ACID CORROSION OF REINFORCED CONCRETE PIPES – THE BURIED FACTS

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ABSTRACT

Acid corrosion of concrete pipes is a well documented degradation mechanism for this product which is used as a vital component of New Zealand's infrastructure. This paper will review and update the various acid attack mechanisms that are common to the industry and outline design solutions accordingly. All acid attack mechanisms are not equal and are often confused in this regard with the provision of sulfate resistance. The paper will clarify these issues.

The mechanism of biogenic sulphuric acid attack, which may occur in concrete sewer pipes, will be reviewed, and the work carried out in the USA to understand the significant factors outlined. American EPA had published a design manual involves various equations that allow a design prediction of rate of sulphide built up in pipe networks, and estimation of concrete pipe wall attack rates. Simplified Excel modeling spreadsheet based on this design approach has been developed. Design examples presented in this paper indicate that well designed and maintained concrete pipelines could safely last for their nominated life; on the other hand, examples of some limited severe cases, indicate that protecting with inert PVC or PE lining, or active measures to reduce sulphide concentration may be needed.

New Zealand laboratory mineral sulphuric acid attack tests have been completed by various agencies and companies on pipe samples with different SCM. While positive laboratory results were achieved, site performance did not always meet the expectation. European research in this area has found that biogenic sulphuric acid attack has a different mechanism to mineral acid attack, therefore; laboratory and field behavior is quite different. Attempts in Europe to develop a field representative, bench-top, biogenic acid attack test will be presented.

Australian pipe companies, through the Australasian industry body, CPAA; have researched acid attack on pipes due to acidic soils and dissolved CO_2 and developed methods to predict depth of attack for various acid concentrations and pipe age. Examples of utilizing the CPAA methods to provide design solutions to achieve 100 years design life in aggressive acidic soil and groundwater situations of major highway projects in NZ, will be presented.

Future solutions and methodologies to support the industry in this particular range of aggressive concrete pipe environments will complete the presentation.

KEYWORDS

Acid attack, Sulphide attack, Wastewater pipes corrosion, Concrete pipe corrosion, Life of pipes, Aggressive Environment.

1 INTRODUCTION

Hydraulic cement concrete has poor resistance to acid attack. Acid attack to concrete is a surface attack in which acid reacts with both hydrated and un-hydrated alkaline cement compounds. In most cases the chemical reactions form water-soluble calcium compounds which are then leached away. Acids also dissolve calcareous aggregates in the same way as the hydraulic cement compounds. Siliceous aggregates on the other hand, are resistant to acid attack, however they are eventually lost from the surface of concrete during the acid attack process when the binding cement matrix is dissolved.

Concrete pipes are manufactured to a very high quality standard to comply with the requirements of the relevant National Standards. It is well known that concrete resistance to aggressive environments is increased when the concrete has high cement content, low water cement ratio, low water absorption, is subjected to effective curing, and is produced under an accredited quality assurance system. These characteristics match those of concrete pipes produced in Australia and New Zealand to AS/NZS 4058:2007 requirements.

Tests on actual concrete pipes installed in acidic environments for various periods in both Australia and New Zealand (CPAA 1987), indicate that these pipes can safely achieve their design 100 year life period despite being installed in acidic soils with pH values ranging between 4.5 and 5.5. The results of this investigation has been adopted by AS/NZS 4058:2007 where Table E1 of the standard (AS/NZS 2007), reproduced in (Table 1) indicates the maximum allowable limits for 100 years design life in various aggressive environments. To assess conformance of any proposed pipe installation to AS/NZS 4058:2007 Table E1, a specific assessment should be undertaken.

Table 1: Concentration of impurities (Table E AS/NZS 4058:2007)

Constituent	Soil Classification		
	Clay/stagnant	Medium	Sandy/flowing
Chloride (mg/L) max.			
Unrinforced concrete	No limit	No limit	No limit
Reinforced concrete	20000	20000	20000
Sulphates (mg/L) max.			
Type GP - general purpose Portland cement	1000	1000	1000
Type SR - sulphate resisting type Portland cement	10000	10000	10000
Acidity			
Acid pH (min)	4.5	5.0	5.5
Exchangeable soil acid (mL of 0.1M NaOH consumed by 100g air dried soil, max.)	70	50	30
Aggressive CO_2 (mg/L) max.	150	50	15

For a comprehensive assessment of installations in acidic environments, it is essential to differentiate between exterior surface acid attack and interior surface acid attack, and for the latter, between acidic effluent attack and sulphide attack (Biogenic Acid Attack or Microbial Induced Corrosion (MIC)). Exterior acid attack, although chemically the same as interior attack may involve a completely different environment and mechanism which will be discussed in detail.

When an acidic soil or ground water is encountered, its effect on concrete is governed by pH, total acidity, ground water conditions, and backfill materials. Table 1 show that a ground water pH of less than 5.5 with free flow along the pipe indicates a potentially aggressive situation where special analysis should be undertaken. In an installation with no movement or slow movement of ground water, the acid in contact with the concrete pipe will be neutralized forming a natural zone which stops further corrosion. The standard allows the aggressive pH level to be reduced to 4.5 in such situations. In both cases the life of the pipe can be extended by providing extra ("sacrificial") cover to reinforcement.

Acidic effluent may be a source of interior acid attack of concrete pipes. Acidic stormwater effluent may result from mining activities or leaching from acidic soils, while sewage acidic effluent is limited to disposal of acidic waste from industrial sites. In both cases the attack is limited to the submerged area or the invert of the pipe and the conditions and limits of attack are similar to that of exterior attack of free flowing ground water.

Section 2 of this paper will cover this corrosion process in detail, it also includes a design procedure to achieve the required life where acidic attack is expected and illustrates how this procedure has been adopted in an actual project to design pipes for the specified 100 year life.

In sanitary sewers where the concentration of all aggressive elements is significantly below the limits stated in Table 1, interior acid attack to the crown of the pipe may occur as a result of the hydrogen sulphide mechanism. Under favorable anaerobic microbial conditions sewage may generate hydrogen sulphide that remains dissolved in the sewage effluent. When fluxed to the unsubmerged crown of the pipe and dissolved in moisture it forms a weak acid which is not capable of corroding the concrete. However if sufficient oxygen, nutrients, and moisture is available, various sulphuric oxidizing bacteria can colonize the concrete surface and convert the hydrogen sulphide to sulphuric acid and the process may continue with different types of bacteria until the pH of the concrete is reduced to values around 1-2. (Scrivener and De Belie 2013)

Scientific knowledge in understanding both the biological and physico-chemical processes behind the generation of sulphides in the wastewater stream, the kinetics of fluxing of hydrogen sulphide gas, and the formation of the sulphuric acid in the crown of the pipe, allowed the development of design processes to control hydrogen sulphide generation in existing sewers and to predict levels in new sewers. Pipe design methods have been also developed such that if the problem cannot be alleviated by proper system design, then the concrete pipe can still be designed to meet the required service life (Pomeroy 1991).

