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Acid Resistance of Sewer Pipe Concrete

Plagiarism Declaration

I, **Ntseuoa Motsieloa**, know that plagiarism is wrong. I declare that this is my own work and that each significant contribution to, and quotation in this project from the work of other people has been attributed, and has been cited and referenced where applicable.

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Abstract

The corrosion of sewer pipe concrete is a global problem, especially in warm climates in which biogenically generated sulphuric acid attacks the concrete and lowers its structural integrity. The Virginia Experimental Sewer is a ‘live sewer’ in South Africa for investigating acid resistance of concrete made with different cement/aggregate combinations. In previous studies, Calcium aluminate cement (CAC)/dolomite concrete was found to perform well in this aggressive sewer environment. However, due to the cost limitations of CAC in pipe infrastructure, it was decided to investigate the use of CAC blends with fly ash (FA) and ground granulated blast furnace slag (ggbs) with the following percent replacement: 15 %, 25 % and 40 % for FA and 25 %, 40 %, 50 % and 60 % for ggbs.

FA and silica fume (SF) were also blended in Portland cement (CEM I 42.5 R) concrete to make binary mixes of 70 % PC: 30 % FA, 90 % PC: 10 % SF, and a ternary mix of 72 % PC: 20 % FA: 8 % SF. Duplicate specimens are installed in the Virginia Sewer to determine a material factor (M_F) for these various blends, i.e. a ratio relating the corrosion rate of any concrete to that of PC /Siliceous concrete in a given sewer. This will enable the results to be incorporated in the Life Factor Method (LFM) when designing sewers which demand a better material performance than plain PC /dolomite concrete.

Standard tests such as tensile splitting, compressive strength, and durability index tests were performed on all the samples to assess the quality of the concrete specimens for application in sewer pipes. Generally, the CAC concretes had low OPI values (< 10) and high sorptivity values (> 11 mm/$\sqrt{\mathrm{hr}}$ for CAC/FA specimens and > 9.5 mm/$\sqrt{\mathrm{hr}}$ for CAC/ggbs specimens). However, the porosity of CAC concretes was less than that of PC concretes because it uses higher proportion of mixing water for its high early strength development and thus reduces the free water, which forms the voids. The acid insolubility test and laboratory acid resistance test (pH = 1.0) were performed to measure the neutralisation capacity and acid resistance of the specimens. Portland cement concretes generally performed better than the plain CAC concretes in the acid resistance test. However, the blended CAC concretes had higher acid resistance than a plain CAC concrete. The blended CAC concretes with the extenders had low strengths but did not undergo any conversion such as occurs in a plain CAC concrete. A converted CAC concrete with high porosity was more acid resistant than an unconverted concrete. Thus, it is clear that the high acid resistance of CAC concrete in aggressive environments is not only a function of its porosity or permeability, but also of its hydration products.

Concrete pipe sections of different cement/aggregate combinations are installed in the Virginia Experimental Sewer to investigate corrosion at the crown of the pipe, which cannot be simulated by laboratory tests. Although a dolomite aggregate increases the neutralisation capacity of the concrete, preliminary results indicate that PC/DOL concrete samples exhibit a differential corrosion rate in the paste and the aggregate due to differences in their alkalinity, which could be detrimental. Therefore, an appropriate cement/aggregate combination that will provide slow uniform corrosion is preferable for acid resistant sewer pipe concrete. The performance of PC dolomite concrete blended with supplementary cementitious materials (fly ash, ggbs and silica) in a 'live sewer' is variable with PC/FA/DOL samples having highest mass loss of about 4 % followed by PC /SL/DOL at 3 % and PC/SF/DOL samples at 2 % for data taken in October 2011. The CAC concretes on the other hand are performing well thus far with zero mass loss because these concretes gained mass due to formation of complex aluminates; however slight corrosion was noticed by visual inspection.

KEY WORDS

Acid resistance, Sewer pipe concrete, Calcium aluminate cement, Fly ash, Slag, Portland cement concrete

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Dedication This thesis is dedicated to my parents Mr Lebina Bernard Motsieloa and Mrs Mapule Motsieloa for the love they have given me, but most importantly I would like to thank God because it is his grace that this work is completed.

Cover photos

Top: Concrete pipes at Rocla Concrete Manufacturing (Photo by Alaster Goyns)
Bottom: CAC/SIL concrete pipe after 14 years in a service life exposed to biogenic acid corrosion i.e. plain calcium aluminate cement concrete with siliceous aggregate (Photo by Alaster Goyns).

Concrete nomenclature

Acid resistance	The ability of the concrete to resist/neutralise an acid environment
Acid insolubility/acid solubility	acid dissolution of concrete in an acid
Durability index tests	Tests used to measure resistance of concrete to transport of fluids and ions responsible for deterioration mechanisms
Gypsum	Calcium sulphate di hydrate ($CaO.SO_3.2H_2O$)
Hygroscopic	Ability to absorb water molecules from the atmosphere
Ettringite	Calcium sulphoaluminate ($3CaO.Al2O_3.3CaO.SO_4.32H_2O$)
False set	Significant loss of plasticity without releasing heat of hydration
Flash set	Rapid early loss of workability, leading to stiffening of the wet concrete, it results from imbalance of the sulphates and aluminates in a concrete
Pozzolan	An inorganic material, either natural or artificial, which hardens in water when mixed with calcium hydroxide (lime) or with materials that can release calcium hydroxide (Portland cement clinker).

Microbiology nomenclature

Abiotic	Produced without living organisms, occurring in the absence of life
Acidophile	An organism that grows optimally in an acid (generally below pH of 5)
Antibiotic	A molecule that can kill or inhibit the growth of the micro-organisms.
Antimicrobial agent	A chemical substance that can kill microbes or slow their growth
Autotroph	An organism that can reduce carbon dioxide to produce organic carbon for biosynthesis.
Autotrophic aerobe	See autotroph

Biofilm A biologically active layer on a surface or interface, consisting of complex association of micro-organisms, microbial products, water, and suspended dissolved solids.

Biochemical Oxygen Demand (BOD) An indicator of the amount of dissolved oxygen (DO) needed to biologically degrade the organic compounds in a aquatic environment

Biocide see anti microbial agent

Biogenic Produced or formed by microorganisms, such as sulphuric acid in sewer pipes.

Desulfovibrio A genus of Sulphate Reducing Bacteria which occurs in mud and sediments of sewerage in the sewer pipes

Electron acceptor A low molecular weight inorganic or organic species (compound or ion) that is reduced in the final step or electron transfer process

Electron donor A low molecular weight inorganic or organic species (compound or ion) that is oxidised in the first step or electron transfer process

Neutrophile An organism with optimal growth range in environments between pH5 and pH 8

Sulphate reducing bacteria (SRB) A bacteria which can use elemental sulphur as terminal electron acceptor in an anaerobic respiratory metabolism.

Sulphide oxidising bacteria (SOB) A bacteria which can use elemental sulphur as terminal electron donor in an anaerobic respiratory metabolism

Mixotroph An organism that obtains its energy by the oxidation of an inorganic substrate

Sulphur substrate Nutritious elements or compounds of sulphur to bacteria in the sewer pipes

Thiobacillus A mixotrophic bacteria which is found in soil, mud soil sediment in the sewer pipes, mine drainage and hot springs. Most species obtain energy by oxidising sulphur and/or reduced sulphur compounds (sulphides, sulphite and thiosulphate)

Thiobacillus thioparus Species that are found in the thiosulphate liquid media with optimum growth at temperature of 28 °C, optimum growth at pH 6 – 8 and growth ceases below pH of 4.5

Thiobacillus thioxidans Species that use thiosulphate and elemental sulphur as electron donors; found within approximate pH range 0.5 – 6.0 and have optimum growth within pH 2 – 4

Thixotropic of a concrete to appear stiff before being compacted/vibrated, but quickly fluidify under either compaction/vibration

Standard tests

SANS 6242, **2008:** Acid insolubility test of aggregates. South African National Standards

SANS 5863, 2006: Concrete tests – Compressive strength of Hardened Concrete. South African National Standards

SANS 6251, 2006: Concrete tests- Density of hardened concrete, South African National Standards

SANS 6253 2004: Concrete Tensile splitting test, South African National Standards

SABS 676, 2003: Concrete pressure Pipes, South African Bureau of Standards

University of Cape Town Durability Indexes Test Manual. 2009 - Permeability, Sorptivity and porosity

Abbreviations

CAC – Calcium Aluminate Cement

ggbs – Ground granulated blastfurnace slag

HAC - High alumina cement

FA - Fly ash

LFM – Life factor method

OPC – Ordinary Portland cement used

PC – Portland cement

SA – South Africa

mM – milli molar

M – Molarity

M/H - Manhole

SF – Silica fume

SIL - Silecious aggregate

SL - Slag

N – Normality

UCT - University of Cape Town

US - United States of America

Cement chemistry notations

A – Al_2O_3

C - CaO

H – H_2O

S – SiO_2

F – Fe_2O_3

Some examples

C_2AS =Gehlenite (2CaO. Al_2O_3 .SiO_2)

CA = Mono calcium aluminate (CaO.Al_2O_3)

AH_3 = Gibbsite (Al_2O_3.3H_2O)

CAH_{10} = Monocalcium aluminate decahydrate (CaO. Al_2O_3.10 H_2O) – a metastable hydrate

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Chapter 1: Introduction, background and study objectives

1.1. Background and problem identification

Biogenic corrosion of sewer pipe concrete and waste water conveyance systems is currently a global problem for most countries especially in warm climates e.g. South Africa (Alexander *et al.,* 2008), Belgium (Zhang *et al.,* 2008), United States (Gualdalupe *et al*., 2010) and France (Lamberet *et al.* ,2008). With this type of deterioration, the sewer pipes fail prior to their intended service life. The design life of sewers in South African (SA) cities had recently been 40 years (Da Silva, 2009), however many of the sewers in older SA cities are older than 40 years and have not been replaced or rehabilitated. Increasing urban population and industrialisation brings about the need to rehabilitate and research new methods of building long lasting sewers. However, the rehabilitation and replacement of these underground structures is expensive because closure of roads for excavation causes delays and hence becoming even more expensive. The Virginia Sewer is a typical example of such problem in which there is work that is currently being undertaken on the performance of sewer pipe concrete materials. Figure 1.1 below is an example of deteriorated calcium aluminate cement concrete made with dolomite aggregate, due to exposure in a 'live sewer' for a period of 14 years at Virginia Experimental Sewer.

Figure 1.1 Deteriorated CAC/DOL sewer pipe concrete after 14 years of service at Virginia Experimental Sewer

1.2. Social and economic factors

The consequences of structural failure of sewer pipes can result in catastrophic situation in which the sewage can flood the streets. This situation is dangerous to human health and the environment because hydrogen sulphide gas is odorous and toxic. Hydrogen sulphide (H_2S) is acid forming gas that was reported by EPA (1991) to have resulted in a number of deaths due to the exposure of workers in confined areas of sewers. Since sewers are underground structures, the leakages of a failed sewer pipes may mix with ground water and this can affect the life of the ecosystem in a given environment. This may go unnoticed for years and later the sinkholes and cavities created may pose extreme risk of property damage and danger to public. The economic implications of sewer pipes corrosion are astonishing. A study done in 1989 by Los Angeles County showed that about $150 million was needed to repair or replace a 25 mile damaged sewer, and the city of Houston estimated $477 million on the rehabilitation of its sewers (EPA, 1991). The consequences of acid corrosion are destructive, the closure of roads for repair and rehabilitations cause havoc and this may cost more than the repair itself. In recent studies of corrosion costs (Koch, 2011), it is estimated that the corrosion cost of water and sewage systems is far higher than that of other sectors, estimated at $36.0 billion per year in the United States (US) with this quantifying the indirect costs as well (Figure 1.2). Although the cost is determined based on the factors that are different from SA, relative to other sectors the corrosion cost of water and sewage systems is higher.

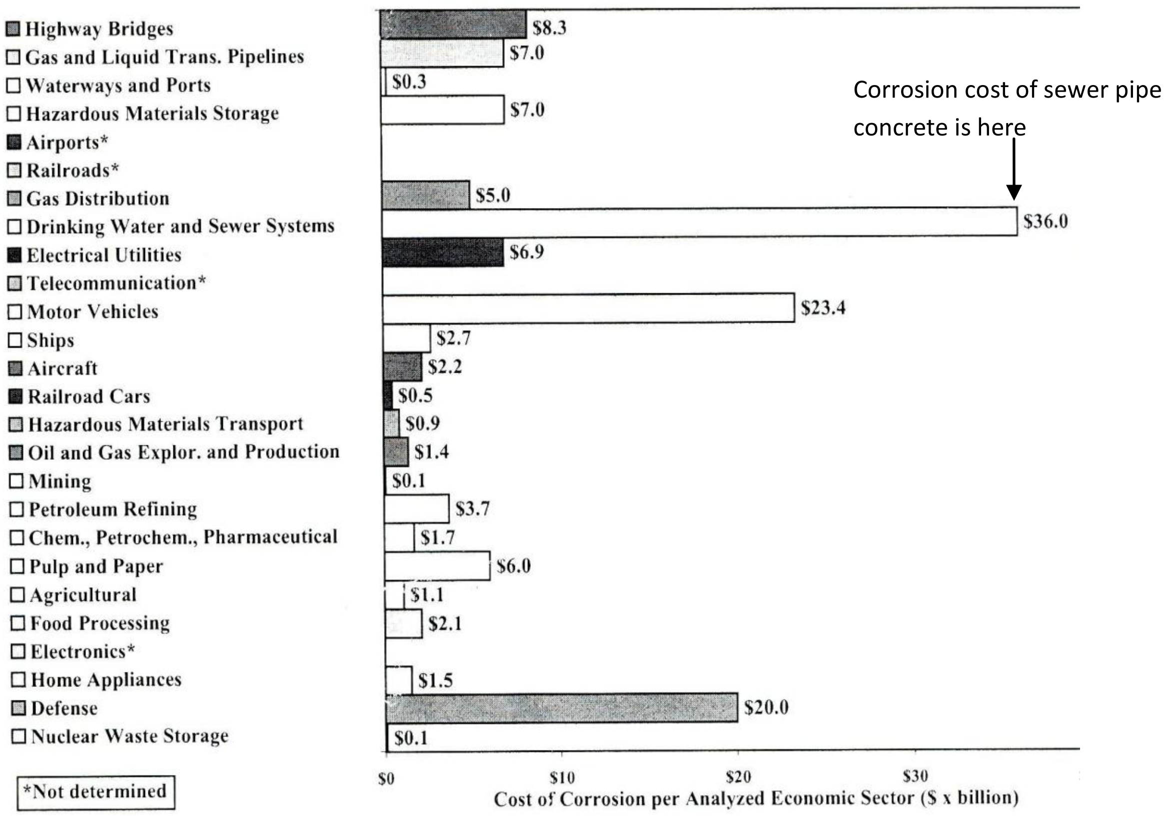
1.3. Investments in drainage infrastructure (sewer pipes)

Cement is one of the top world trading commodities that creates value for building of infrastructure for human use. However, only a small fraction of the income derived from the manufacturing and marketing of cements is spent on research and development of new cements (Bensted, 2002). Preferred concrete properties are dependent on the properties of the hydrated cement paste and cement is more costly when compared to other constituent materials in concrete. Thus, cutting edge solutions in cement properties advances knowledge in concrete materials. In the 21st century, the financing of infrastructural projects such as sewers from government to investment banks has risen. Due to aging and deteriorating of sewer pipe infrastructure by biogenic acid corrosion, there is a need to improve durability of sewer pipe concrete through optimal material designs; thereby improving security for investment and returns on the project for both the investor or tax payers and the owner.

