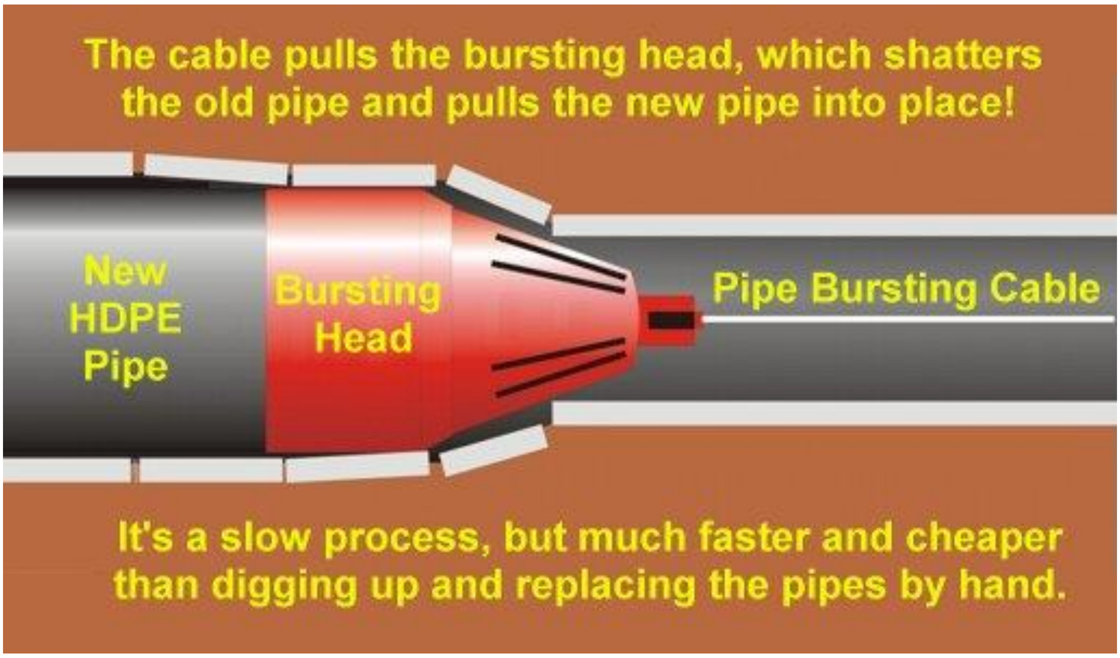

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Figure 10 – SHOWING PIPE CRACKING AND REPLACEMENT.

4.17 THE EFFECT OF SULPHIDES AT THE WASTEWATER TREATMENT WORKS.

4.17.1 Corrosion of Infrastructure.

Where wastewater containing sulphides discharges into a wastewater treatment works there is likely to be corrosion of concrete surface and of steel structures as well. Stainless steel relies on a thin oxide layer to produce corrosion resistance. Sulphides tend to damage this oxide layer and so reduce its resistance to corrosion.

4.17.2 Odour Release.

Most wastewater entering a treatment works will have a pH value in the range of 7.0 to 7.5. In this range, about 50% of the sulphide species present is hydrogen sulphide gas. This together with organic sulphur contain compounds are responsible for the odours at the inlet to a wastewater treatment works.

Turbulence caused by passing through a screen or a flow meter will encourage the release of odours.

Any treatment of the wastewater in the sewer will reduce the potential for odour release at the wastewater treatment works.

4.17.3 Effect on Electrical Panels.

Electrical panels contain copper wires and other components. When the copper is exposed to air containing moisture, it develops a surface film of copper oxide (Cu_2O). This film is a very tough layer that protects prevents further corrosion of the underlying copper. Because the copper oxide layer is very thin and is a good conductor of electricity, the presence of this oxide layer does not create a problem.

When hydrogen sulphide is present, then a completely different scenario occurs. The hydrogen sulphide reacts with the copper oxide forming copper sulphide. This copper sulphide flakes off and the bare copper is exposed. This again gets protected with the copper oxide layer, but this is converted to copper sulphide and the process repeats itself.

The reactions are:

$$4\,Cu + O_2 \longrightarrow 2\,Cu_2O$$

$$Cu_2O + H_2S \longrightarrow Cu_2S + H_2O$$

Contact faces on electrical contactors are often coated with silver. Hydrogen sulphide reacts with silver directly as shown below:

$$4\,Ag + 2\,H_2S + O_2 \longrightarrow 2\,Ag_2S + 2\,H_2O$$

This silver sulphide grows “whiskers” that can cause a short circuit.

Where hydrogen sulphide could cause a problem in electrical panels, one method to prevent this would be to blow air from a clean source into the panel to prevent hydrogen sulphide from entering the panel.

Another maintenance matter often overlooked by maintenance staff is the need to tighten all electrical connections once per year. As the electrical wires contain a number of individual wires, they compress after a time and result in a loose connection. This will result in heat being generated at the connection point. This heat when transferred to the PVC cover of the wires result in hydrochloric acid being formed. This will attack any iron or zinc galvanised components in the panel.

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