Section 3 of this paper will cover the mechanism of this corrosion process in detail. It also includes a review of various design solutions to minimize the generation of hydrogen sulfide in sewers, methods to predict levels in the proposed network of an actual project, and pipe design procedures to achieve the required design life.

2 CORROSION DUE TO ACIDIC GROUND WATER AND EFFLUENT

2.1 MECHANISM OF ACID ATTACK

Acid attacks the surface of concrete pipes by reacting with the readily available free lime in the concrete and after neutralizing all the free lime the pH of the concrete starts to decrease rapidly. At low pH levels, calcium silicate hydrate, which forms most of the cementing material, starts to decompose releasing CaO which is then neutralized by reacting with the acid. As a result of this acid – alkaline reaction, a layer of calcium sulphate hydrate is formed on the surface of the concrete. This layer is removed in the presence of moving water and with continuous replenishment of acid, the reaction will continue and more of the concrete surface will corrode. If the calcium sulphate layer is not removed the acid has to diffuse through this layer before further reaction can take place, thus causing a substantial slowing of the reaction.

Aggressive CO2 forms carbonic acid when dissolved in water and will have the same effect on concrete as other type of acids. Some ground waters, with reasonably high pH values, may have high amounts of dissolved CO2 that will attack the concrete, therefore, the concentration of CO2 must be investigated and a solution evaluated as part of the design process.

It is usually assumed that the service life of the pipe ends when all concrete cover over the reinforcement is corroded due to the acid attack. When acid starts to attack the pipe reinforcement, the pipe should be replaced or properly repaired to maintain structural integrity and extend service life.

From the above summary, we can conclude the following:

- The acid needs to be strong enough to attack the surface of the concrete, acid with pH below 5.0 is considered aggressive and below 4.0 is highly aggressive to buried concrete pipes.(ACPA 1991)
- Acid attack will not progress without acid replenishment, this can only take place through leaching of acid rich water from the contaminated soil, and attack will not progress without the presence of water.
- Significant ground water movement around the pipe is required to remove the corrosion layer from the surface of the pipe, attack will slow with reduced groundwater movement.
- Humic acid, usually present in highly organic and peaty soils, is not considered highly aggressive to concrete due to the fact that its calcium salts are insoluble in water so that reaction stops due to reaction products clogging the voids in the concrete matrix(BRE 2005).

Support of the above points is illustrated in the response to a question by one of the readers of Concrete Construction Staff (CCS 1987), specifically a letter by T.P. Lees of the Cement and Concrete Association published in the Concrete magazine (British), February 1986, reporting findings that concrete buried in soils with pH of 3.5 to 4.5 for 20 years had shown "no sign of any attack". T.P. Lees believes that where the pH isn't caused by industrial waste but by native acids, where the pH is 3.5 and more, and where there is no flow of water across the concrete, concrete will not corrode with time.
For internal acid attack on the inside surface of the pipe, the effect will be similar to that of freely flowing water outside the pipe, however, the average flow levels inside the pipe should be considered as most pipes are not flowing full for significant proportions of the pipeline life.

2.2 NGARUAWAHIA PROJECT EXPOSURE CONDITION

The information and test results submitted to Humes indicates that mild exposure to an acidic soil and CO2 is anticipated in some areas along the pipe alignment. Following is a summary of the available information:

Table 2: Ngaruawahia project water analysis

Sample No.	Sample Date	Location	Chainage	pH	Free CO2
WQ1/6A	1 July 2011	van Dam/Williams	940	6.3	19.5
7A	8 August 2011		1900	5.5	72
8C	26 July 2011		2090	4.6	137
8B	8 August 2011		2280	6.0	87
8A	26 July 2011		2520	6.3	35
10C	26 July 2011		3280	6.1	55
10A	8 August 2011		3860	4.9	175
11B	26 July 2011	Howard Rd.	4140	4.7	164
11B	25 July 2011	Howard Rd.	4140	4.6	127
12B	26 July 2011		4660	4.5	106
12A	26 July 2011		4940	4.2	?
WQ2/14B	1 July 2011	Ormsby	5920	4.7	120
14A	26 July 2011		6140	4.2	?
15A	1 August 2011		6860	4.1	?
M1-021	1 August 2011		7100	6.2	60
WQ3/17B	22 June 2011	Simpson's Farm	1780	6.6	9.7
17C	1 August 2011		7520	6.1	27

- The above table shows all pH and CO2 results of water samples collected from the work area
- No information available regarding the type of soil and its permeability in the test area.
- No information available regarding the position of water table and its seasonal movement at the pipes installation depth.
- It is assumed that the low pH values are due to presence of decomposed organic deposits “peat” in the proposed construction area.
- It is assumed that the prevailing acid in the soil is sulphuric and organic acids
- Fletcher Construction indicates that for external condition, soil type and permeability is “Medium” and no free flow along pipes is expected.
- Design drawings indicates pipe grade of less than 1%
- No test results available in locations of culverts M2-008 and culverts M3 to M6, this area is considered non contaminated non aggressive by Fletcher Construction, however, further tests are in the progress to confirm this.
- There are no report of industrial contamination in the work area.

2.3 CONCRETE PIPE DESIGN

The project specification required all buried components to be designed for a 100 years service life. Humes proposed to design pipes so that it could achieve this target by considering the following factors that effect both acid resistance and the expected life of the pipes:

2.3.1 CONCRETE COVER

Pipes intended for use in the contaminated areas should be designed with a concrete cover that exceeds the depth of attack during the 100 year service life of the pipes, as recommended in section E2.3 of AS/NZS 4058:2007 when the exposure limits exceeds the limits of the standard.

Humes Concrete (Australia) have conducted research work for the Concrete Pipe Association of Australia (CPAA) with published results in the technical papers section of the CPAA website (CPAA 1988). This research includes an evaluation of the limit of concentration of acid and CO2 adopted by CPAA and recently adopted by AS/NZS 4058:2007 as shown in Appendix E of the standard (AS/NZS 2007).

The results of this research indicates that for standard pipes with 10mm cover, the specified 100 years service life could be achieved when pipes are installed in an acidic soil of a minimum pH ranging from 4.5 to 5.5 depending on type of soil as shown in (Fig. 1) below.