1.4. Objectives and scope of the research

This project focuses on establishing understanding of the performance of concrete when exposed to acidic conditions through the analysis of the samples that had been installed in Virginia Experimental Sewer since October 2004. Based on the knowledge of concrete deterioration science, various factors i.e. cement blends are considered for application in concrete technology to improve acid resistance of concrete. The solution to the corrosion problem of any structure does not only encompass the design for corrosion resistance but must encompass strategies shown in Figure 1.3.

The chart involves various strategies in corrosion control program and includes how the current research fits into corrosion control program.

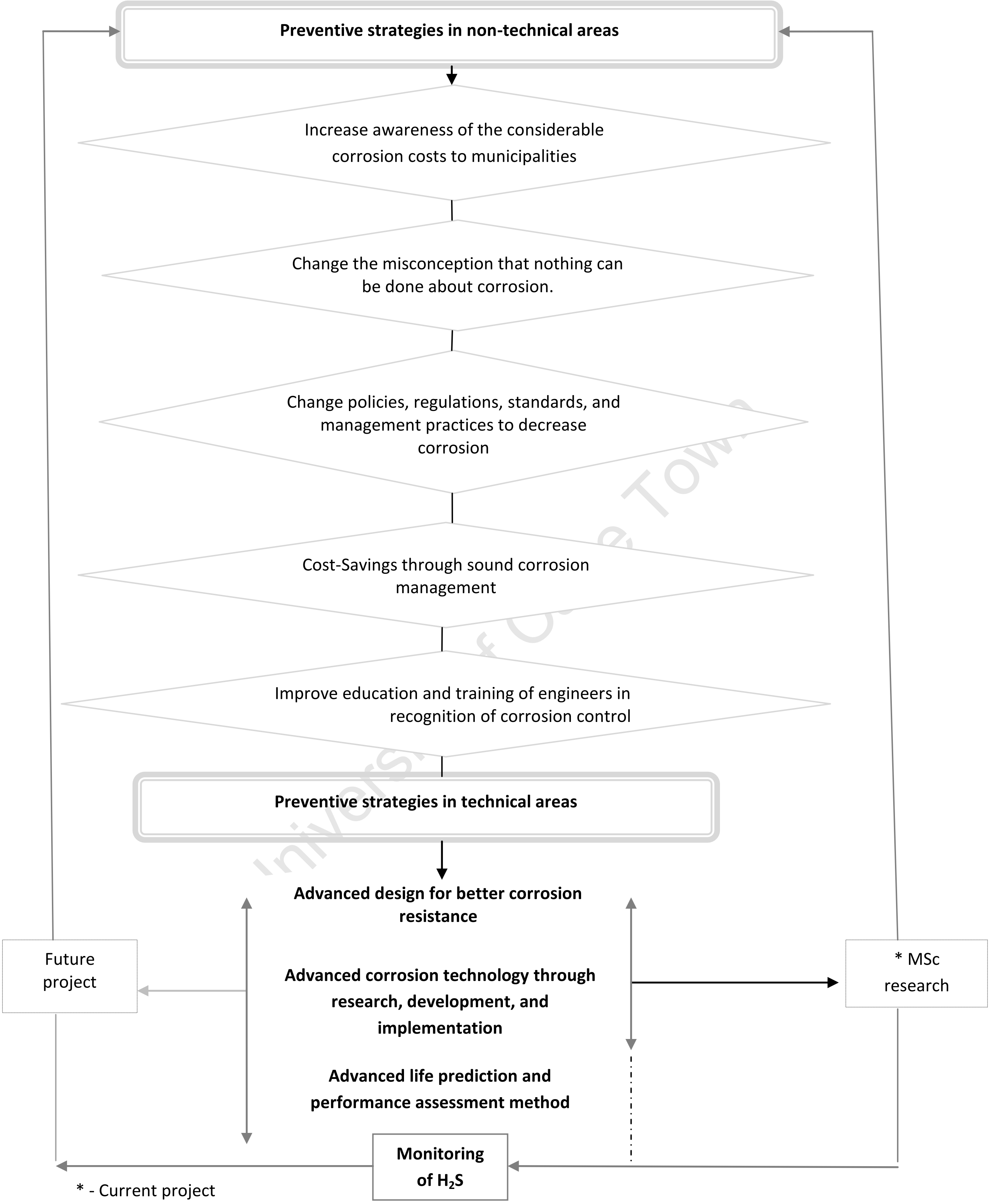


Corrosion cost of sewer pipe concrete is here

Figure 1.2 Summary of estimated cost of corrosion for industry sectors analysed in the US in corrosion studies (Koch, 2011).

This research is based on an ongoing project at Virginia Experimental Sewer where acid resistance of sewer pipe concretes is investigated for upgrading the existing Life Factor Method (LFM) through incorporation of material factor (MF) i.e. the ratio relating the corrosion rate of any concrete to that of a mostly attacked Portland cement (PC)/Siliceous concrete by biogenic sulphuric acid in a given sewer.

The use of Portland cement in sewer pipe applications is a disadvantage due to shorter service life because of biogenic corrosion. However, Calcium aluminate cement (CAC)/dolomite is used as sacrificial liner to a PC/siliceous host pipe concrete. The cost of CAC is about 4 -5 times that of PC, which is a limiting factor for application in sewer pipes. Thus, it was decided to investigate the use of CAC blends with fly ash (FA) and ggbs in a dolomite aggregate concrete mix.



* - Current project

Figure 1.3 Corrosion control program and significance of this project (adapted from Koch, 2011

The research project has two phases:

a) The **first phase** involves the primary objective of investigating physico-chemical properties of concretes with different blends of cements in a laboratory. The aim of this phase is to determine the mass loss and hydrogen ion consumption of these concretes as a measure of the rate of acid attack and acid resistance through provision of neutralisation capacity respectively. Various concrete types under investigation for application in sewer pipes are viz:

- 85 % CAC: 15 % FA
- 75 % CAC: 25 % FA
- 60 % CAC: 40 % FA
- 75 % CAC: 25 % ggbs
- 60 % CAC: 40 % ggbs
- 50 % CAC: 50 % ggbs
- 40 % CAC: 60 % ggbs

FA and silica fume (SF) were also blended in Portland cement concrete to make both binary mixes of 70 % PC: 30 % FA, 90 % PC: 10% SF and a ternary mix of 72 % PC: 20% FA: 8 %SF. Duplicate specimens are installed in the Virginia Experimental Sewer to determine a material factor for these various blends so the existing life factor method or any other corrosion prediction model can later (years) be developed to predict corrosion rate.

The physico-chemical properties of the concrete investigated in the laboratory are; strength (compressive & tensile), density, permeability, porosity, acid insolubility and hydrogen ion consumption in acid solution at pH = 1.0. According to Fourie (2007) hand compacted specimens gave concrete of similar to slightly higher quality to that of sewer pipes manufactured using the roller suspension method. Thus, the physico-chemical properties of the concretes were used to assess the efficiency of compaction method at 28 days, the early age strength tests were used to assess cracking/breakage potential of a newly cast pipe immediately after the steam curing. The results for the tests were compared with those of sewer pipe to check the suitability of the concretes to be used in aggressive sewer environment.

b) The **second phase** involves the secondary objective which is to analyse the concrete pipe section ‘lids’ in a ‘live sewer’ that were installed in October 2004 by Concrete Manufacturer’s Association (CMA) to assess biogenic corrosion at the crown of the pipe in which laboratory acid test fails to simulate the acid resistance. The corrosion of these samples is investigated and reported, the hydrogen sulphide gas is also monitored to assess the corrosion potential of the manholes in which these samples are installed.

1.5. Dissertation outline

Chapter 2 discusses the following:

- The nature of biogenic corrosion in sewer pipes
- Microbial succession and stages of biogenic corrosion in sewers
- Factors affecting biogenic corrosion
- Modelling of biogenic sulphuric acid attack in sewers using a life factor method and its implementation by a material factor concept as studied in Virginia Experimental Sewer
- Concretes of high acid resistance
- Why use concrete pipe if it has a drawback of corroding?
- Control of hydrogen sulphide in sewer pipe systems
- Surface coatings of sewer pipe concrete

Chapter 3 discusses materials, their mix proportions and the preparations of the specimens. These include:

- Basis of concrete mix design for use in sewer pipes
- Preparation of specimens for similar tests to standard test methods such as compressive strength, tensile strength, density, acid insolubility and hydrochloric acid resistance test
- Effectiveness of the hydrochloric acid test to determine rate of acid attack

Chapter 4 gives the results, analysis and discussion from previous test methods for the following concrete groups:

- Portland cement/fly ash/silica fume concrete
- Calcium aluminate cement/fly ash concrete
- Calcium aluminate cement/ggbs concrete

In Chapter 5 the history and background of Virginia Experimental Sewer project is stated. The analysis of concrete lids sections made of the following various mixes that have been exposed to biogenic acid attack in a 'live sewer' is also discussed:

- different aggregates i.e. a blend of dolomite crusher sand and siliceous sand,
- different binders i.e. calcium aluminate cement (CAC) and rapid hardening Portland cement (PC) i.e. CEM I 42.5 R
- use of supplementary cementitious materials (fly ash, slag and silica fume) in either OPC and CAC
- different cement contents i.e. 16 %, 18 % and 23 %

- cement aggregate combination i.e. CAC/DOL or CAC/SIL

Chapter 6 discusses conclusions, limitations of the research and the recommendations for ongoing/ future work at Virginia Experimental Sewer.

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Chapter 2: Literature review

2.1. Introduction

The biogenic corrosion of wastewater conveyance infrastructure dates back when Olmstead & Hamlin first mentioned it in the literature in 1900, when deterioration was theorized to be solely due to the chemical attack of hydrogen sulphide generated from the wastewater (Gualdalupe *et al*., 2010). Further research by Parker (1945), incorporated action of bacteria on the deterioration of concrete in which microbial agents were incorporated by isolating sulphur-oxidizing bacteria from the surface of a corroding concrete sewer pipe and demonstrating their ability to grow and produce acid in sewage. Thus, the nature of concrete corrosion in sewer pipes is initiated by the microorganisms that produce sulphuric acid which deteriorates such structures through the process termed “Microbially Induced Concrete Corrosion” (MICC) (Roberts *et al.,* 2002).

The biogenic corrosion of sewer pipe concretes is well studied in the literature; however, there are some gaps that need be studied extensively. Thus, the aim of this chapter is to review most relevant studies to biogenic sulphuric acid attack, then apply the following strategies:

- Understand the cause of biogenic acid attack
- Explore the factors contributing to formation of acid attack
- Identify those gaps so later the prevention of the attack can be applied
- Explore different concrete types that can perform well in acid attack
- Identify the test methods that can be employed to simulate the biogenic corrosion and hence predict the service life of the sewers pipes exposed to aggressive acid environment
- Most importantly to understand the composition of calcium aluminate and its hydration products to explain its behaviour when exposed to acid attack

2.2. Nature of biogenic acid attack on sewer concrete pipes

The mechanism of MICC involves two types of bacteria, which are found to be common in most sanitary systems (Vaidya, 2010), such bacteria are classified as: (1) sulphate reducing bacteria (SRB e.g. *Desulfovibrio sp.*), (2) Sulphide oxidising bacteria (e.g. *Thiobaccilus thioxidans).* The first are active in anaerobic conditions and reside at the bottom of the pipe in the sewage mud and in the slime layer (biofilm) on the inside wall of the pipeline. These species reduce sulphur compounds and produce hydrogen sulphide (H_2S) gas into the sewer pipe atmosphere (Neethling *et al.,* 1989). The later are known as *Concretevorous* i.e. concrete eaters; these are the species that convert present H_2S to Sulphuric acid (H_2SO_4). The oxidation of H_2S to pure H_2SO_4 occurs after either diffusion or sorption of the H_2S gas into the concrete or the biofilm on the surface of the pipe wall generated by other colonies of bacteria.

Although the MICC might simply be thought as conversion of H_2S to H_2SO_4 that attacks concrete, a series of reactions occur from the reduction of sulphur from its parent compounds to the formation of sulphate ions (SO_4^{-2}) that contributes to formation sulphuric acid (Roberts, 2002). The acid formation on the other hand, occurs simultaneously with ecological succession of micro-organisms on concrete surfaces exposed to H_2S (Islander *et al.,* 1991). Islander *et al* grew various *Thiobacillus* bacteria and developed a hypothesis that different types of bacteria contribute to biogenic acid attack of concrete by sulphuric acid in which these bacteria quantify the stages of MICC as discussed below.

2.3. Microbial succession and stages of MICC

A freshly placed concrete has a pH of approximately 11-13 depending upon the mix design (Vaidya ,2010). The high alkalinity of concrete is due to the presence of lime from the hydration products of the hydraulic cements; this high pH is not habitable by most micro-organisms (Davis *et al.,* 1998). However, the self-protection of concrete from the biogenic attack of concrete does not last forever as corrosion later happens. There are about three stages of MICC as shown in Figure 2.1. The first stage is abiotic pH reduction of the concrete surface i.e. does not involve living organisms; the pH of the concrete pipe is slowly reduced by its interaction with carbon dioxide (CO_2) and H_2S gases which are commonly present in the sewage (Vaidya, 2010, Islander *et al.,* 1991 & Davis *et al.,* 1998). These gases form weak acids i.e. carbonic acid by CO_2, thiosulphuric acid and polythionic acid by H_2S respectively. The acids neutralise the concrete surface and thus lower the pH to around 9.0 (Islander *et al.,* 1991).

Thiobacillus bacterium has identified characteristics of converting H_2S to sulphuric acid and is the first bacteria to colonise the concrete at pH = 9.0 (Vaidya, 2010). With sufficient nutrients temperature and oxygen, these species thrive on sulphur compounds as the substrate attach to the concrete surface and reproduce (Roberts *et al.,* 2002). There are five species of *Thiobacillus* that contribute to MICC and these are; *T. thioparus, T. novellus, T. intermedius, T. neapolitanus and T.thioxidans* (Islander *et al.,* 1991) (Table 2.1). The first four species are known as neutrophilic sulphur-oxidising micro-organisms (NSOM) i.e. thriving between pH range of 5 – 8 and the last two are known as acidothilic sulphur oxidising micro-organisms (ASOM), thriving fastest in highly acidic medium generally below pH of 5.0.

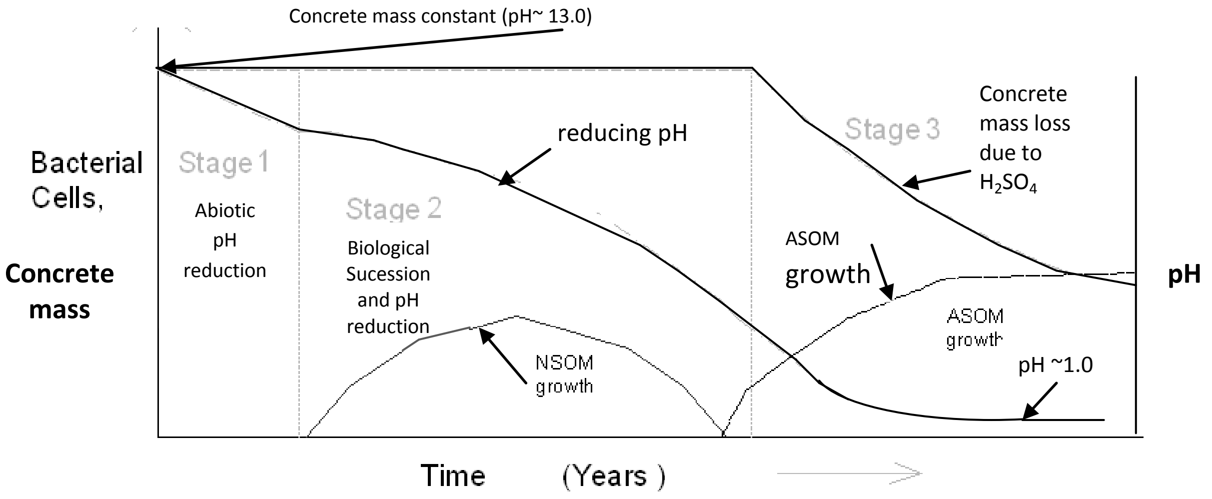


Figure 2.1 Sketch of theoretical stages of biogenic acid attack and physical properties of concrete with time during the deterioration process, (Not to scale) (adapted from Roberts, 2002)

ASOM are thus bacteria that are found mostly in severely corroded sewers with pH values usually less than 1.0 (Alexander, Goyns and Fourie, 2008). From a microbiological point of view both the NSOM and ASOM micro-organisms have specific lifestyle and characteristics when exposed to concrete surfaces typical to those that cause MICC (Table 2.1).

Table 2.1 Five species of *Thiobacillus* and their characteristics (adapted from Roberts, 2002)

`Thiobacillus Species	pH range for growth	Lifestyle	Sulphur substrates	Products
T. thioparus	4.5 -10	autotrophic aerobe	thiosulfate, H_2S, thiocyanate	sulphur, polythionic acids
T.novellus	5.0 – 9.2	Mixotroph	thiosulfate	sulphur
T. intermedius	1.8 – 9.0	Mixotroph	thiosulfate	polythionic acids, sulphuric acid
T.neapolitanus	4.0 -9.0	Autotroph	H_2S, S, thiosulfate	polythionic acids, sulphuric acid
T.thioxidans	0.5 – 4.0	Autotroph	thiosulfate, Sulphur	sulphur, sulphuric acid

After colonisation of micro-organisms has been successful on the concrete surfaces, the NSOM produce some acidic products and convert sulphide to elemental sulphur and polythionic acids (Roberts *et al.,* 2002). Hence, acidic metabolic products accumulate on the concrete surface and this further reduces the pH of concrete (Stage 2) because they react with lime. Sulphate reducing bacteria in the biofilm partition primary sulphate compounds into elemental sulphur preferably in anaerobic conditions (Vincke *et al* 1999). Hydrogen sulphide (H_2S) is then formed in the presence of oxygen, moisture and increased temperature. The ASOM like *T. thioxidans* then begin to colonise and oxidise the secondary sulphur compounds i.e. H_2S and polythionic acids to substantial amounts of sulphuric acid thus completing sulphur cycle as shown (Figure 2.2) (Islander *et al.*, 1991, Fourie 2007 and Vaidya, 2010).

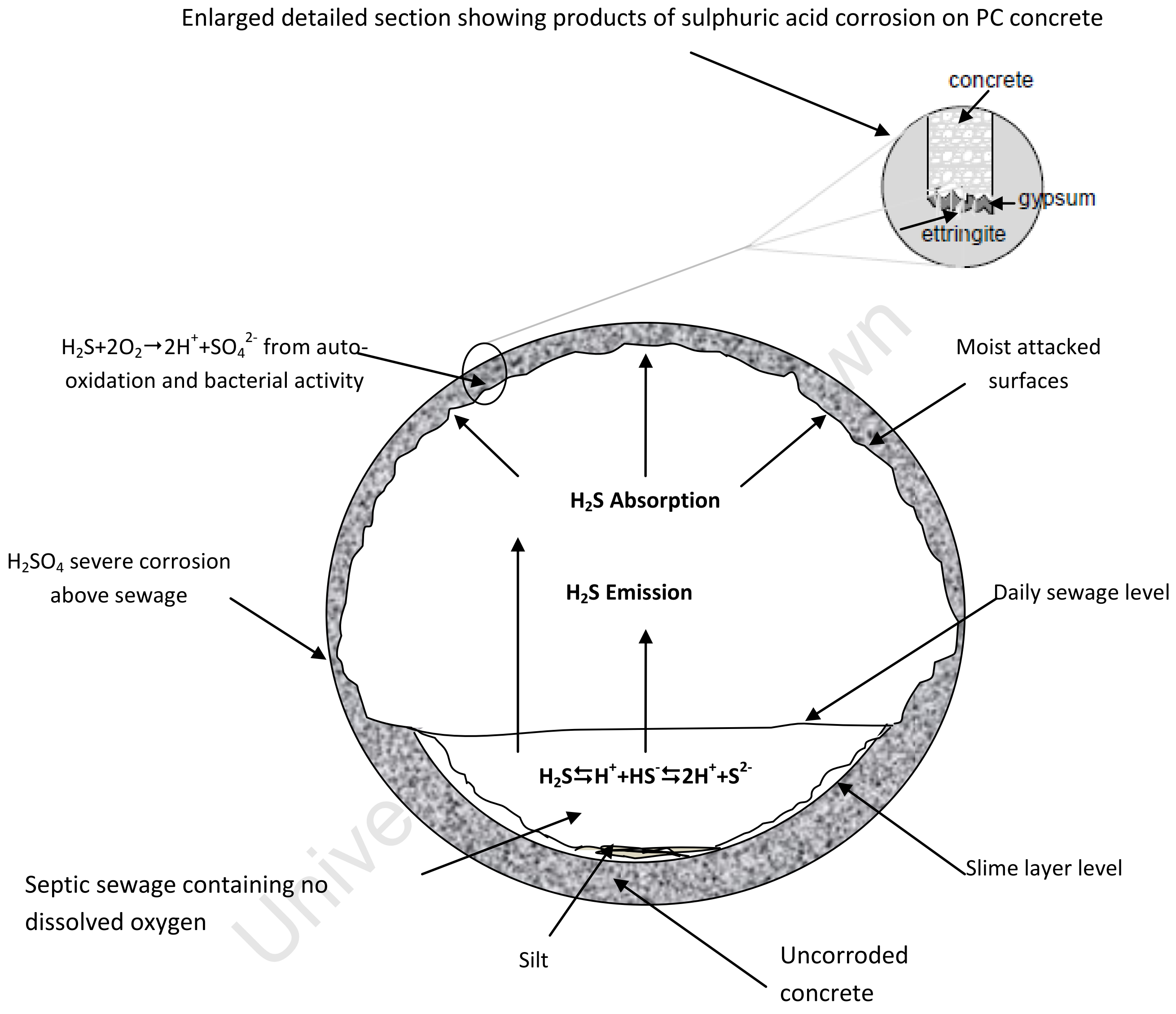


Figure 2.2 Hydrogen Sulphide emission and acid attack processes in a sewer concrete pipe adapted from (Fourie 2007 & Roberts *et al.,* 2002).

The third stage of MICC involves the action of acidophilic oxidising micro-organisms (ASOM) in the biofilm or slime layer above the sewage flow level, their subsequent growth and acid generation (Islander *et al.,* 1991 and Gualdalupe *et al.,* 2010). ASOM actually sustains concrete corrosion due to excretion of acidic products with which the biogenic sulphuric acid generated reacts with the cementitious material to produce a corrosion layer characterised by gypsum ($CaSO_4$ of various hydration states) and ettringite (Figure 2.2). These two products are reported by various researchers Davis *et al.,* (1998), Roberts *et al.,(* 2002) and Hewayde *et al.,* (2007) to expand and hence increase the internal pressure of the sewer pipe concrete which then decreases the structural integrity of the pipe. However, gypsum layer is an insoluble salt and can inhibit the diffusion of aggressive ions (H^+) during the acid attack, and could be washed away at sewage daily level. Thus, more pronounced failure is not just due to acid attack but intertwined with abrasion erosion due to flowing sewage carrying suspended particles. Furthermore, ettringite is an unstable product and thus at low pH values it becomes soluble and during heavy flows it is also washed off hence exposing new concrete surface for further acid attack (Zivicaa, 2002).

2.4. Factors affecting acid attack

Concrete acid attack, either due to pure acid or biogenic acid is due to the interaction of the acid and the cement based materials (hardened cement paste), both of which are of complex in nature (Zivicaa, 2002). Proper understanding of this interaction requires knowledge of cement chemistry and understanding of bacterial colonies causing the attack. The factors that accelerate or inhibit the rate of acid attack need be understood in both design and construction of sewer pipe concretes. This can aid in the selection of the constituent materials for concrete in the sewage environment thereby increasing the service life of such structures. At this stage, one supposes that the hydraulic design of sewer pipes is the least problem and responsibility is on concrete materials engineers to develop competent materials in aggressive sewer environments. However, the effect of hydraulic design on acid corrosion must not be ignored.

2.4.1. Effect of cementing materials

Cementing materials are used in the range of about 16 - 30 % of the concrete mix depending upon the mix design. It is the hydraulic characteristics of the cement that set and hardens to produce a structural material that can be used for example in sewer pipes. Thus, cements contribute significantly in inhibiting or promoting acid attack on concrete surfaces. Cementing materials are the major species of the concrete constituents that take part in the acid chemical reaction; this is solely due to their basicity being high for Portland cement because of high content of portlandite (Alexander *et al.,* 2010).

The use of pozzolans such as fly ash and silica fume was found in the literature to be of little significance in improving acid resistance of Portland cement concrete (Pavlik *et al.,* 1997, Bajza, 1989) as cited by Allahverdi and Škvára, (2000). However, silica fume produces high acid resistant Portland cement concrete due to modification of the microstructure, refinement of the pore structure and reduction of calcium hydroxide in pozzolanic reaction that increases calcium silicate (Zivicaa, 2002, Chandra, 2002 and Alexander, 2011). Due to their fineness, especially silica fume, the pozzolans are able to fill the pores in the concrete and hence could decrease the penetrability of concrete by aggressive ions. The efficiency of pozzolan type to replace free lime, the fineness of the pozzolan, the curing procedures used are all the critical factors that if well taken into account the pozzolans could have significantly improved acid resistance (Zivicaa, 2002).

Calcium aluminate cement is one type of high alumina cement that is used mostly in aggressive environments with high acid resistance and performs well when used in sewer pipe applications (Alexander, 2001, Scrivener, 1999). Unlike Portland cement concrete that has a high CaO content of about 60 - 65 % and produces free lime on hydration which readily reacts with the acid, CAC has 36 - 42 %. Thus, the key performance of CAC is due to absence of calcium hydroxide and its stable hydration products i.e. alumina hydrates which are stable even at pH between 3 and 4, in which Portland cement would be attacked by acid (Scrivener, 1999). However, it must be noted that no cement can sustain acidic environment forever.

2.4.2. Intrinsic or concrete factors

2.4.2.1. Cement content

The proportions of concrete constituent materials are the key elements that determine properties of the concrete. During the acid attack process, hydrated cement paste reacts with the acid and the acid is consumed proportionally as the acid-cement reaction proceeds (Zivicaa *et al.,* 2002). Sulphuric acid reaction with Portland cement concrete involves reaction with a) calcium hydroxide (CH) and calcium silicate hydrate (C-S-H), b) gypsum and tricalcium aluminate hydrate (C_3A) to form ettringite and its analogues (Monteney, 2000). The reactants in a) and b) above are functions of a cement content and thus the rate of reaction increases with the increase of cement content. The corrosion of Portland cement concrete can then be simply characterised by Equations 2.1, 2.2 and 2.3 consecutively (Bassuoni and Nehdi, 2007);

$Ca\,(OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O$ (gypsum) ……………………………………………………………………………(2.1)

$CaSiO_2.2H_2O+H_2SO4 \rightarrow CaSO_4 + Si\,(OH)_4 + H_2O$ ……………………………………………………………………… (2.2)

$3CaO.Al_2O_3.12H_2O + 3(CaSO_4.2H_2O) + 14\,H_2O \rightarrow 3CaO.Al_2O_3.3CaOSO_4.32H_2O$ (ettringite) …………… (2.3)

Although cement content is a controlling factor for hydration reactions of the concrete and microstructure development, increasing cement content decreases acid resistance of concrete (Hewayde, 2007). In his investigation, Hewayde carried out 3 samples of concrete specimens of cement content viz; 310, 445 and 570 kg/m^3 at w/c of 0.35 respectively and immersed them in sulphuric acid solution of pH 0.3 (Figure 2.3). The specimens from various concrete mixtures were soaked in sulphuric acid solutions with pH of 0.3 and examined after 1, 2, 3, 4, 6, and 8 weeks of immersion. At each date, the specimens were removed from the acid bath, carefully rinsed with water, and oven dried at 105 °C until constant mass. The mass loss due to immersion in sulphuric acid and wetting-drying cycles were used as a measure of concrete degradation. The results show that if the cement content is kept as low as possible, the acid resistance was improved considerably.

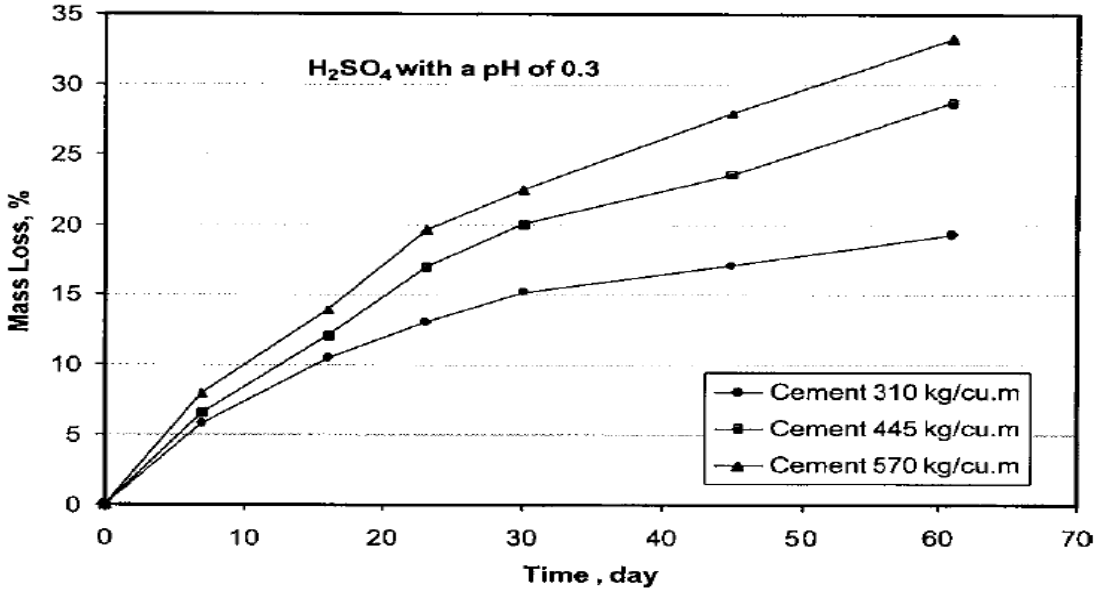


Figure 2.3 Mass loss versus time for concrete specimen with cement content of 310, 445 and 570 kg/m^3 immersed in H_2SO_4 solution with pH of 0.3 (Hewayde, 2007).

Although binder content in concrete mixes increases neutralisation capacity of the concrete, high content of this parameter could ultimately result in a more porous corroded layer promoting acid diffusion (Beddoe, 2005). Thus, overall acid uptake becomes high hence promoting the rate of acid attack. In sewer pipe concretes, the commonly used binder content is between 16 - 23 %, which corresponds to 400 to 570 kg/m^3 if one assumes total constituents of 2500 kg/m^3.