(Fig.2) shows the relationship between depth of CO2 attack on concrete after 100 years of exposure and the concentration of free CO2 in the ground water around the pipe and indicates that a maximum limit of 20 ppm is acceptable for pipes with 10mm cover and a design life of 100 years.

Both figures indicate that the CPAA and AS/NZS 4058:2007 limits are based on depth of attack, and hence, depth of cover on concrete of 10mm which is specified as the minimum limit of the standard. They also indicate that the proposed design limits are conservative compared to the depth of attack on actual pipes.

Arrows on the drawings show the actual tested values of pH and CO2 in the project which exceed the standard limits for pipes with 10mm cover. Therefore pipes were designed with extra cover to accommodate for the extra depth of corrosion anticipated in the low pH and high CO2 areas as measured at some points along the project alignment.

CO2 values in (Fig 2) are based on aggressive CO2 concentration rather than the “free CO2” concentration tested in this project; the figure also indicates that the curves and the standard limits are conservative compared to the measured corrosion values. Based on the conservative nature of the curves and the use of “free CO2” results, the design for durability in this project could use an attack depth less than that obtained from the curves for some culverts.

Figure 1: Estimated depth of attack due to acid (CPAA 1988)

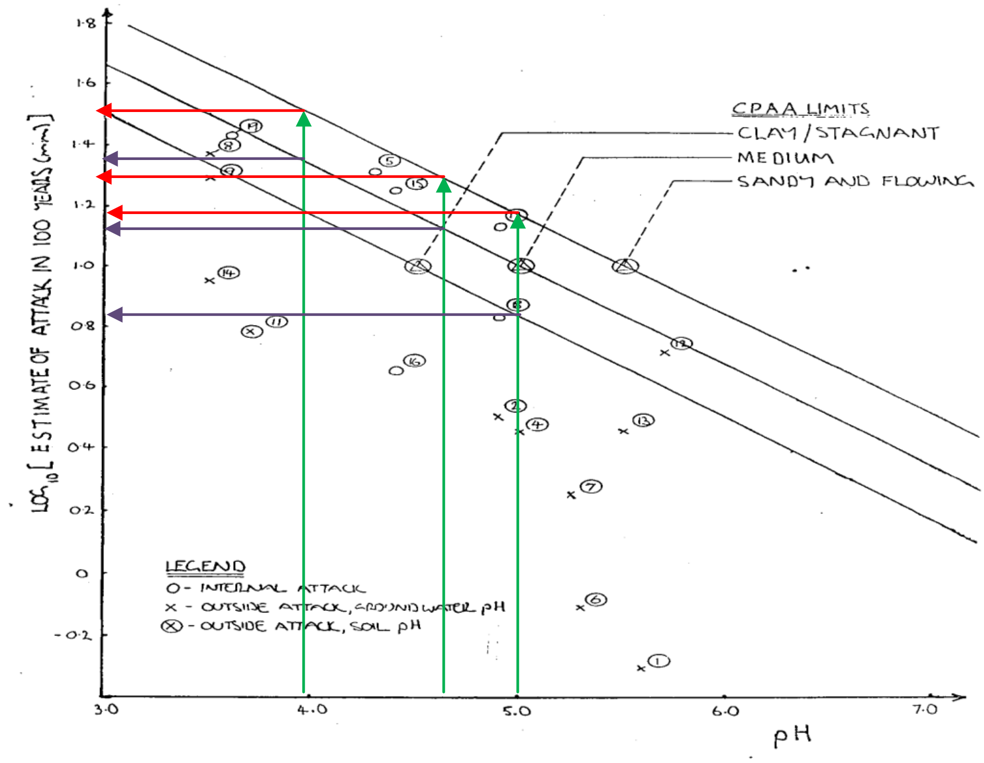


Figure 2: Estimated depth of attack due to CO_2 (CPAA 1988)

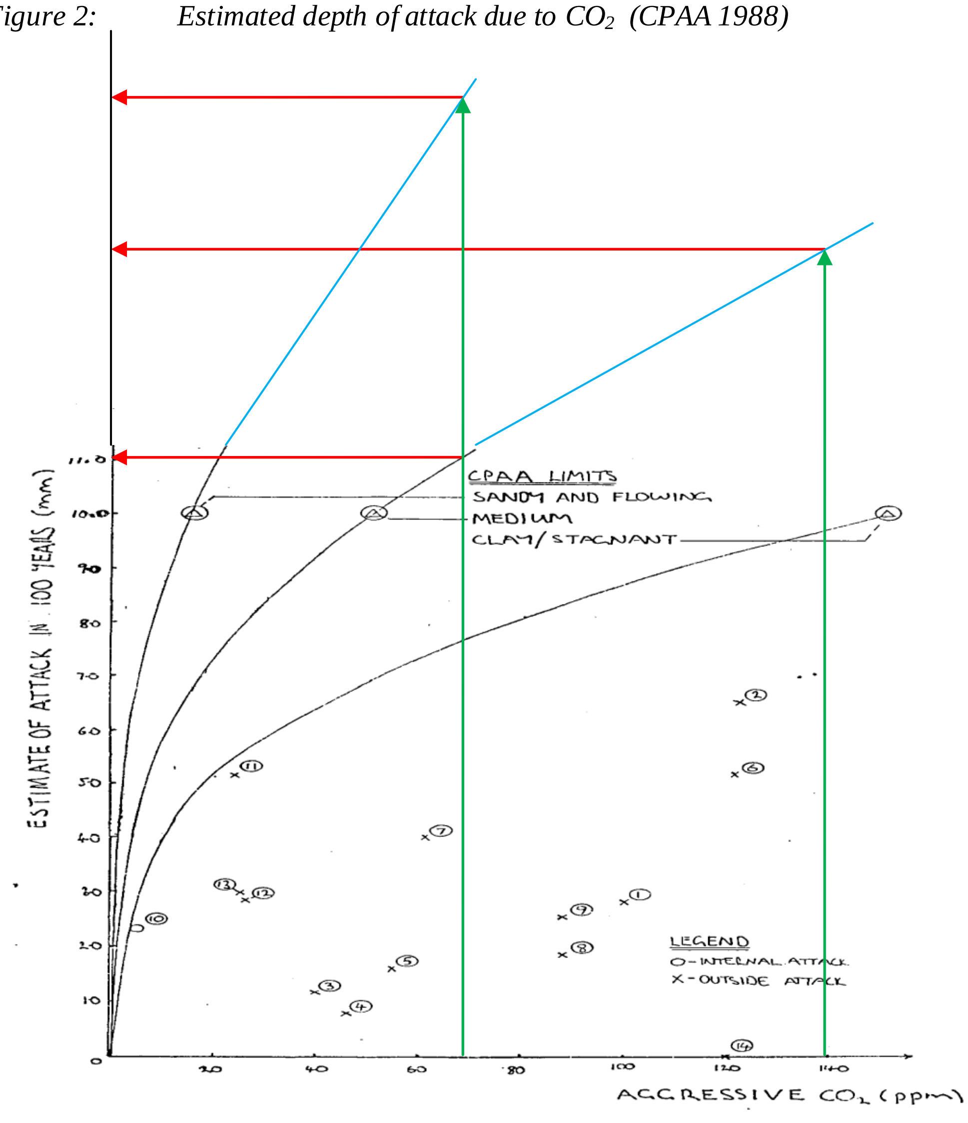
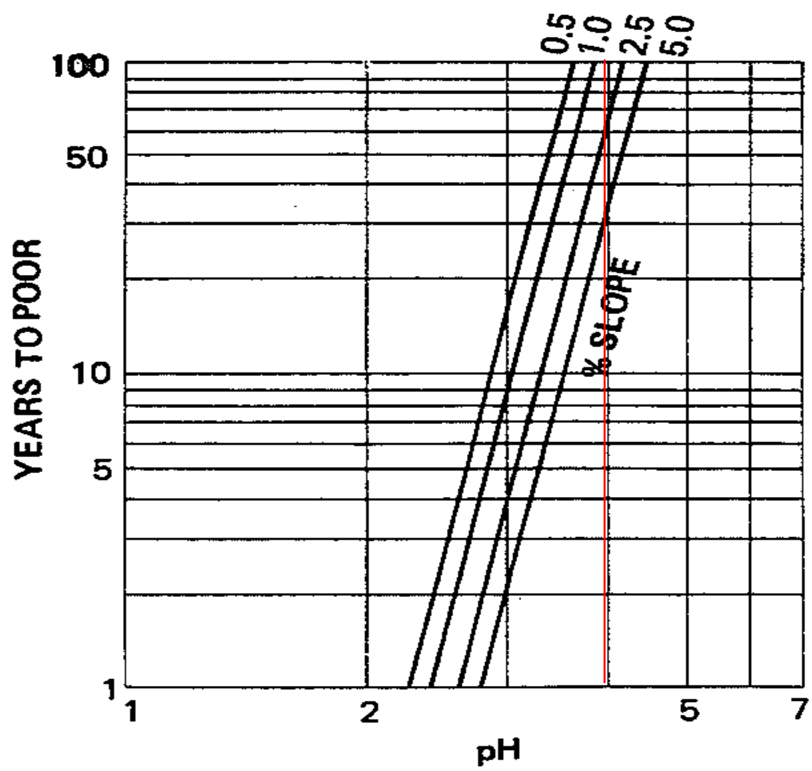


Table 3 Estimated depth of concrete attack for 100 years service life of pipes for Ngaruawahia Project

Soil Classification	Clay/stagnant	Medium	Sandy/flowing
pH 5	8.9	10.0	15.1
pH 4	15.1	18.2	27.5
pH4.7	8.0	14.0	20.0
CO_2 72ppm	8.0	11.0	15.0
CO_2 140ppm	9.0	14.0	About 20

The above results agree with the results of a ten-year study conducted by the Ohio Department of Transportation of more than 1600 stormwater pipes in all areas of the state, which shows that a 100 years service life could be achieved when standard pipes (with 20-25mm cover as per ASTM Standards) are installed at less than1.5% slope in acidic soil with pH value of 4.0 as shown in (Fig. 3) below (ACPA 1991).

Figure 3: Concrete pipe culvert life (ACPA 1991)

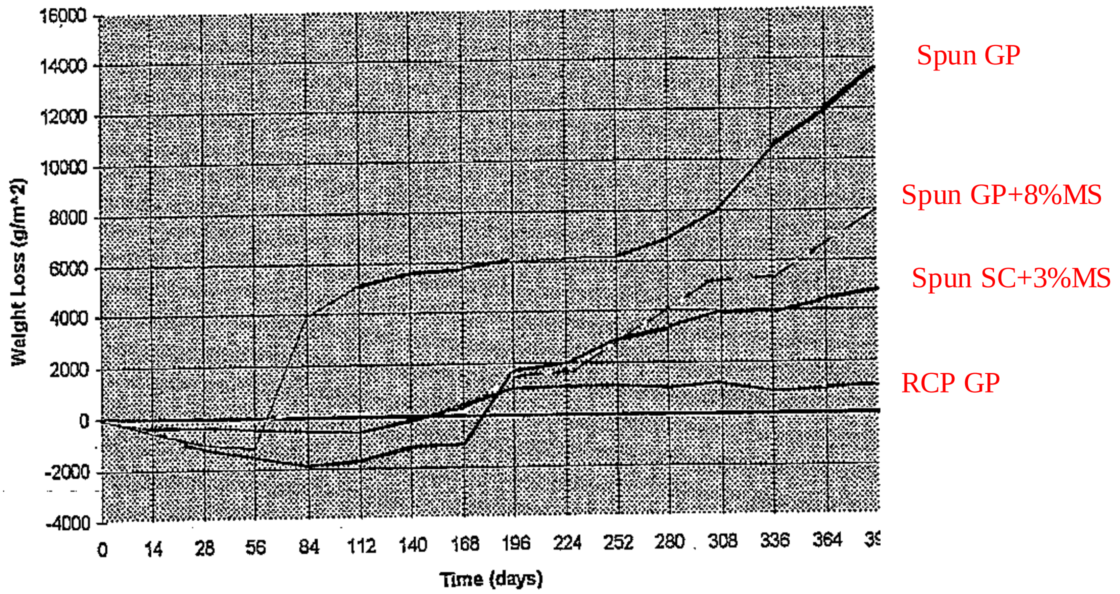


2.3.2 WATER-BINDER RATIO

Precast concrete pipes are produced with low water-binder ratio regardless of which production method is used. AS/NZS 4085:2007 notes that a maximum water-binder ratio of 0.4 should be used to achieve the required water absorption. It has long been recognized that a lower water binder ratio results in an improved microstructure of the cement paste and hence resistance to aggressive environments. This is one of the reasons attributed to the high performance of concrete pipes compared to cast insitu concrete where higher water binder ratios are typically used (and being particularly so in the earlier development years of the 20 the century).

Humes VT pipes are produced using water binder ratios substantially lower than the minimum standard values. For example a water binder ratio of 0.35 is used by Humes in the Papakura VT plant and as a result the cement paste microstructure will be superior to that required by the standard (with a 0.4 ratio).