2.4.2.2. Water/cement ratio

In sewer pipe manufacturing, a low water cement ratio (w/c) of 0.36 and less with low water content is used (Fourie, 2007). These are typically dry mixes used for suitability of casting method i.e. roller suspension preferred to limit the chances of mixing water being driven off by centrifugal forces during rotation of the mould. W/c ratio affects the durability of a fully compacted concrete and lowering w/c ratio improves mechanical properties of concrete and acid resistance (Hewayde, 2007). However, this is affected by different properties of the acid i.e pH, for w/c ratio less than 0.5; the converse is true, i.e. acid resistance of concrete increases with the increase in w/c ratio depending on the pH and concentration of the acid (Figure 2.4). This trend is explained by the content of the cement per m^3, which provides high concentrations of free lime in a hardened concrete that reacts with the acid. The cement content is high for low w/c ratio and low for high w/c ratio. Concrete of low w/c ratio i.e. less than 0.36 (sewer pipe concrete) is dense and has low permeability and so the ingress of the aggressive acid ions (H^+) is highly inhibited and attack becomes a surface reaction as opposed to penetration of ions into the concrete. Thus if the w/c ratio is to be kept low, the cement content must be kept sufficient for hydration reactions to develop. Then the water content must be adjusted to meet the required compaction of the concrete.

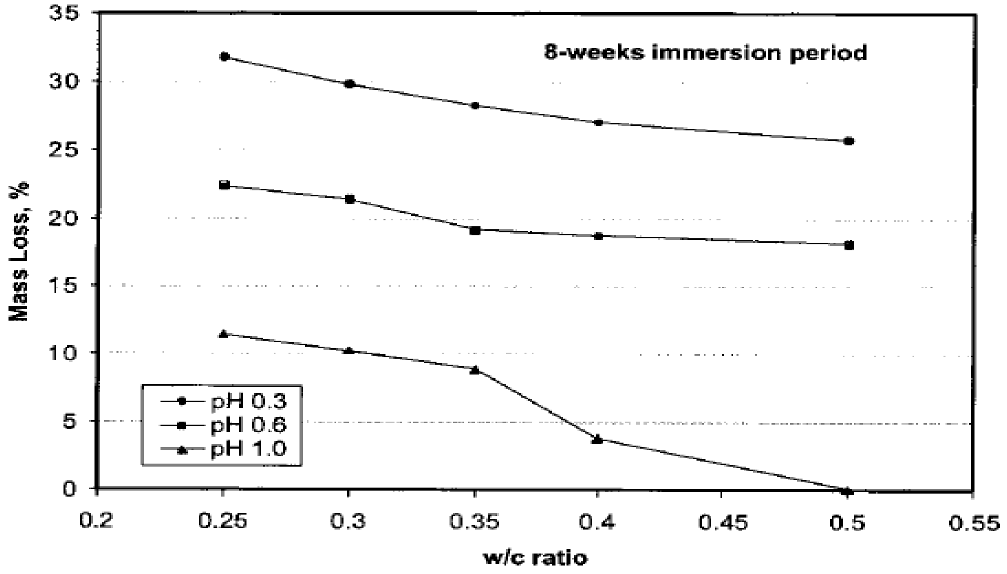


Figure 2.4. Mass loss of concrete specimens with various w/c ratios immersed in sulphuric acid solutions with pH values of 0.3, 0.6 and 1.0 (Hewayde, 2007).

2.4.2.3. Aggregates

The reactivity of the aggregates in a concrete with the acid depends mainly on two factors, namely; 1) its neutralisation capacity in an aggregate- binder-concrete system (Beddoe *et al.,* 2005) and 2) its acid insolubility (Fourie, 2007). Most researchers (Alexander, 2001 & Chang, 2005) have studied the use of siliceous aggregates and calcareous aggregates on acid resistance of concrete. Due to their insolubility in acid, the siliceous aggregates such as granite, do not react with the acid and do not provide any neutralising effect to stop the attack. It is only the cement paste that is attacked by the acid thus the aggregate could protrude and eventually fall out hence exacerbating the attack and affecting transport properties, thus lowering structural integrity of the concrete pipe.

The calcareous aggregates such as dolomites and limestone provide a sacrificial effect on concrete exposed to acid attack (Chang, 2005 & Goyns, 2004). The service life of sewer pipes using limestone aggregates is longer than that using siliceous aggregate by 3–5 times in South Africa (Barnard 1967) as cited by (Chang, 2005). This is because limestone or dolomite aggregates contain more dissolvable carbonate ions and increase neutralisation capacity of the concrete to acid attack. However, it must be noted that potential neutralisation capacity of the dolomite aggregate could not be described as a function of the concrete porosity. At low porosity i.e. dense concrete, the acid attack is a surface reaction and porous solution of corrosion products containing acid ions and dissolved aggregate particles provide a medium for transporting acid further inside the concrete (Beddoe *et al*., 2005).

The diffusion paths of the ions within the concrete depend on the porosity, permeability and sorptivity of the hardened cement paste (Hearn *et al.,* 1994 & Chandra, 2002). However, aggregate size controls the direction of diffusion path and the amount of aggregate and its grading curve for a particular mix controls the degree of tortuosity (Beddoe *et al.,* 2005 & Hewayde, 2007). A high acid resistant concrete can be created by the use of densest packing of aggregate and binder particles in which the cement content can be less than that used for conventional concrete mixes (Huttl, 2000) as cited by Beddoe *et al*., (2005).

2.4.2.4. Concrete porosity

The hydration reaction of the cement either Portland cement or calcium aluminate cement release some water molecules when the new hydrates are formed thus inevitably generating the voids on hardening (Hearn *et al.,* 1994). Some of the voids are from the spaces that were previously occupied by unreacted mixing water.

The pore structure of the concrete is the result of the w/c ratio and the cement content (Zivicaa *et al*., 2002). The chemical resistance of concrete is a function of its pore structure in which the permeability of concrete as a transport phenomenon controls the ingress of the acid ions from the surface into the concrete. Zivicaa *et al.* (2002) indicated that a cement content of 300–400 kg/ m^3 is sufficient to get a satisfactorily low permeability and a sufficient acidic resistance of concrete if the w/c ratio is kept below 0.5. However, for concrete to be used in sewer pipe application the maximum w/c ratio is 0.36 for the reasons outlined in Section 2.4.2.2. Part of concrete porosity is affected by the degree of compaction, curing and addition of pozzolanic materials which are fine to reduce the pore sizes of a hardened cement paste, thus inhibiting transport of aggressive substances into the concrete (Chandra, 2002). Therefore, based on the information of all the factors that affect porosity and durability of concrete then interrelations of these factors to pore structure of the concrete was developed as shown in Figure 2.5.

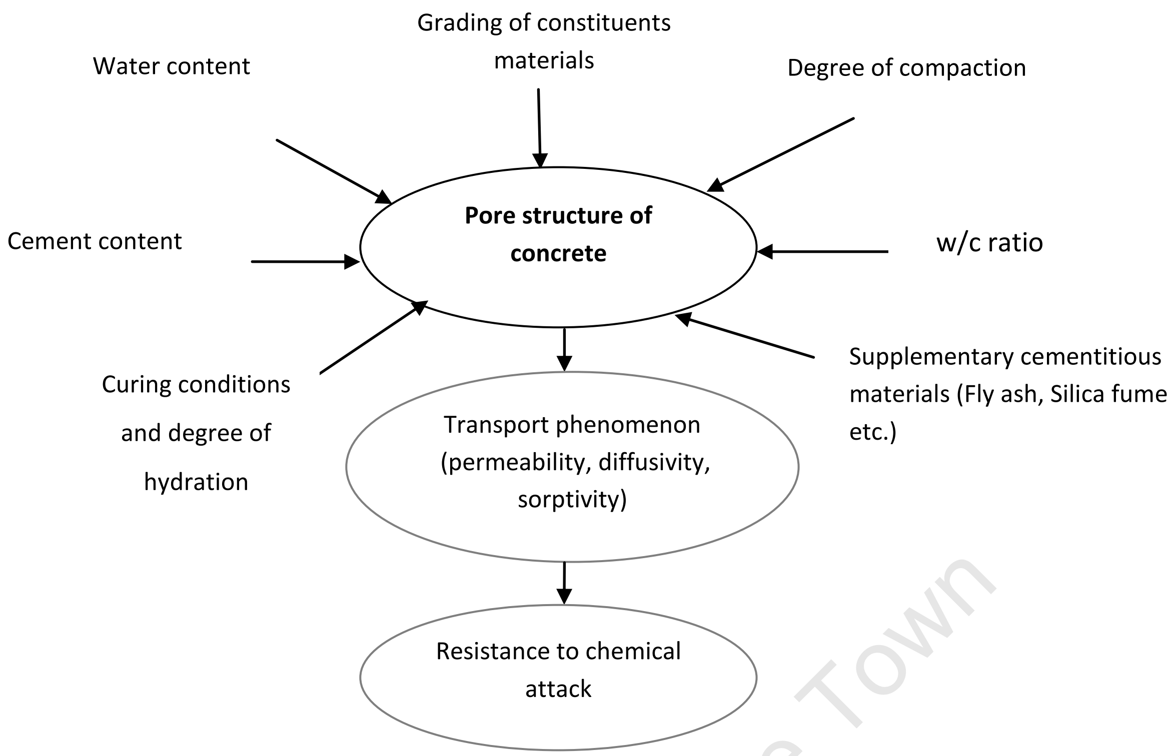


Figure 2.5 Inter-relationships of factors affecting concrete porosity and resistance to chemical attack (Adopted from Zivicaa *et al.,* 2002)

2.4.2.5. Transport mechanism

When dry concrete specimens are subject to hydrogen sulphide in a sewer pipe, the hydrogen sulphide (liquid or gaseous) produced enters the concrete pores by capillary suction or surface diffusion depending on the phase of the hydrogen sulphide (Hearn *et al.,* 1994). The alternative wetting during high effluent flows can oxidise H_2S to sulphuric acid and thus increasing the uptake of the sulphuric acid by concrete to promote the corrosion rate of the concrete (Hewayde, 2007). Normally the sewer pipe concrete is moist-saturated due to continuous flow of sewage that enables the bacterial colonisation. Thus the ingress of the acid into the concrete occurs mainly by diffusion. In the case of sulphuric acid attack that forms gypsum and ettringite for Portland cement concrete; the expansion of the gypsum may generate the tensile stresses and hence cracks that open ways for transportation of aggressive acid ions within the concrete.

2.4.3. Extrinsic factors

2.4.3.1. Curing time

It is mentioned above that some authors have regarded the use of pozzolanic materials as of little significance in improving acid resistance of concrete. However, it seems that in some cases this could be due to insufficient curing, because the hydration products of pozzolanic concrete take time before reaching maturity and stability due to slow heat of hydration (Iowa State University, 2004). Fahutti & Hughes (1988) cited by Allahverdi (2000) investigated the effect of curing on acid resistance of hardened cement pastes and concrete cubes. In their experiment, the specimens were cured in water for 7, 14, 28 days respectively each and were then immersed in 2 % sulphuric acid solution for a period of 50 days. The results for pastes of w/c = 0.417 revealed that increasing curing time from 7 to 28 days reduced the mass loss by 75 % after the exposure to acid attack. Sewer concrete pipes are precast units that are steam cured at temperature of about 50 ° C to accelerate hydration reactions, maturity and strengths so rapid turnover is increased, and this has a positive effect on acid resistance as an inferred function of maturity and microstructure development.

2.4.3.2. Acids and their salts

The rate of chemical reaction depends on the nature and type of its reactants (Ebbing *et al.,* 2009). Likewise the rate of acid attack depends on the strength of the acid and its ability to dissociate. In sewer pipes the conditions are very aggressive and the pH can go as low as less than 1.0 (Fourie, 2007). In addition, the severity of the acid attack depends on the solubility of the calcium salt formed (Zivicaa *et al.,* 2002 & Fourie, 2007). Soluble salts such as calcium nitrates and chlorides are removed by leaching into acid solution and increase porosity of the concrete thus axcerbating the corrosion. On the other hand, insoluble salts such as $CaSO_4$, or gypsum layer formed from sulphuric acid remain in the corroded layer and protect the concrete from further attack by the acid especially for high dense concrete whereby corrosion happens mostly at the surface (Allahverdi, 2000).

2.4.3.3. Other factors

The biogenic reaction kinetics of the acid and the concrete is mainly affected by temperature; this is explained by the commonality of biogenic sulphuric acid attack of sewer concrete pipes and warm climates. As cited by Allahverdi (2000), Mehta (1985) carried an experiment investigating the effect of temperature on acid resistance of a number of concrete specimen to acids; HCl, H_2SO_4 ,and lactic acid each of 1 vol %. No difference was found with specimen immersed in 45 °C and 20° C. However, temperature is a very significant factor in controlling acid resistance of concrete to acid attack of sewer pipes because it sustains the growth of the acid causing bacteria (Islander *et al*., 1991, Scrivener 1999 & and Gualdalupe, 2010). Therefore, the findings by Mehta were only applicable for pure acid attack not for biogenic acid attack.

Other factors contributing to sewer pipe corrosion are attributed to: 1) hydraulics design, 2) H_2S generation and 3) H_2S release into the sewer pipe headspace (EPA, 1985). Long retention times of more than 1 hour and sewage with high biochemical oxgen demand in order of 100 mg/l, may deplete available dissolved oxygen and hence promote the generation of sulphides (Goyns 2008). This is higher for sewer lines running on flat terrains. Velocities that are less than 0.6 m/s and not self cleansing allow settling of the sludge deposits, silt accumulation and formation of slime layer that promotes colonisation of the bacteria (EPA, 1985). However, excess velocities, that are greater than 1.5 m/s allow turbulance that enables the release of hydrogen sulphide into the pipe (Santry 1963). It must be noted that high velocities also increase the abrasion erosion of the pipe by suspended solids. Sharp junctions at manholes need be avoided as high velocities and turbulence at the pipe junctions or at change of slopes promotes the release of hydrogen sulphide and obstructs flow causing long retention times. When sewers are joined upstream, gradients should be adjusted so that entry velocities and energy lines correspond as shown in Figure 2.6.

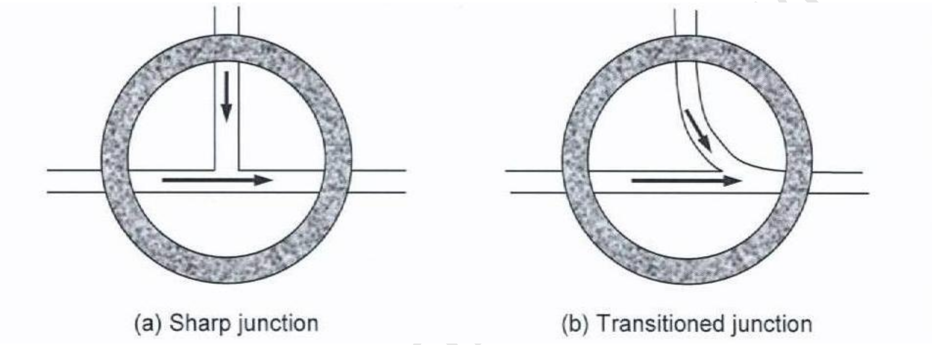

(a) Sharp junction
(b) Transitioned junction

Figure 2.6 The connection between the connector and lateral to enable smooth flow that does not cause turbulence and increase of the retention time in the sewer pipes (Goyns, 2008).

A drop of energy line at downstream Manhole 2 shown in Figure 2.7 may result in turbulence flow and adjusting the grade so the flow is similar at Manhole 1 can limit the generation of hydrogen sulphide. Therefore, drops must be avoided as much as possible in manholes of sewer pipes where biogenic corrosion can be a problem.

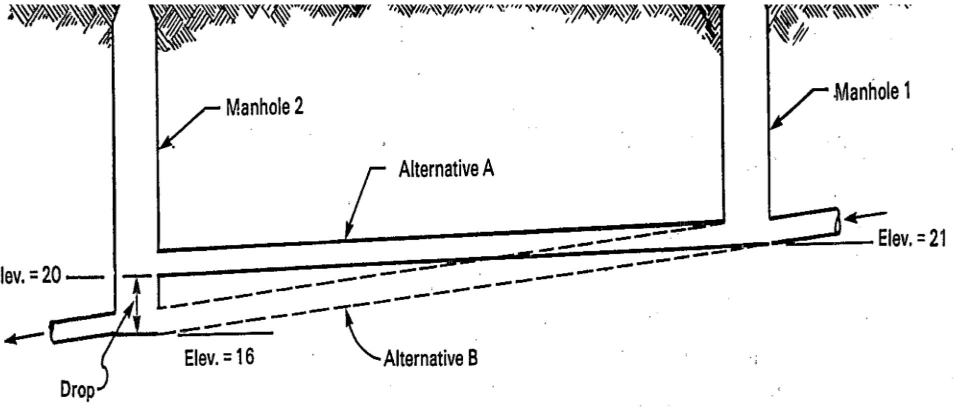


Figure 2.7 Alternative sewer grading design to limit the turbulence at Manholes (EPA, 1985)

2.5. Modeling of biogenic sulphuric acid attack

Two types of modelling tools are used in practice to predict the rate of acid attack on concrete structures and assess the estimation of the material's remaining life. Such models are empirical equations based on regression analysis of the experimental data and mathematical models based on the theoretical analysis of corrosion process (Allahverdi, 2000). Mathematical modelling of biogenic acid attack has not been researched much and goes beyond the scope of this thesi. However such models need be formulated and/or modelled into computer programmes etc so that the engineers in practice could use the models to predict the rate of attack of the sewer pipe concretes in design.

2.5.1. Empirical models

Most of the empirical models available from the literature are related to chemical acid attack but not necessarily microbiological acid attack. Gualdalupe (2010) investigated the corrosion rate of concrete specimens subjected to microbiological acid attack using the Equation 2.4 below. This model can be used for quality control of specimens when designing acid resistant sewer pipe concrete.

$$C_r = \frac{1}{A \times \rho} \times m \quad \ldots\ldots \quad (2.4)$$

Where:

C_r = the concrete corrosion rate typically given in mm/yr.

A = Surface area of the concrete specimens

ρ = the density of concrete in (g/cm^3), and m is mass loss per day, this can be converted to mm/year for estimation of the real sewer pipe concrete in service.

2.5.2. Life Factor Method

Life factor method is an empirical method that was proposed by (Parkhurst and Pomeroy, 1976) as cited by (Goyns, 2008) to predict corrosion rate of sewer pipe concretes. The key derivation equations are based on 1) sulphide generation, 2) release of hydrogen sulphide and its absorption into slime layer subsequently to 3) generation of sulphuric acid for a given type of waste water. The derivations are presented in Equations 2.5 to 2.15.

Consider Sewers flowing partly full:

$$S_{lim} = \frac{M_{sf}}{m_s} \times \mathrm{EBOD} \times (sv)^{-3/8} \times \frac{P}{B} \quad \ldots\ldots \quad (2.5)$$

Where:

S_{lim} = limiting sulphide concentration (mg/ℓ)
M_{sf} = flux coefficient for sulphide generation in slimes layer of gravity sewers (m/h)

m_s = coefficient to account for sulphide loss from oxidation and escape into atmosphere
s = energy gradient of wastewater stream (m/m)
v = mean velocity of sewage (m/s)
P = wetted perimeter (m)
B = wastewater stream width at the surface (m)
EBOD = effective biochemical oxygen demand of effluent (mg/ℓ)

$$\mathrm{EBOD} = \mathrm{BOD_5} \times 1.07^{\mathrm{T}-20} \quad \text{…… (2.6)}$$

Where:

$\mathrm{BOD_5}$ = biological oxygen demand of sewage measured after 5 days

T = temperature (°C)

When a sewer flows full as in the case siphon, there is no release of the H_2S in the pipe, it only accumulates in the effluent and a concentration of such a closed conduit is estimated using the Equation (2.7)

$$S = M\ (t) \times [EBOD] \times (\frac{4}{D} + 1.57) \quad \text{…… (2.7)}$$

Where

S = Sulphide concentration in effluent in mg/l

M = Sulphide flux coefficient in a full pipe m/hr

t = Flow time in sewer reach in hr, with constant slope, diameter and flow
D = Internal pipe diameter pipe in m

Downstream sulphide concentration is then calculated as;

$$\mathrm{S_2} = \mathrm{S_1} + [\,\mathrm{M}\,(\mathrm{t_2} - \mathrm{t_1}) \times \mathrm{EBOD} \times \left(\frac{4}{\mathrm{d}} + 1.57\right)] \quad \text{…… (2.8)}$$

Where:

S_2 = sulphide concentration at time t_2 mg/ℓ)
S_1 = sulphide concentration at time t_1 (mg/ℓ)
d = diameter of pipe (m).

However, when the pipe is flowing partly full there is an air/water interface, thus the sulphide accumulation in the effluent is slower than it would be in an equivalent system with the pipe flowing full. The difference is due to the sulphides that get absorbed into the slime layer over the length of the pipe. This is the most normal case in the sewer pipe whereby the pipes are flowing partly full.

$$\frac{\mathrm{dS}}{\mathrm{dt}} = \mathrm{M}' \frac{\mathrm{EBOD}}{\mathrm{R}} - \mathrm{m} \times \frac{\mathrm{S(sv)^{3/8}}}{\mathrm{dm}} \quad \text{…… (2.9)}$$

Where:

M' = Effective sulphide flux coefficient for H_2S generated in slime layer when there is open channel flow in a gravity system, constant expressed m/hr
R = Hydraulic radius of flow area in m
m = Sulphide loss coefficient due to oxidation and escape into atmosphere
S =Total sulphide concentration in mg/l
d_m = Mean hydraulic depth = flow area / flow width in m
Ds/dt = The rate of change of concentration of sulphide mg/l.hr

The first term on the right-hand side contributes to formation sulphides by a slime layer, whereas the second term accounts to loss of sulphide due to oxidation in the sewer atmosphere (EPA 1985),

At equilibrium, $\frac{\mathrm{dS}}{\mathrm{dt}} = 0$

$$\therefore \quad \mathrm{M}' \frac{\mathrm{EBOD}}{\mathrm{R}} = \mathrm{m} \times \frac{\mathrm{S}(\mathrm{sv})^{3/8}}{\mathrm{dm}}$$

Solving for S, the theoretical upper limit at equilibrium when the generation of sulphide balances the losses yields;

$$\mathrm{S} = \mathrm{S}_{\mathrm{slim}} = (\mathrm{M}'/\mathrm{m})\ \mathrm{EBOD}\ (\mathrm{sv})^{-3/8}\ (\mathrm{P}/\mathrm{W}) \qquad \text{(2.10)}$$

Where:

P = Wetted perimeter in m

W = Flow width in m

The limiting value cannot be reached theoretically but asymptotically (EPA 1985). However, when a sewer flows as an open channel gravity system and receives the discharge from a closed system, the [S] concentration may exceed the limiting value; the H_2S can be stripped rapidly from the effluent to re-establish equilibrium between gas concentrations in the sewer atmosphere and effluent (Goyns 2008). The downstream sulphide generation (S_2) is then calculated from Equation 2.11;

$$S_2 = S_{\mathrm{lim}} - \frac{(S_{\mathrm{lim}} - S_{1)}}{\log^{-1}\left[\frac{m(sv)^{3/8} t}{2.31 dm}\right]} \qquad \text{(2.11)}$$

Where:

$t = t_2 - t_1$ in hr
S_1 = Sulphide concentration at time t_1, mg/l
S_2 = Sulphide concentration at time t_2, mg/l

Sulphides Released from the Sewer

When dissolved sulphides in the effluent have been determined the rate of H_2S releases i.e. H_2S flux, can be calculated as follows:

$ø_{sf} = 0{,}69 \times (sv)^{3/8} \times J \times DS$ ………………………………………………………………………… (2.12)

Where:

$ø_{sf}$ = hydrogen sulphide flux from sewage (g/m^2/h)
s = energy gradient of wastewater stream (m/m)
J = fraction of dissolved sulphide present as hydrogen sulphide (function of sewage)
DS = average annual dissolved sulphide concentration in wastewater (mg/ℓ) (0,2 to 0,3 mg/l less than the total sulphide concentration) (Goyns 2008).

Assuming all the sulphides are absorbed into the moist slime layer on the sewer pipe wall, and H_2S flux into the pipe wall is calculated from Equation 2.13.

$ø_{sw} = 0{,}69 \times (sv)3/8 \times J \times DS \times (W/P)$ …………………………………………………………………… (2.13)

$ø_{sw}$ = Hydrogen sulphide flux into the pipe wall (g/m^2/h)

W/P = Ratio of stream width to pipe wall perimeter above water surface.

Acid Formation and Concrete Corrosion

The corrosion of the sewer pipe concretes is determined accordingly with the rate of oxidation of H_2S flux on the pipe walls (Goyns 2008). The estimate of average corrosion rate in mm/year is given by Equation 2.14;

$C_{avg} = \frac{11.5k}{A}\Phi_{sw}$ ……………………………………………………………………………………………………… (2.14)

Where:

c_{avg} = Average corrosion rate (mm/year)
k = Coefficient of efficiency of acid reaction with concrete considering a fraction of acid remaining on the sewer wall (0.3 to 1.0 for complete reaction).
A = Alkalinity of the concrete (0.16 to 0.23 for granite aggregates, 0.9 for calcareous aggregates and 0.4 for mortar linings)
11.5 - Converts $ø_{sw}$ in g/m^2/h into c_{avg} units of mm/year.

At the end of the sewer life cycle, the life factor method can be modified (Equation 2.15) by applying additional concrete cover over reinforcement to check if the sewer pipe can still be serviceable (Goyns 2008).

$Az = 11.5\,k\,\Phi_{sw}\,L$ ………………………………………………………………………………………………(2.15)

Where:

z = Additional concrete cover over reinforcement (mm)

L = Required design life of sewer line (years)

The term Az on the left hand side is referred to as a life factor and compares different concrete types based on their neutralisation capacity to slow acid reaction over the reinforcement cover. Whereas the term on the right hand side constitutes the conditions within the sewer, in terms of high generation of the sulphides and release of the sulphides into the sewer atmosphere etc..

2.5.3. Virginia Experimental Sewer and Implementation of a Life Factor Method

The limitation of a life factor method is that its originality was based on Portland cement concrete; however, there has been different cement materials used in sewer applications such as CAC liners which has different alkalinity to OPC. The method did not also take into account the effect of aggregate fall out and difference in alkalinity of different concrete mixes (Goyns, 2008). The performance of different pipe materials was assessed in Virginia Experimental Sewer (Table 2.2). Using different corrosion rates for each material, the concept of material factor (M_F) was implemented to calculate the corrosion rate of pipe materials in a ‘live sewer’ subject to a given set of conditions (Goyns, 2004). M_F is a dimensionless coefficient that relates corrosion rate of each concrete to that of the most susceptible Portland cement/siliceous aggregate concrete in biogenic acid attack. However, enough data is needed to fully characterise the material factor for each concrete type.

The significance of Virginia Experimental Sewer is to investigate the biogenic acid resistance of the sewer pipe concrete at crown of the pipe as a laboratory hydrochlroric acid test cannot simulate such conditions in a ‘live sewer’. This ‘live sewer’ is used for investigation of M_F for different types of concretes i.e. Portland cement with supplementary cementitious materias (SCMs), calcium aluminate cement with SCMs with different aggregates, this is fully discussed in Chapter 5.

Material factor model is a modified life factor method in which the corrosion rates of concrete made of different cements and aggregates with differing alkalinity can be estimated using Equation s 2.16 and 2.17. M_F is a factor that controls bacterial metabolism and provide neutralisation capacity in sewers with the later being less critical although not negligible (Alexander *et al.*, 2008).

$$C_{avg} = M_F \frac{11.5k}{A} \Phi_{sw} \quad \text{......} \quad (2.16)$$

$$Az = M_F \times 11.5\,k\,\Phi_{sw}\,L \quad \text{......} \quad (2.17)$$

Example of a Material Factor Concept:

In design, Portland cement/siliceous aggregate concrete is used as a standard with alkalinity of 0.16. Then using Equation 2.17,

$$Z_{\mathrm{PC/SIL}} = 72 \times \; \mathrm{k}\,\Phi_{\mathrm{sw}}\,\mathrm{L} \quad \ldots\ldots \quad (2.18)$$

When comparing alternative materials Equation 2.19 is used,

$$Z_{\mathrm{ALT}} = 72 \times M_{\mathrm{F}} \times \mathrm{k}\,\Phi_{\mathrm{sw}}\,\mathrm{L} \quad \ldots\ldots \quad (2.19)$$

Table 2.2 Measured and estimated corrosion rates and material factors for different concretes (Goyns, 2003).

MATERIALS (Cement/Aggregate)	**5 year estimate**		**12 year estimate**		**14 year measured**		**Material factor (M_F)**
	Total (mm)	**Average** (mm/yr)	**Total** (mm)	**Average** (mm/yr)	**Total** (mm)	**Average** (mm/yr)	
Portland cement/Siliceous	>30	>6,0	>64	>6,0	> 105	> 7.5	1.00
Portland cement / Dolomite	10 – 15	2 – 3	20 – 30	1,7 – 2,5	55	3.9	0.40
CAC/Siliceous	5 – 10	1 – 2	10 – 15	0,8 – 1,2	35	2.5	0.29
Fibre Cement	10 – 12	2 +	20 - 25	1,7 – 2,1	-	-	0.32
CAC/Dolomite *	3,0	0,6	7,2	0,6	8,4	0,6	0.12
CAC/ALAG *	Less than CAC/DOL-no mass loss after 17 months in sewer & pH >6,4						

NB: *Value estimated using hydrochloric acid resistance test in the laboratory

2.6. Concretes with high acid resistance

The corrosion of sewer pipe concrete does not only affect the municipalities but the public. Thus, the need for rethinking concretes that are acid resistant over the service life of the sewer lines is vital. The research focuses more on calcium aluminate cement concrete and thus the properties and behaviour of this concrete will be discussed from anhydrous cement phase point of view to hydrated phases in a concrete.

2.6.1. Calcium aluminate cement concrete

Calcium aluminate cement (CAC) dates back to 1848 when first prepared by Ebelman by heating mixtures of alumina and lime and to 1856 when Sante Claire Deville prepared the product by mixing water and corundum aggregate in order to prepare crucibles which could be heated to high temperatures (Robson. 1962). However, Fremy in 1865 is the one who is recognised in the literature to have been accredited as a pioneer of this work (Bensted, 2002). The first manufacture of calcium aluminate cement in the market had been referred to as ‘high alumina cement’ (Robson, 1962) until in the 1970s when it was superseded by ‘calcium aluminate cement’ (Bensted, 2002). However, these terms are used interchangeably in the literature and calcium aluminate cement concrete is the concrete made from CAC cement.

2.6.1.1. Mineralogy of calcium aluminate cement (CAC)

Like pure Portland cement (CEM I), Calcium aluminate cement contains the oxides of calcium, silicon, aluminium, and iron. The aluminates and silicates contained in commercial CACs are meyenite ($C_{12}A_7$), monocalcium aluminate (CA), belite (βC_2S) and gehlenite (C_2AS); these phases are shown in Figure 2.8.

However, the percent composition of the oxides in a CaO +MgO, Al_2O_3+Fe_2O_3 and SiO_2 system is significantly different to that of Portland cement as shown in Table 2.3. The high temperature requirement for refractory concretes makes calcium aluminate cements (CACs) to be produced with a wide range of Al_2O_3 (36- 80 %), i.e. from dark grey low alumina to white high alumina (Bensted 2002). The content of alumina is used as the classification criteria as shown in Table 2.3. However, the mineralogy or phases of the unreacted low alumina cement is reported to be the same as that of the high alumina cement (Robson, 1962).