Figure 4 – Weight loss of various pipe samples in 1% sulphuric acid solution (Humes 2000)



The results of the research work carried out by Humes in 2000 (Humes 2000) shown in Fig. 4 Indicate that RCP which was produced using a water binder ratio of 0.35 (similar to that currently used in VT production) shows much lower weight loss compared to that of spun pipes produced with same type of cement and water binder ratio of 0.4.

2.3.3 SUPPLEMENTARY CEMENTITIOUS AND POZZOLANIC ADDITIVES

Research work on the durability of concrete in aggressive environments agrees that the replacement of part of the cement by fine Pozzolanic materials improves the concrete resistance to acid attack. In 1985 Mehta (Mehta 1985) found that acid resistance of concrete containing 10% Microsilica by weight of cement has a two fold better resistance to sulphuric acid compared to normal low w/c ratio concrete. In a paper published in 1996, Wecharatana and Liskowitz (1996) indicate that concretes containing 15% to 50% Fly Ash exhibit excellent acid resistance when compared to conventional concrete. In more recent work published in 2008, Rahmani and Ramzanianpour (2008), and Murthi and Sivakumar (2008), indicate that concrete made of a ternary blend of Silica Fume – Fly Ash – Cement performs better with regard to acid resistance than that made of a binary mixture of ether additives and both blends perform better than the control Portland Cement concrete.

Humes research results shown in (Fig 4) also clearly show that for the same water binder ratio concrete, the addition of Microsilica and slag cement improves the long term acid resistance of the concrete as compared to the control.

Most research work agrees that the reasons for such improvement in acid resistance is attributed to a combination of factors which could be summarized as follows:

- Dilution – additives reduce the amount of calcium oxide rich cement that reacts with the acid
- Materials - Pozzolanic materials react with the free lime generated from cement hydration; free lime is a weak highly alkaline product that immediately reacts with acid upon exposure.
- Cement Paste Structure – Pozzolans reactions reduce concrete permeability, porosity of cement paste, and improve the microstructure; all these factors are believed to impair the ingress of the attacking materials into the matrix thus improving resistance.

2.3.4 RECOMMENDED PIPE DESIGN

Based on the available information, Humes recommended the following design requirements to achieve and exceed the 100 years minimum service life for the concrete pipe in the contaminated areas of the project:

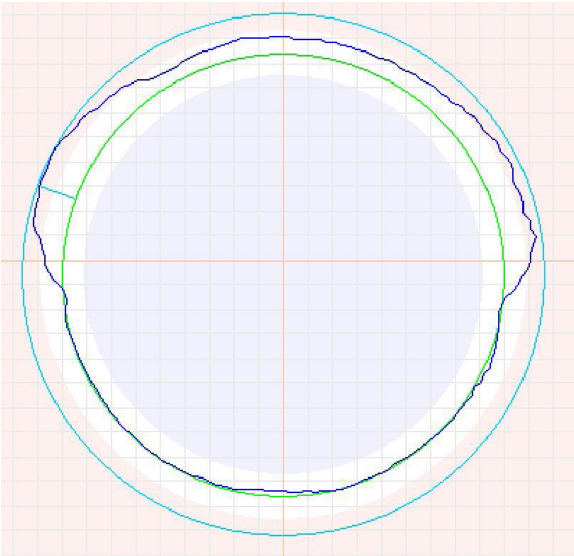
- Minimum external and internal concrete cover to reinforcement = 20mm for pH values more than 5 and CO2 less than 72 and more than 15.
- Minimum external cover to concrete 20mm and internal cover 30mm for pH between 4 and 5 irrespective of CO2 content
- Maximum water binder ratio= 0.35
- Cementitious materials = GP Cement + 15 to 20% Fly Ash
- Apply curing membrane to allow for slow curing of the fly ash
- Design to be reviewed if new information indicates changes in exposure condition.
- An aggregate exposure might be observed on the internal surface of the pipes after a few years of service due to the acid attack; however this will not affect the integrity of the pipes as per this design.

3 INTERIOR SULPHIDE CORROSION OF WASTEWATER PIPES

Also called “Biogenic Acid Attack” or “Microbial Induced Corrosion (MIC)” this process involves a complicated bio-chemical and physico-chemical mechanism that results in the conversion of the organic sulphate in the reasonably inert domestic wastewater, when conditions are favourable, to sulphuric acid which attaches to the concrete matrix in the unsubmerged crown of the pipe, causing severe corrosion in some cases.

Confusion prevails regarding sulphate, sulphide, and sulphuric acid attack on wastewater pipes. Concentration of sulphates in domestic wastewater is usually in the range of 50 to 100 mg/ L which is much less than the maximum allowable limit of 1000 mg/L limit for aggressive sulphates stated by AS/NZS 4058. Domestic wastewater is usually alkaline (pH = 7 to 8) and does not contain sulphuric acid (or any other acid) that may attack the concrete. Hydrogen sulphide gas is too weak to attack the concrete, but it does attack any exposed metals. However concrete corrosion to the extent shown in (Fig 5) has been observed in “live” concrete pipes that only carry domestic wastewater. How then does this happen?

Figure 5 – Laser profile of 450mm wastewater pipe after 40 years (Clearwater Systems 2010)



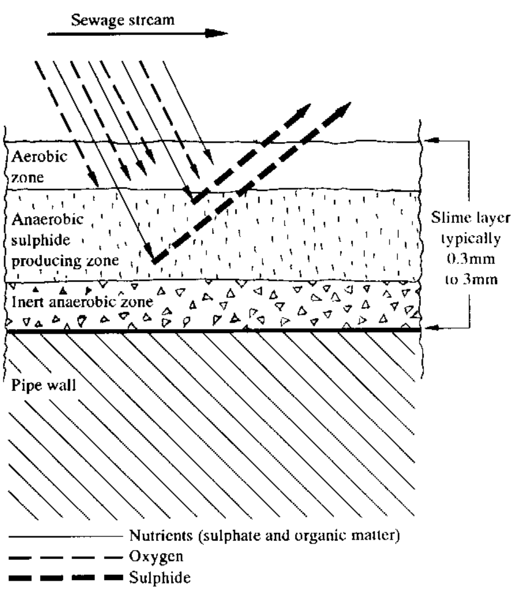
This type of corrosion is not due to wastewater sulphates, sulphides, or acids, but is the result of the final stage of the bio-physico-chemical process of sulphate conversion in the pipe interior to sulphuric acid which attacks the surface of the concrete.

To control this type of attack in wastewater networks, it is important to understand the mechanism of sulphate conversion, factors affecting the extent of conversion, methods of control and best design practices to achieve the required life of concrete pipe under actual service conditions.