Table 2.3 Composition ranges for calcium aluminate cements (Scrivener, 1999)

Grade	**Colour**	**CaO**	**Al_2O_3**	**SiO_2**	**Fe_2O_3 FeO**	**TiO_2**	**MgO**	**Na_2O**	**K_2O**
Standard low alumina	Grey or buff to black	36–42	36–42	3–8	12–20	<2	~ 1	~ 0.1	~ 0.2
Low alumina, low iron	Light buff or grey	36–42	48-60	3–8	1–3	<2	~ 0.1	~ 0.1	~ 0.0.5
Medium alumina	white	25-35	65–75	<0.5	<0.5	<0.05	~ 0.1	~ 0.2	~ 0.05
High alumina	white	<20	≥ 80	<0.2	<0.2	<0.05	~ 0.1	~ 0.2	~ 0.05

In this research, the interest is on standard low alumina grade with 36 - 42 % Al_2O_3 produced by Kerneos with product brand named 'Cement Fondu' with buff to dark colour. Various phases of CACs are discussed in the next section.

CA (Monocalcium Aluminate)

Monocalcium aluminate phase is by far the most important phase of CACs with proportion of about 60- 70 % responsible for high early strength (Bensted, 2002). It is a slow setting especially if cooled from molten condition, but subsequently hardens rapidly (Robson, 1962). In practice, the maxiumum hydraulic activity at early ages is obtained by slowly cooling the molten clinker in order to allow the fullest gowth of CA crystals (Bensted, 2002).

$C_{12}A_7$ (Meyenite)

Meyenite is found in small proportions of ~ 2-5 % in CACs with its content increasing with the ratio of CaO/Al_2O_3 if other contents are constant (Bensted, 2002). Although this compound appears in small amounts it is predominantly controlling factor for rapid hydration of CACs and thus if its content is substantially increased the cement tends to set quickly (Robson, 1962)

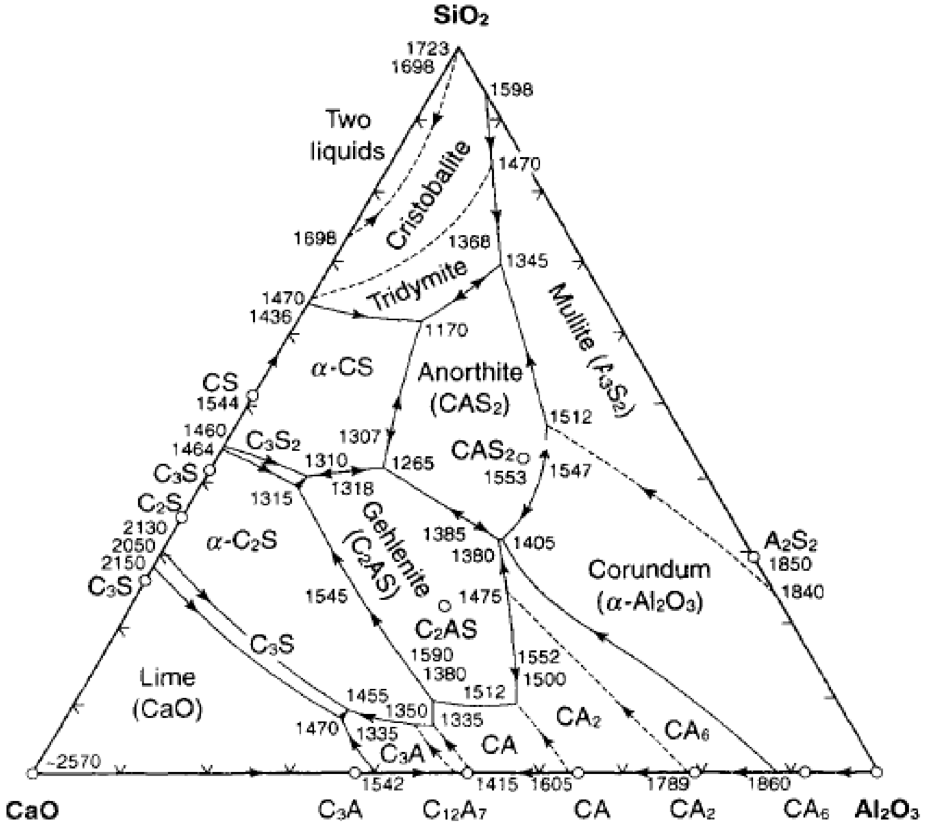


Figure 2.8 The phases of hydraulic and latent hydraulic cement materials in a ternary system of CaO – Al_2O_3 – SiO_2, (Macphee *et al.,* 2004)

β-C_2S (Belite)

This is the compound that appears as small rounded particles in a CAC particularly in CACs with no more than 5 % of SiO_2 (Bensted, 2002), similar to ordinary Portland cement clinkers, dicalcium silicate hydrates slowly even in CACs so that its contribution to concrete strength at early age is insignificant.

C_2AS (Gehlenite)

CACs with significant amount of silica content are reported in the literature (Bensted, 2002, Fernández *et al.,* 2008 & Hidalgo, 2009) to have C_2AS as a regular constituent. Like β-C_2S, C_2AS has very slow hydraulic activity and inevitably causes a significant reduction in strength hardening properties of CAC concrete. It is for this reason that the silica content in calcium aluminate cement is kept low (Robson, 1962) i.e. *circa* 3-8 % for low alumina calcium aluminate cement and *circa* less than 0.2 % for high alumina calcium aluminate cement (Bensted, 2002). Thus, even when CACs are blended with pozzolans and latent hydraulic binders that have high contents of silica, there is a limit of percent replacement so that certain strength properties can be achieved.

The use of CAC in South Africa is not that common and this could be due to; 1) failure of some buildings in the UK in the early 1970s failed due to the 'conversion' reactions resulting in strength loss in the performance of the structures which led to a 'ban' on its use in structures (Concrete Society, 1997). 2) High cost; CAC is 4 - 5 times more costly than ordinary Portland cements (Scrivener, 1999); probably because of high prime cost of bauxite and high temperatures of firing at 1600 °C (Neville 1995) as compared to slightly less temperatures firing limestone in case of Portland cement at 1400 - 1450 °C. However, the use of CAC outperforms PC in aggressive environments such as sulphates, chloride attacks and acid attacks and refractory applications. The data available in the literature regarding the good resistance of CAC to chemical attacks is only based on the unitary mixes i.e. 100 % CAC mixes (Alexander, 2001), Alexander, 2008, Alexander, 2011 and Scrivener *et al.,* 1999).

2.6.1.2. Hydration mechanisms and conversions of CAC

When water is added to the anhydrous phases of CAC the formation of the hydration products follows the dissolution of such phases (Bensted, 2002). The hydration reaction of CAC is mainly a function of both temperature and the moisture. Using CA as the main cementing compound, the hydration mechanism of this phase is as follows:

- The initial hydration reaction of CA occurs below the temperature of 15 °C with $\mathrm{CAH_{10}}$ as the main hydration product as shown in Equation 2.20 a) and above 15 °C $\mathrm{C_2AH_8}$ is formed shown by Equation 2.20 b). At high temperature of about 60 °C, a more stable C_3AH_6 compound is formed as shown in Equation 2.20 c) (Bensted, 2002).

  $CA + 10H \rightarrow CAH_{10}$ ………………………………………………………………………………………. (2.20 a)

  $2CA + 11H \rightarrow C_2AH_8 + AH_3$ ……………………………………………………………………………. (2.20 b)

  $3CA + 12H \rightarrow C_3AH_6 + 2AH_3$ (Gibbsite) ……………………………………………………… (2.20 c)

The initial hydration products CAH_{10} and C_2AH_8 formed at low temperature are regarded as metastable i.e. thermodynamically unstable with regard to stable hydrates formed at higher temperature C_3AH_6 and AH_3 (Figure 2.9). The transition of the hydration products of CACs as a function of temperature and moisture changes the morphology of these products from unstable hexagonal crystals to stable cubic crystals (Concrete Society, 1997).

The porosity of the stable hydration products of CAC concretes is higher than that of unstable products and hence compressive strength of CAC concrete at the time of test is lower than that at service life. This reduction in strength of CAC concrete under hydration mechanisms is termed '**conversion'** and it was for this reason that led to the ban of CAC concrete in construction early in the 1970s in the UK.

Gosselin *et al.,* (2008) investigated the microstructure development of calcium aluminate cement accelerated by lithium sulphate. Lithium sulphate was used to produce a very fast setting and initial strength development owing to the formation of ettringite.

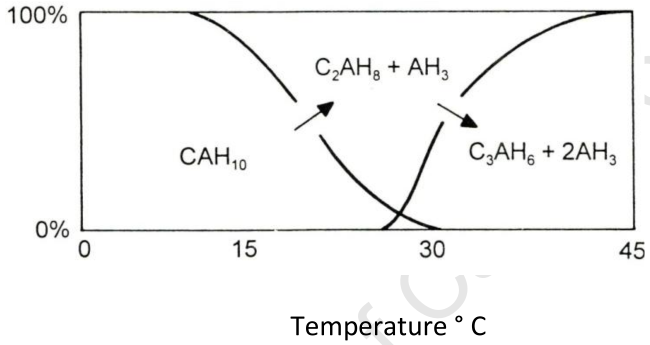


Figure 2.9 Temperature dependence of calcium aluminate hydrates formation (Concrete Society, 1997)

The porosity was measured by the Mercury Intrusion Porosimetry (MIP) and the pore volume (percentage) is shown in Figure 2.10, which confirms from the image analysis that the samples cured at higher temperature (70 °C) have higher porosity than respective samples cured at 20 °C as shown in Figure 2.11.

Thus, it can be noted that conversion mechanism of CAC concrete or mortars is a slow process at low temperatures but can be accelerated at high temperature. A well-planned use of calcium aluminate cement concrete is to expose control specimens to a high temperature at 38 °C, at 100% relative humidity in which the maximum conversion and stable strength occur at about 7 days as shown in Figure 2.12. For the relevance of this research, in sewer pipe manufacturing the newly cast pipes are subject to steam curing at temperature of 50 °C for 4 hours. In reality, the conversion reactions are not yet complete for these pipes but are after 24 hours of steam curing.

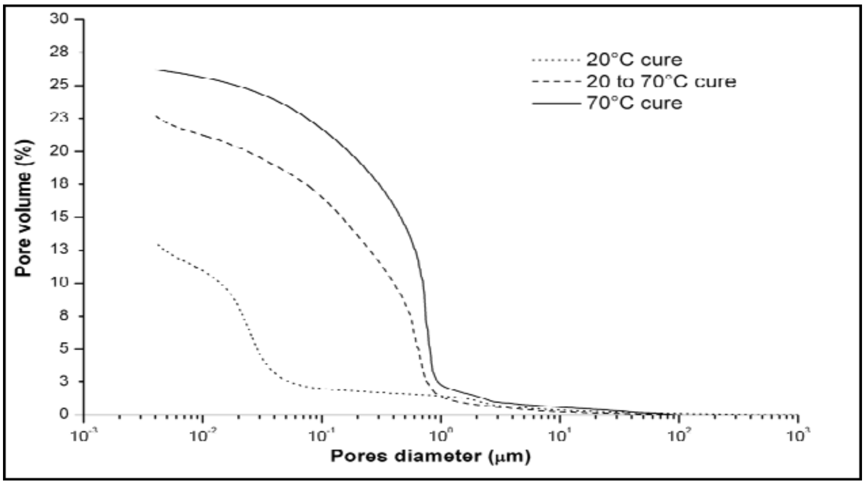
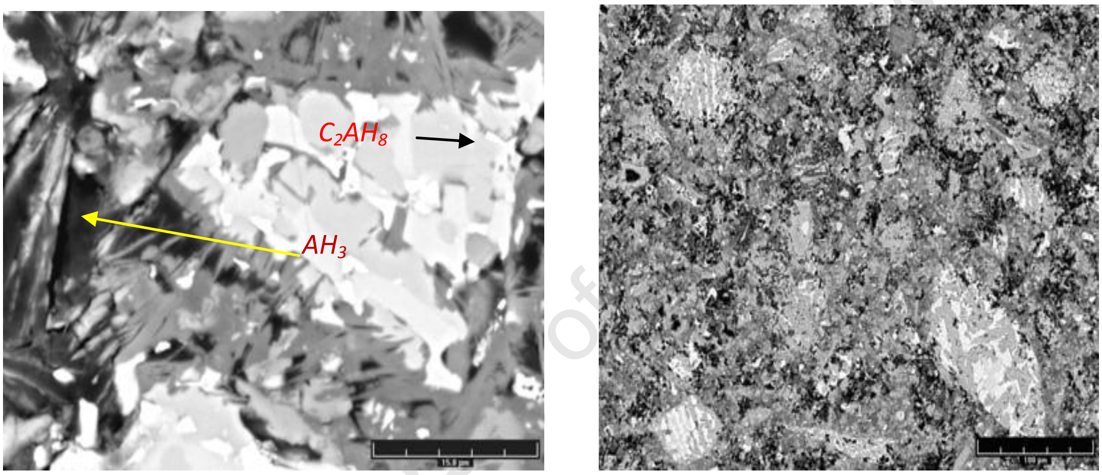


Figure 2.10 MIP results (cumulative pore volume) of CAC pastes cured at 20°C, 20 to 70°C and immediately at t after 24 hours 70°C curing (Gosselin *et al.,* 2008)



a) Unconverted microstructure of C_2AH_8 (brighter sheets) is intermixed with AH_3 (darker) after 3 hours

b) Converted microstructure of (C_3AH_6) with significant porosity after 24 hours

Figure 2.11 SEM observations of CAC hydrated at 70°C, adapted from (Gosselin *et al.*, 2008)

Low w/c ratio concrete mixes in the range of 0.3 - 0.36 typical of those used in sewer pipe manufacturing plants cannot be affected by conversion because of their high density and less porosity (Figure 2.13). Such concretes take long time before hydration can fully take place and hence the conversion reactions will follow later when hydration reactions are complete.

Different types of aggregates can have a significant effect on conversion of CAC, with relatively pure limestone exhibiting strengths of about 20 % higher than CAC concretes containing siliceous aggregates (Ideker, 2008). Apparently this is because in the presence of limestone, a phase $C_{10}AH_8$ of hydrated calcium aluminate cement concrete transforms to $C_4A(CaCO_3)H_{11}$ (mono-carboaluminate)

(Bensted, 2002). Conversely, purely siliceous aggregate sources may exhibit strengths about 20% lower than CAC concretes with silico-calcareous aggregates upon conversion.

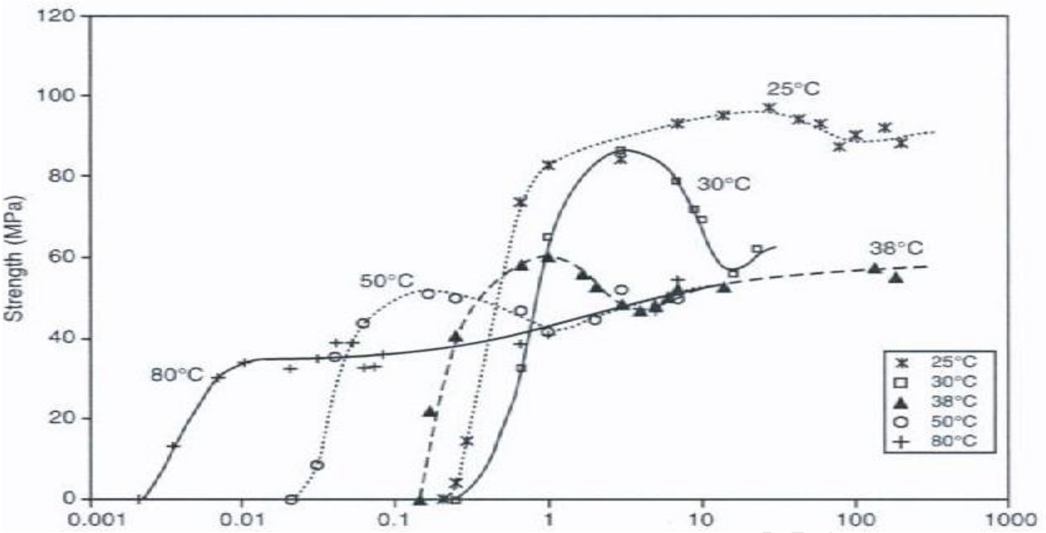


Figure 2.12 The impact of temperature on the conversion and strength development of calcium aluminate cement concrete in isothermal curing (Scrivener, 2003).

2.6.1.3. Acid resistance of CAC concrete

When the conversion reactions of CAC had taken place, the two stable hydration products C_3AH_6 and AH_3 react with the acid giving three typical chemical reactions as shown below.

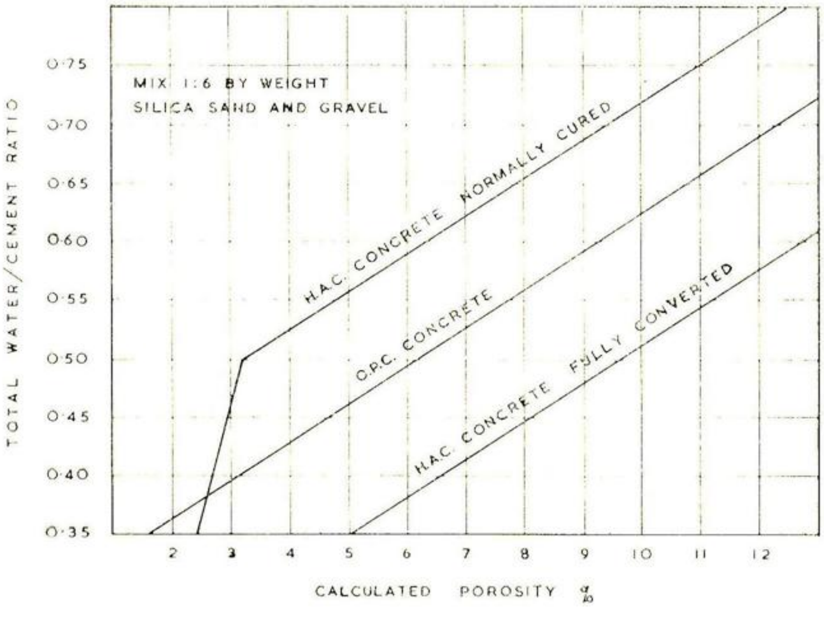


Figure 2.13 Porosity of HAC concrete (normally cured and fully converted) compared with that of ordinary Portland cement concrete; sourced from (Robson, 1962)

$C_3AH_6 + 6H^+ \rightarrow 3CA^{2+} + 2Al(OH)_3 + 6H_2$ ………………………………………………………………………… (2.21)

At pH around 3.5 the alumina hydrate or AH_3 dissolves and in so doing the reacting acid is neutralised as shown in Equation 2.22

$AH_3 + 6H^+ \rightarrow 2AL^{3+} + 6H_2O$ ……………………………………………………………………………………………… (2.22)

The overall neutralisation reaction is shown by Equation 2.23

$C_3AH_6 + AH_3 + 24\ H^+ \rightarrow 3CA^{2+} + 6AL^{3+} + 24H_2O$ ……………………………………………………………………… (2.23)

In both Equations 2.23 and 2.24 aluminium hydroxide or alumina gel is formed, and thus neutralisation capacity is self-created from the acid reaction. The alumina gel created encapsulates the hydration products from further acid attack (Zivicaa, 2002). CACs also exhibit a bacteriostatic effect i.e. the life of the micro-organisms is put at dormant stage due to alumina gel (Alexander, 2001). Since the corrosion of sewer pipes is biogenic in nature the use of CAC in sewer pipes improves the service life of the pipes. Other than stable acid resistant hydration products, the absence of calcium hydroxide in a hydrated CAC also makes it more competent in aggressive acid environment. There is a minimum threshold at pH of about 4 where gibbsite or Al (OH_3) dissolves and thus provide better biogenic corrosion resistance due to bacteriostatic effect of the aluminium ions (Scrivener, 2003).

2.6.1.4. Blends of CAC with other binders

Blending of CAC with other binders is proposed in this research such that the cost of CAC could be reduced without affecting the performance of the sewer concrete pipe during service life.

CAC – PC Blends

CAC–Portland Cement blends are known because of high early setting and hardening behaviour which makes them usable for non-structural applications such as screeds, tile adhesive, grouts and rapid hardening repair mortars (Scrivener, 2003). However, flash set and fast setting can arise with range of CAC-PC percent replacements and this cannot be predicted but can be evaluated through experiments (Bensted, 2002). The fast setting and flash set is primarily due to the gypsum content and calcium hydroxide with high pH from OPC in which gypsum reacts with rapidly reacting CAH_{10} and C_2AH_8 to form ettringite $(C_3A.3CS.H_{32})$ (Bensted, 2002). The strength of CAC-PC blend is reduced considerably as PC replacement is increased until a minimum is reached that is lower than the either CAC or PC alone (Table 2.4). The effect of fast setting and flash setting of the CAC-PC mixes can make it difficult for the mixes to be used in pipe manufacture thus limits the combination for use in this project.

Table 2.4 CAC – OPC Compressive strengths of 1:2:3 concrete at water/cement ratio of 0.55 (Bensted, 2002) NB : Below 60 % CAC the strength reduction is acute

CAC (%)	**OPC (%)**	**Compressive strength (MPa)**				
		3h	**6h**	**24h**	**7 days**	**28 days**
100	0	0	8.3	46.9	62.1	70.3
90	10	10	10.3	37.9	51.7	56.6
75	25	1.7	11	22.6	40	42.8
60	40	2.1	6.9	17.2	21.4	22.0
40	60	5.5	6.2	8.3	10.3	11.0
25	75	3.4	4.1	5.5	9.7	12.4
10	90	0.3	0.7	2.1	7.6	11.7
0	100	0	0	4.8	20.7	34.5

CAC – Fly ash Blend

The conversion reactions of CAC cements during hydration leading to reduced strength of the CAC concrete/mortars over time had brought about the use CAC with other binders to see if this could be reduced. In her study, Fernandez (2008) investigated mixtures of different CAC/FA ratios viz. 90/10, 75/25, 60/40 and 50/50, using CAC as a control group the results indicated that the increase of fly ash reduces the mechanical strength of the mortar at older age as shown in Table 2.5. At 2 days curing, the increase in fly ash content in CAC/FA system decreases the compressive strength, this is critical for 40 % FA and 50 % FA but not for 10 % and 25 % respectively.

Table 2.5 Mechanical strength of CAC:FA mortars (MPa) at w/c ratio of 0.4 and total binder to sand ratio of 3 to 1 (Fernandez , 2008).

	2 days		**28 days**		**180 days**	
	Flexural (MPa)	**Compressive (MPa)**	**Flexural (MPa)**	**Compressive (MPa)**	**Flexural (MPa)**	**Compressive (MPa)**
Plain CAC	6.9	71.3	7.2	89.4	5.4	80.0
10 % FA	8.8	70.3	7.4	91.0	5.1	72.2
25 % FA	8.4	63.5	5.1	70.1	4.3	60.6
40 % FA	6.4	47.0	3.3	37.5	3.2	39.1
50 % FA	5.8	31.4	3	31.4	3.8	52.5

However, at longer curing times the higher FA contents in CAC/FA system do not tend to reduce the compressive strength, this is due to complete reactions of the silica from fly ash with aluminates to form a more stable hydration product- C_2ASH_8, known as stratlingite or gehlenite hydrate. The proportion of the mix made up of the calcium aluminate hydrates is less than in pure CAC and so the effects of the conversion reaction on the strength of the concrete are greatly reduced.

CAC is not used for production of structural sewer pipe but as a lining (Goyns, 2001), the reduction in strength cannot be such a critical parameter but a series of tests need be performed on these blends so that proper blends can be specified for design and construction purposes of such pipes. However even in non-structural applications it is prudent to take sufficient care; this could be done by using low w/c ratio for mortars.

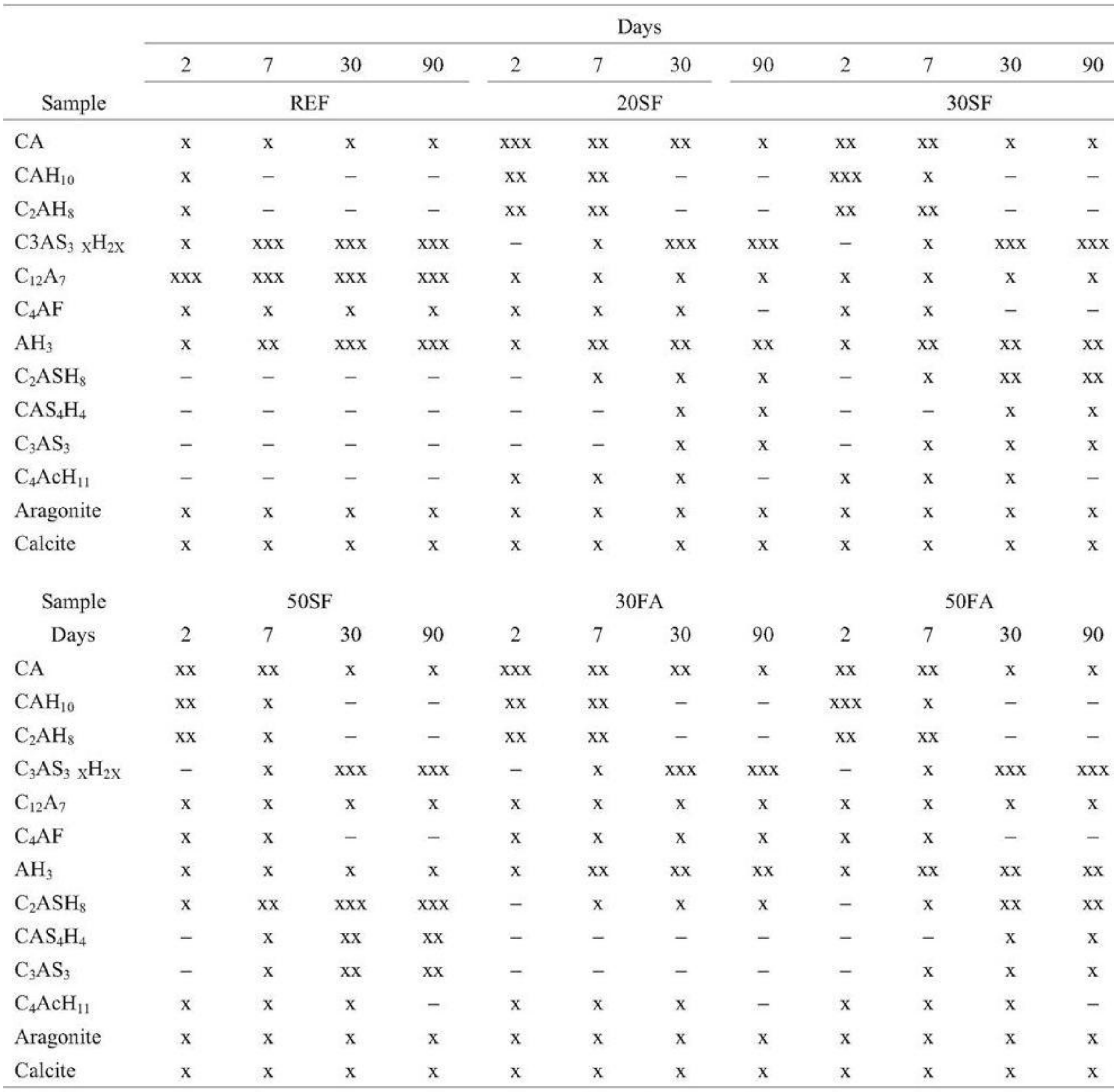
In a study done by (Hidalgo *et al.,* 2009) various products of hydration of blended Calcium aluminate cement concretes with high silica mineral additives i.e. fly ash and silica fume are presented in Table 2.6.

CAC – GGBS

Conversion of CAC is a function of the temperature and the humidity (Bensted, 2002). In the case of sewer pipes in service there is high temperature and humidity in the sewer pipe atmosphere that can promote the conversion reactions. The steam curing of the newly cast concretes may cause conversion to about 17 % (i.e. 4 hours of total 24 hours) (Scrivener, 2003). A study done by Majumdar (1992) on CAC/ggbs blends had shown that the conversion reactions are reduced with addition of ggbs as shown in Table 2.7 thus improving stability of the hydration products. He reported that the presence of ggbs in blended CAC is responsible for the formation of stratlingite in the hydrated product and the possibility of the reactions leading to 'conversion' phenomenon to proceed is inhibited. However, the compressive strength is lowered with addition of ggbs and pozzolans due to the modified chemistry on hydration caused by high silica content in ggbs and fly ash (Quillin *et al*., 2001).

A CAC/ggbs blend is also found from the literature to provide good chemical resistance similar to that of pure CAC; 50/50 blend is typically found to give optimum resistance to sulphate attack (Majumdar, 1992). The blend also performs well on storing in sulphate solution, aggressive marine water and acid water environments (Quillin *et al.,* 2001). Thus this could make CAC/ggbs system a candidate for selection in aggressive environment like sewer pipe linings. However, there is no work done in the case of sulphuric acid attack in sewers. Other than reducing the total cost of pure CAC and reduction of carbon dioxide emissions for production of pure CAC cements, this thesis seeks to check the performance of the blended CAC in acid attack in a 'live sewer'.

Table 2.6 Mineralogical composition of CAC mixes blended with fly ash and silica fume at different times (Hidalgo *et al.,* 2009).