3.1 MECHANISM OF SULPHIDE CORROSION

Sulphide corrosion of concrete pipes (and wastewater treatment plant components) is the last stage of the Sulphur Cycle in wastewater that involves a complicated bio-physico-chemical processes. In wastewater pipes, a layer of slime builds up on the submerged pipe wall, very thin where the stream is swift, but a millimeter or more in thickness where it is slow. The slime layer is the site of intense micro- biological action, and it is here that sulfate reduction can take place and the following sulphur cycle starts (Pomeroy,1991)

Figure 6: Cross section of slime layer (Pomeroy 1991)



I. In the anaerobic part of the slime layer (Fig 6), anaerobic bacteria of the genus Desulfovibrio colonize. These bacteria reduce the organic sulphate ions of the wastewater to sulphide ions. The sulphide ions then combine with hydrogen ions to form dissolved hydrogen sulphide gas H_2S and hydrosulphide ion (HS^-), depending on pH. At neutral pH = 7, the distribution is 50/50. At pH = 6 the distribution is 90/10 H_2S/HS^-.

II. Sulphides diffuse out of the zone where they are produced, part of it being oxidized in the aerobic part of the slime zone to thiosulfates, while the remaining portion escapes from the slime layer into the stream. If ample is oxygen present, almost all the sulphides will be oxidised in the aerobic zone, but if the oxygen availability is low, more sulphides will escape to the stream. When this condition prevails, the sewer may show "sulphide build-up" and the concentration in the stream progressively increases as the wastewater moves down the pipe line. However, some oxidation takes place in the stream while some H_2S gas escapes to the atmosphere, hence, at a certain stage, concentrations reach a steady state where losses equal production and no further build up occurs.

III. Hydrogen Sulphide gas is released from the wastewater stream to the pipe atmosphere. The release of H_2S from solution is accelerated under turbulent conditions and higher temperature.

IV. The released gas serves as a food source for another group of aerobic bacteria which colonize the walls and crown of the pipe above the water line. Bacteria of the Thiobacillus family convert the combination of moisture and hydrogen sulphide gas to Sulphuric Acid (H_2SO_4). Various strains of this bacteria, each of which is capable at flourishing at different pH levels, produce enough sulphuric acid to reduce the pH of the concrete from its initial value of 9 down to 1 and 0.2 in some cases (Ref)(Fig). This pH level is highly aggressive to all Cementitious materials.(Scrivener and De Belie, 2013))

V. The hydrogen ions of the acid attack the calcium hydroxide of the hydrated cement of the concrete pipes, while sulphates combine with the calcium ions to form gypsum ($CaSO_4$), a soft soluble corrosion product. If the concrete aggregates are lime stone or dolomitic limestone, they will also react with the acid to form soft, soluble corrosion products. Silica based aggregates do not react with acid, however, they will be lost from the concrete matrix when the binding cement is corroded.

3.2 DESIGN TO CONTROL SULPHIDE CORROSION

Control of sulphide corrosion is possible in most cases if the factors affecting the sulphur cycle are well understood, and the net work is designed with sulphide corrosion in mind. In certain cases it may be preferable that the design to reduce sulphide build-up is supervised by a process engineer with a sound knowledge of the bio-chemical processes associated with wastewater.

It is now well recognized that the most cost-effective method to control sulphide corrosion in wastewater networks, is to do an overall system design to control sulphide generation and build-up in the network. This design may involve, but not be limited to, a thorough hydraulic design of the network that minimizes sulphide generation by introducing special mitigating features. Networks also need to be operated, monitored, and maintained so that sulphide build-up remains within design levels at all times.(US EPA, 1974)

The use of corrosion resistance pipe materials alone, without considering sulphide generation**,** may not be a wise solution in most cases. Excessive amounts of sulphide in the network generate bad odours and cause substantial H&S issues during network access and maintenance. Wastewater with high concentrations of dissolved sulphides also cause odour and metal corrosion problems in treatment plants.

To design a corrosion free wastewater network, or components within the network, to achieve the target design life, engineers need to understand the factors affecting the sulphur cycle in the network, apply engineering design methods to break the cycle whenever feasible, or, alternatively, to design to accept a certain degree of corrosion that does not exceed the design life cycle of that component.(US EPA 1974 & 1991)

3.2.1 SULPHIDE GENERATION IN WASTEWATER NETWORKS

3.2.1.1 Wastewater Characteristics

I. **Dissolved Oxygen**: Low DO favours proliferation of anaerobic bacteria and subsequent sulphide generation. High dissolved oxygen in the wastewater also allows oxidisation of most of the sulphide generated in the anaerobic zone, and hence reduced sulphide build-up in the stream.

II. **Biochemical Oxygen Demand (BOD):** High soluble BOD encourages more microbial growth and more DO depletion

III. **Temperature**: High temperature increase microbial growth rate, lowers DO solubility.

IV. **Concentration of** Sulphur **Compounds**: Sulphides are generated from decomposition of organic sulphate compounds in the wastewater, the concentration of the sulphur ion at the end of the process cannot exceed that of the original wastewater in the sulphate form.

V. **Industrial Discharges**: Unlike domestic wastewater, industrial wastewater may have soluble sulphides, high sulphates concentration, high BOD, high temperature, low pH, and high grease content. All increase sulphide generation and need to be carefully monitored and controlled.

VI. **pH Level**: Low pH wastewater fluxes more H_2S to the pipe atmosphere than that with high pH.

3.2.1.2 Hydraulic Characteristics of Gravity Networks

I. **Velocity:** Adequate velocity prevents deposition of solids which can cause flow obstruction and increase sulphide generation, reduce the thickness of the slime layer, and provides surface re-aeration which helps to maintain aerobic conditions and prevent sulphide generation.
Velocity in pipes is controlled by flow rate, slope, and pipe diameter. All the above factors should be considered in the hydraulic design to minimize potential sulphide generation.

II. **Depth of Stream:** Shallow wastewater stream flows encourage re-aeration due to increased contact area availability on stream surface, and a larger air gap on top of the stream.

III. **Turbulence:** Turbulence of the fresh aerobic wastewater increases DO concentration in the wastewater stream.

IV. **Junctions and Drops:** Both features cause turbulence and re-aeration of wastewater stream. It has been found that drops have a number of folds more aeration effect than flow velocity, therefore they are effective in preventing sulphide generation in fresh wastewater.

3.2.1.3 Sulphide Generation in Pressure Mains, Wet Wells, and Siphons

In pressure mains with detention times longer than, say 10 minutes, there can be considerable sulphide build-up even in NZ temperature conditions, as strictly anaerobic conditions are most likely to prevail. This also happens when wastewater is retained for long periods in large wet wells of Pumpstations or pass through siphons.
High sulphide concentration from pressure mains or Pumpstations wet wells are sometimes discharged to gravity mains where the next part of the sulphur cycle starts.
Total sulphide generation in a pressure main is directly proportional to wastewater BOD and temperature in most prediction formulas(Pomeroy, 1991), however, Thistlethwayte(Pomeroy, 1991), includes in his formula both sulphate content of the wastewater and velocity.

3.2.1.3 Sulphide Generation in small sewers

The flow in small sewers serving a small number of homes can be highly variable with cycles of wetting and drying of the small diameter pipe surface where the slime layer develops. In addition there are frequent connections along the way which adds more aerated flow. The combined effect of these factors may limit the generation and build up of sulphide in this part of the wastewater network. In the prediction of total sulphide generation in a net work, it might be more realistic to assume zero dissolved sulphide content, although theoretical calculations might give a different result. (Pomeroy 1991 & US EPA 1974)

Severe sulphide corrosion is nevertheless observed in some small sewers. The reason for this seems to be the accumulation of paper and other debris in the pipe which causes the formation of semi-stagnant pools where anaerobic conditions prevail.

3.2.1.4 Prediction of sulphide generation in wastewater networks

After a series of scientific breakthroughs starting in the 1950's, it is now possible to predict the generation of sulphide in both existing and new wastewater net works. A number of empirical equations have been developed in the 1970's that allow a reasonably accurate prediction of the amount of sulphide generated in any known part of the wastewater network (Pomeroy 1991 & US EPA 1974).

To facilitate the use of these equations in designing wastewater net works, a spread sheet has been developed to calculate sulphide generation in both partially filled pipes (gravity pipes) and pipes flowing fill such as pressure pipes and siphons. In both cases, two of the most popular formulas were used to allow for engineering judgment in selecting design parameters.

(Figs. 7 & 8) show an example of the sulphide prediction in both gravity pipes and pressure pipes. It is evident from the numbers that sulphide generation in pressure pipes is a number of folds larger than that of partially flowing gravity pipes when all other conditions are the same.

Figure 7: Prediction of sulphide concentration in typical gravity pipe

PREDICTION OF SULPHIDE CONCENTRATION

INPUT DATA

Pipe Diameter, mm	750
Steam Velocity, m/s	0.5
Depth of stream in pipe %	50
Energy Gradient of stream, m/m	0.01
pH of wastewater (select value)	7.5
Average annual dissolved sulphide in wastewater [DS]*,mg/L	N/A
Efficiency coefficient for acid reaction, 0.3 - 1.0	N/A

INPUT DATA

BOD of wastewater	250.00
Temperature of wastewater, ^{o}C	22.00
Initial sulphide concentration, mg/L	0.00
Sulphate concentration in wastewater, mg/L	65.00

PREDICTION OF SULPHIDE BUILD-UP IN PARTLY FILLED PIPES

Rate of build-up (median prediction), mg/L-hr	0.49
Rate of build-up (conservative prediction), mg/L-hr	0.49
Limiting Sulphide concentration, mg/L	1.64
The half-life of the process, hours	2.30

PREDICTION OF SULPHIDE BUILD-UP IN FILLED PIPES

Rate of build-up , mg/L-hr (Pomeroy)	N/A
Rate of build-up , mg/L-hr (Thistlethwayte)	N/A

Figure 8: Prediction of sulphide concentration in typical pressure pipe

PREDICTION OF SULPHIDE CONCENTRATION

INPUT DATA

Pipe Diameter, mm	750
Steam Velocity, m/s	0.5
Depth of stream in pipe %	100
Energy Gradient of stream, m/m	0.01
pH of wastewater (select value)	7.5
Average annual dissolved sulphide in wastewater [DS]*,mg/L	N/A
Efficiency coefficient for acid reaction, 0.3 - 1.0	N/A

INPUT DATA

BOD of wastewater	250.00
Temperature of wastewater, °C	22.00
Initial sulphide concentration, mg/L	0.00
Sulphate concentration in wastewater, mg/L	65.00

PREDICTION OF SULPHIDE BUILD-UP IN PARTLY FILLED PIPES

Rate of build-up (median prediction), mg/L-hr	N/A
Rate of build-up (conservative prediction), mg/L-hr	N/A
Limiting Sulphide concentration, mg/L	N/A
The half-life of the process, hours	N/A

PREDICTION OF SULPHIDE BUILD-UP IN FILLED PIPES

Rate of build-up , mg/L-hr (Pomeroy)	1.95
Rate of build-up , mg/L-hr (Thistlethwayte)	0.76

3.2.1.5 Prevention of Sulphide Generation in Existing Systems

The EPA Process Design Manual for Control of Sulphide in Sanitary Sewage Systems (1974) involves detailed design procedures and methods to prevent or at least reduce sulphide generation in existing wastewater systems. All processes are based on implementing physical or chemical methods to break the sulphur cycle, either by preventing sulphide generation in the slime layer, or neutralizing the already generated sulphide by oxidation or precipitation. Below is a summary of these methods, for detailed design methods, designers could refer to the EPA manual which includes calculations, examples, and case studies:

I. **Oxidation:** It is evident from the previous discussion that the presence of oxygen in sufficient quantities in the wastewater stream plays an important role in sulphide generation and build up. Little or no build up is expected if the oxygen concentration in the stream is 0.1 mg/L or more. This level of DO could be maintained by avoiding any unnecessary oxygen depletion and supplementing more oxygen to the system where it is inadequate.
   - Avoiding unnecessary oxygen depletion due to long detention times in wet wells and tanks, and wastewater backup.
   - Injection of compressed air into pressure mains
   - Injection of oxygen into pressure mains
   - Insert falls, drops, and other high turbulence facilities where dissolved sulphide contents are still very low.
   - Insert properly designed U-Tube Aeration structures
   - Insert air lifts
   - Add aeration facilities to wet wells, special tanks, and retention tanks.
   - Add facilities to achieve in-line augmentation of the oxygen supply in gravity lines
   - Ventilation

II. **Chemical Methods:** Chemicals can control sulphide by either of two ways; a) by reacting with sulphides already present in the stream to oxidise it, precipitate it, or converted it to unharmful form of sulphur compound; and b) by killing the sulphide producing bacteria or altering the atmosphere so that the sulphate reduction is inhibited. Commonly used chemicals are:
   - Chlorine to oxidise sulphides to sulphates and prevent sulphide build up in chlorinated wastewater.
   - Metallic salts, such as iron, zinc, and other metals react with dissolved sulphites to precipitate insoluble sulphides.
   - Hydrogen Peroxide is widely used in pressure mains and gravity sewers. It oxidises H_2S to elemental sulphur.
   - Strong alkalis to control pH including sodium hydroxide and lime.

III. **Control of Industrial Waste:** Strict limitation of low pH discharges, allowing high pH discharges, limitation on BOD level, and soluble sulphides are some of many control actions that could be considered to control sulphide generation in the network.

3.2.1.5 Prevention of Sulphide Generation in the Design of New Networks

Previously discussed methods to predict sulphide generation in wastewater system allows designers to alter their network hydraulic design to eliminate, or at least reduce the generation of sulphide.

Designers can control their design to have adequate velocity to prevent deposition of solids and provide surface aeration to the wastewater stream. Depth of stream in pipes could be changed to improve aeration. Well designed drops, junctions, and jumps in locations where sulphides are not yet generated, will increase re-aeration and prevent sulphide generation down stream of the structure.

In Pumpstations and pressure mains there is no opportunity for re-aeration , therefore, they are in most cases the source of most sulphides generated in the system. The EPA Process Design Manual for Control of Sulphide in Sanitary Sewage Systems includes details of various design methods to prevent sulphide formation in this part of the network.

Control of industrial discharges is also an important factor that should be considered during design.

3.3 DESIGN OF CONCRETE PIPES WHEN SULPHIDE CORROSION ANTICIPATED

In some cases it is difficult or not cost effective to design a wastewater network that will be free from the sulphide problem. It is then important to predict the sulphide level expected in each part of the net work and design that part to achieve the targeted life.

Empirical equations have been developed to predict the corrosion of concrete pipes when the level of dissolved sulphides in the stream, stream hydraulics, wastewater properties, and pipe material properties are known.

3.3.1 CORROSION RATE AND LIFE OF CONCRETE PIPES

3.3.1.1 Flux of H_2S to the Pipe Wall

The flux of H_2S to the pipe wall increase with increase of stream velocity and stream energy gradient. Therefore, high velocities and slopes that have been recommended to reduce sulphide generation should be avoided in those parts of the networks where sulphides are present. Turbulence in drops and junctions are another source of high rate of H_2S flux, and should be avoided when possible, or considered as hot spots, in the life design of networks, pipes and structures.

Flux of H_2S also increases with a decrease of the pH of the wastewater stream. Wastewater streams flowing at shallow depths will have less H_2S flux than those flowing at greater depths.

3.3.1.2 Alkalinity of Pipe Material

Unlike other types of acid corrosion, the sulphide corrosion process involves a limited amount of acid available to react with the cement bonded materials. The amount of acid that reacts is limited by the amount of H_2S fluxing to the wall of the pipe and the possibility of some of the acid being lost due to condensation and high wet weather flow.

As this acid reacts, it will penetrate the wall of the pipe at a rate inversely proportional to the acid- consuming capacity of the wall material (Alkalinity). Use of calcareous aggregates in the concrete pipe increases the alkalinity of the concrete and thus increases the resistance to sulphuric acid attack.

3.3.1.3 Pipe Wall Thickness

Pipes are considered to reach the end of their design life when the corrosion of the concrete wall reaches the reinforcement or when the pipe starts to lose its design structural capacity. Pipe wall thicknesses where sulphide corrosion is anticipated, are designed with an extra concrete layer (sacrificial layer) with the assumption that this layer will corrode within the design life of the pipe.

3.3.1.4 Type of Cement

A number of laboratory tests using mineral acid baths to simulate the performance of concrete during the sulfide corrosion process have been carried out in New Zealand and overseas (UniService 2001, Humes 2000, & Scrivener and De Belie 2013). Most test results indicate that SCM modified cement concretes out perform those made from normal Portland cement, sulphate resistant Portland cement, and calcium aluminates cement. These differences, however, do not correspond to those observed in the field, where CAC concrete usually exhibits the best performance compared to other cements which generally show a similar poorer performance.

To better simulate the actual combined effect of biological activity and the acid effect on the corrosion process, a number of tests have been developed in Europe which aim to improve the modeling of the sulphide corrosion process by using actual bacterial growth to produce the acid (Scrivener and De Belie 2013). Results of these tests confirm the field observations that all types of cement have approximately the same resistance to sulphide attack with the exception of CAC, which has better resistance. Observations during some of these tests indicate that when the pH of the CAC cement is reduced by bacterial action to 3-4, $Al(OH)_2$ increases in solubility and this may facilitate the entry of aluminum ions into solution, which inhibits the activity of the bacteria.(Scrivener and De Belie 2013).

3.3.1.5 Use of Bactericide Admixtures

Bactericide admixtures have been developed in recent years to prevent bacterial growth on the surface of the pipe and hence stop the formation of sulphuric acid that attacks concrete.(Bell et al, 1999) Companies producing such products claim that many city councils are utilizing them in their wastewater structures. However, despite the sound theoretical basis that supports the use of such products, there are no long term tests available and/or an acceptable simulation test to support these claims.

3.3.1.6 Prediction of Life

A spread sheet has been developed to facilitate the prediction of the design life of concrete pipes of various wall thickness made with different types of aggregates (different alkalinity). (Fig. 9) shows an example of the calculation using this spread sheet.

(Table 4) shows the expected life of concrete pipes with different alkalinity and sacrificial layer thickness. The results indicate that it is possible to combine alkalinity and thickness of wall to achieve various design life times

Figure 9: Prediction of sulphide concentration in typical gravity pipe

PREDICTION OF LIFETIME OF CONCRETE SEWERS

INPUT DATA

Pipe Diameter, mm	*750*
Steam Velocity, m/s	*0.5*
Depth of stream in pipe %	*50*
Energy Gradient of stream, m/m	*0.01*
pH of wastewater (select value)	*7.8*
Average annual dissolved sulphide in wastewater [DS],mg/L*	*1.6*
Efficiency coefficient for acid reaction, 0.3 - 1.0	*0.7*

PIPE DESIGN SELECTION

*Select Degree of Resistance***	*5*
*Select Type of Concrete****	*1*

Predicted Lifetime of Sewer, Years	**91.98**

***Values 1 - 5 for concrete cover to reinforcement of 10 - 50mm*

**** 1 For Normal Silica Aggregate concrete*

2 For Calcareous All Aggregate concrete

3 For Calcareous Course Aggregates concrete

Table 4: Estimated life of the concrete gravity pipe using different concrete covers and materials

Type of Aggregates	Thickness of Cover mm				
	10	20	30	40	50
All Silica Aggregates	17	34	52	69	86
All Calcareous Aggregates	73	146	219	292	365
Course Calcareous Aggregates	47	84	142	189	236

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