	Days											
	2	7	30	90	2	7	30	90	2	7	30	90
Sample	REF				20SF				30SF			
CA	x	x	x	x	xxx	xx	xx	x	xx	xx	x	x
CAH_{10}	x	–	–	–	xx	xx	–	–	xxx	x	–	–
C_2AH_8	x	–	–	–	xx	xx	–	–	xx	xx	–	–
$C3AS_3\,{}_xH_{2X}$	x	xxx	xxx	xxx	–	x	xxx	xxx	–	x	xxx	xxx
$C_{12}A_7$	xxx	xxx	xxx	xxx	x	x	x	x	x	x	x	x
C_4AF	x	x	x	x	x	x	x	–	x	x	–	–
AH_3	x	xx	xxx	xxx	x	xx	xx	xx	x	xx	xx	xx
C_2ASH_8	–	–	–	–	–	x	x	x	–	x	xx	xx
CAS_4H_4	–	–	–	–	–	–	x	x	–	–	x	x
C_3AS_3	–	–	–	–	–	–	x	x	–	x	x	x
C_4AcH_{11}	–	–	–	–	x	x	x	–	x	x	x	–
Aragonite	x	x	x	x	x	x	x	x	x	x	x	x
Calcite	x	x	x	x	x	x	x	x	x	x	x	x

Sample	50SF				30FA				50FA			
Days	2	7	30	90	2	7	30	90	2	7	30	90
CA	xx	xx	x	x	xxx	xx	xx	x	xx	xx	x	x
CAH_{10}	xx	x	–	–	xx	xx	–	–	xxx	x	–	–
C_2AH_8	xx	x	–	–	xx	xx	–	–	xx	xx	–	–
$C_3AS_3\,{}_xH_{2X}$	–	x	xxx	xxx	–	x	xxx	xxx	–	x	xxx	xxx
$C_{12}A_7$	x	x	x	x	x	x	x	x	x	x	x	x
C_4AF	x	x	–	–	x	x	x	x	x	x	–	–
AH_3	x	x	x	x	x	xx	xx	xx	x	xx	xx	xx
C_2ASH_8	x	xx	xxx	xxx	–	x	x	x	–	x	xx	xx
CAS_4H_4	–	x	xx	xx	–	–	–	–	–	–	x	x
C_3AS_3	–	x	xx	xx	–	–	–	–	–	x	x	x
C_4AcH_{11}	x	x	x	–	x	x	x	–	x	x	x	–
Aragonite	x	x	x	x	x	x	x	x	x	x	x	x
Calcite	x	x	x	x	x	x	x	x	x	x	x	x

Where: ref is 100 % cac, sf is silica fume, and fa is fly ash numeric number represent % replacement, x: mass < 10 %; xx: mass 10-20 % ; xxx: mass > 20 %

2.6.1.5. Dimensional stability of CAC concrete/mortars

Although CAC concrete has been used over 100 years there is limited information in the literature regarding its volume change and cracking potential (Ideker *et al.,* 2008). Mortars for special applications such as grouting, screeds for underlying pavements or even tile adhesives and lining in sewer pipes would show improved performance if their shrinkage are low (Bier, 2001). Owing to its unique hydration mechanisms and chemical resistance in aggressive sewer environment with sulphuric acids; CAC based mortars are used as liners to host pipes concrete.

Table 2.7 Compressive strength of 10 mm cubes of GGBS and CAC ($C_{12}A_7$) mixtures at three w/c ratios for different curing methods (Majumdar *et al*., 1992).

GGBS :$C_{12}A_7$	**w/c**	**Compressive strength in MPa**												
		24 hr moist air	**7 days**			**28 days**			**180 days**			**1 year**		
			Air	**Water 20 ° C**	**Water 30 ° C**	**Air**	**Water 20 ° C**	**Water 30 ° C**	**Air**	**Water 20 ° C**	**Water 30 ° C**	**Air**	**Water 20 ° C**	**Water 30 ° C**
40:60	0.35	32.1	57	47	50	60	63	54	59	70	69	54	56	65
	0.4	27.4	54	40	46	57	57	51	51	74	66	59	67	53
	0.5	21.8	40	33	37	54	54	35	39	49	48	38	41	44
50:50	0.35	30	45	46	42	68	68	63	57	72	81	57	72	78
	0.4	27.8	49	45	50	64	64	60	54	67	72	52	67	69
	0.5	17.6	30	26	36	40	40	36	33	40	50	32	55	45
60:40	0.35	29.5	48	46	58	68	68	71	51	76	-	61	84	68
	0.4	24.8	44	39	50	55	55	65	48	73	83	51	74	76
	0.5	18.9	31	30	37	42	42	44	38	51	56	36	63	62

When mortars or concretes are completely restrained while drying out or hardening, the normal shrinkage strains are converted to tensile strains and if the ductility of the material is exceeded cracks occur (Robson, 1962). This could be the case for CAC concrete/mortar liners in a sewer pipe when fully restrained by a host pipe normally made of PC/siliceous aggregate concrete. Fully restrained CAC mortars and concretes crack under the influence of this shrinkage stresses at much earlier age (Ideker *et al.,* 2008). This is because the shrinkage stresses develop quickly due to rapid hydration of CAC concrete. Furthermore, the modulus of elasticity of CAC concrete reaches relatively high value at early age and the internal stresses cannot be reduced by creep to the same extent as in Portland cement mix at the same age (Robson, 1962).

In a study to assess the volume change, cracking potential and autogenous shrinkage of calcium aluminate cement mortars at early age, Ideker *et al.,* (2008) used a rigid cracking frame shown in Figure 2.14 to estimate restrained shrinkage cracking of CAC concrete. In their experimental work different concretes were cured at different isothermal temperatures. The results revealed that low curing at temperatures < 30 °C, the shrinkage of the hydrated material predominantly CAH_{10} leads to the generation of tensile forces that create cracks of the specimen. On the other the converted specimens cured at high temperature (70 °C) were less susceptible to cracking. Ideker *et al* (2008) concluded converted CAC has less cracking potential to restrained cracking for the following reason; the release of water upon conversion is used for further hydration of unreacted phases. This result in a decrease in volume of the hydrate hence creating compressive stresses within the hydrate that are opposite to tensile stresses (the source of cracks). Thus, it is clear that the restrained cracking happens at early age for CAC liners, or if there is differential in shrinkage values to that of the host pipe. However, since the CAC hardens quickly when the host pipe is still not hard enough this cracking can be of little significance.

Free shrinkage may also affect the cracking potential of the CAC mortar liners in sewer pipes, however free shrinkage of concrete is generally influenced by the following factors:

- The relative humidity of storage atmosphere
- The size of the specimen
- The type of aggregate if present
- Water/ binder ratio
- The cement paste content of the mortar or concrete

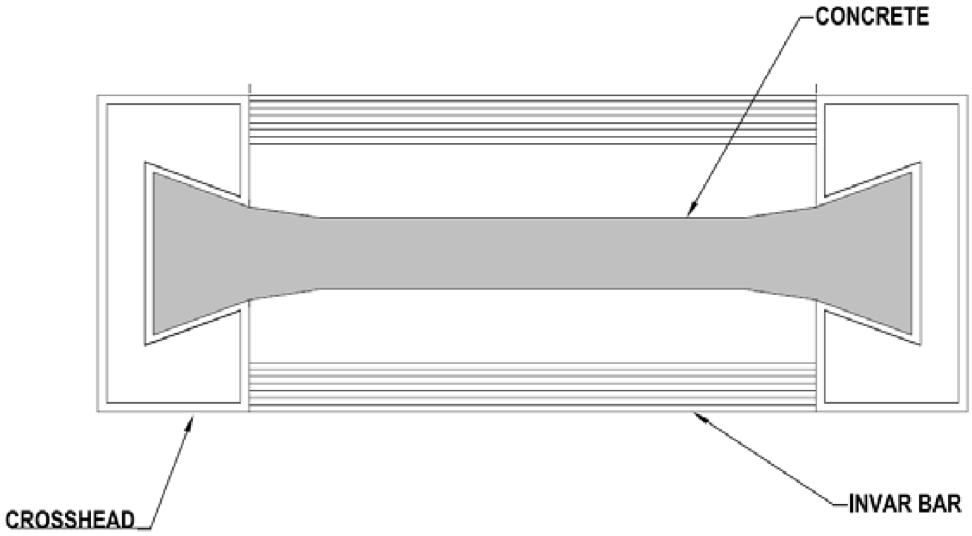


Figure 2.14 Schematic of rigid cracking frame (Ideker *et al.,* 2008)

Drying shrinkage is not a problem for concrete/mortars used as linings in the sewer pipe concretes, because; 1) the humidity is high in the sewer pipe due to constant flowing sewer water and emitted sewer gas i.e. H_2S, 2) Thermal shrinkage is a problem in mass concrete or huge members but the linings are of thickness of order 20 mm plus 5 mm allowance for the interface (Goyns, 2010), 3) Concrete used in sewer pipes is a dry mix with low w/c ratio < 0.36 which makes it denser for applicability of roller suspension method and hence making less susceptible to free shrinkage. Therefore, free shrinkage may not be a problem for high density sewer pipe concrete.

In this research CAC is blended with fly ash and slag and the use of these binders had been reported earlier to reduce the conversion reactions because of the reactions of the silica from these binders and aluminates to form a more stable hydration product- C_2ASH_8, known as stratlingite or gehlenite hydrate. Thus, it would make sense to assume that since converted CAC mortars have no potential to restrained shrinkage cracking, these blended mixes may have little or no restrained shrinkage cracks. However, tests have to be done to verify this but this is beyond the scope of the thesis and is not covered in this research.

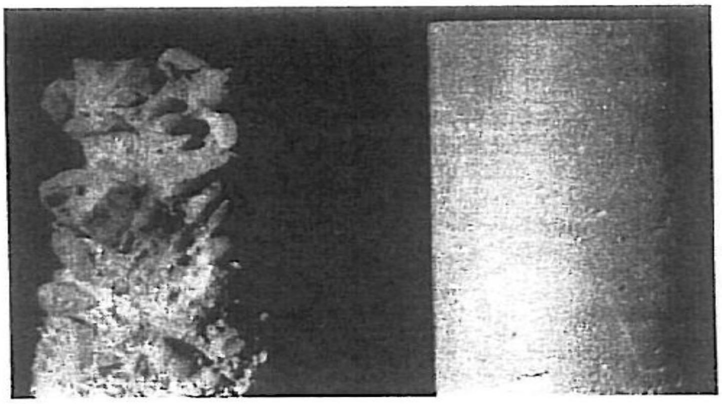
2.6.2. Polymer based concrete

The use of polymers in concrete goes back as far as 1924 when a first patent on hydraulic binders modified with polymers was issued (Pacheco-Torgal *et al.,* 2009). However it was only in the early 1960s when the development of polymer concrete products, mostly pipes took place (Lang *et al.,* 2005). At present three kinds of polymer based concrete are mentioned in the literature due to their different nature (Pacheco-Torgal *et al.,* 2009), these are; a) Polymer modified concrete (PMC) or polymer cement concrete (PCC). PCC consists of aggregates and a binder matrix in which the hydration of cement co-exists with the polymeric phases. b) Polymer impregnated concrete (PIC) in which the concrete mix is impregnated with the monomers of low viscosity typically methyl methacrylate in order to fill the porous structure of a normal concrete. c) Polymer concrete (PC), this type of concrete is composed of aggregates and the polymer matrix without the hydraulic binder and the additive are added during mixing usually in a form of powder and colloidal suspension of latex.

The above polymer based concretes are reported in the literature by Lang *et al*., (2005), Monteney *et al.,* (2000) and Pacheco-Torgal *et al.,* (2009) to have improved acid resistance relative to Portland cement concrete. Various researchers reports that the polymers lead to denser microstructure, smaller discontinuous pores, a better bond between the aggregate and cement matrix, and bridge microcracks relative to pure Portland cement concrete (Vincke *et al.,* 2002). However, the performance depends on the type of the polymers used, although the performance may be better, the cost of concrete pipes with polymers is about 20 – 30 % more than that of Portland cement concrete (Vincke *et al*., 2010). There are different types of polymers available in the market including styrenebutadiene and detailed information regarding the performance on acid attack may be found depending on the mix designs and the type of polymer, the acid resistance may be lower than that of Portland cement concrete (Vincke *et al*., 2002).

2.6.3. Sulphur concrete

Normal hydraulic cement concrete (HCC) or PC sewer pipe is used all over the world and the shortfall of this concrete is its ability to corrode due to biogenic acid attack because of the reaction of portlandite and sulphuric acid. However the use of epoxy coatings and PVC liners are used to prevent this. But the cost of these materials is high and thus they cannot be used for large pipe diameters (Vroom 2000). As studied by Vroom (2000), sulphur concrete (SC) is a primary material that should be considered for sewer pipes usage when exposed to aggressive acid environment. The properties that make SC acid resistant candidate for design incorporation for sewer pipes are mainly impermeability to water and aggressive liquids. Unlike the HCC concrete with open cell structure (pores), SC concrete is reported to be impermeable due to hydrophobic nature of the sulphur and discontinuous closed cell structure. When made with acid resistance aggregate such as siliceous aggregates, Vroom showed that SC is not affected by continuous exposure to strong-acids such as hydrochloric acids (HCl) and sulphuric acid (H_2SO4) Figure 2.15.



Sulfate-resistant HCC after 3 weeks in 20% H_2SO_4

Sulfur concrete after 3 years in the same acid

Figure 2.15 Immersion of sulphur concrete cored samples on acid (Vroom, 2000)

SC is a special type of concrete developed over 30 years ago, the mix preparation of this concrete involves first drying and heating the aggregates to a temperature of 130 – 140 °C, and then adding the hot aggregates , sulphur (either liquid or solid), mineral filler and the STX additive. On cooling SC develops strength and does not need curing. According to Vroom (2000), SC sewer pipes could be produced by dry-cast, wet cast or spun using conventional concrete pipe moulds as well. Although SC exhibit exceptionally high acid resistance than conventional concrete mixes, the high temperature production cost limits its application in concrete technology industry due to high energy cost. However, since the rehabilitation and replacement of damaged sewer pipes courses inconvenience to the public and could be expensive, using life cycle cost analysis SC could be an option for use in sewer pipes.

2.7. Why concrete pipe?

A layman would ask, “why opt for concrete pipes if they corrode?”; concrete pipes have history of a good performance in sanitary sewer and stormwater conveyance systems. However the only challenge is to understand the environment and service conditions for these pipes. For instance acid attack and sulphate attack. Concrete pipe may have a lot of properties that make it best for use by the industry over flexible HDPE pipes and these are viz:

2.7.1. Sustainability

Concrete is used globally as a structural material. Production of hydraulic cement as a constituent material in concrete produces high carbon footprint. However, pozzolans and latent hydraulic binders such fly ash and ggbs as secondary products may be used in the precast concrete plants when casting. This can minimise high content of pure cement as an initiative to save the environment. These cement extenders may also be added to the cement clinker during production of cements to minimise carbon emissions and this may reduce the energy cost as well.

2.7.2. Durability

The use of cement extenders in the literature is found to improve the performance and durability of concrete pipe when exposed to aggressive environments, hence increase the service life of the pipe. This is because the pozzolans are able to reduce the porosity due to reduction of pore sizes which reduces the permeability, sorptivity and diffusivity potential of the concrete pipe. However, if these properties are considerably reduced, one must be aware that the chemical attack i.e. acid attack on a concrete specimen will be concentrated on the aggregate and the concrete surface depending on the pH of the acid. This is the reason why calcareous aggregate has found a common use in sewer pipe manufacturing to increase the neutralisation capacity.

2.7.3. Structural performance

Concrete pipe has high inherent strength with less strength derived from the soil envelope. The use of computer controlled fabricated wire reinforcement cage contributes to high strength performance of the concrete pipe and also helps to resist flexural and lateral stresses (Sherman-Dixie, 2011). In comparison to flexible pipes, concrete pipes have unlimited range of pipe strengths demonstrated prior to installation at the manufacturing plant whereas the strength of the flexible pipe may be different if the backfill material is not well compacted because the strength of a flexible pipe is highly dependent on the soil support. In general when using concrete pipe:

- There is less reliance on quality of installation by the installer
- There is lower embedment material cost i.e. bedding material
- There is less compaction needed
- It is easier to maintain grade and alignment

- There is no excess deflection concerns, because of high flexural strength and it can bridge over uneven bedding without affecting hydraulics of the pipe while flexible pipe can need special consideration for deflection and bending

One most important property of concrete pipe is its mass especially when it is used in marshy environment where there is a potential for flexible pipe to float due to the buoyancy effect. The mass of the concrete pipe counteracts the buoyant force while the flexible pipe may depend on the weight of the liquid, and the weight of the backfill material.

2.8. Control of hydrogen sulphide emission in sewer pipe systems

The solution to biogenic corrosion of sewer pipes must incorporate other expertise such as waste water studies to control H_2S because stages of microbially induced concrete corrosion dictates that H_2S gas is the factor contributing to the formation of H_2SO_4. Although remedial measures for sewer pipes corrosion cannot totally be inhibited, interactive measures available could be employed to retard the corrosion process (Parker, 1945 and Zhang, 2008), such measures are:

- Optimizing the sewer hydraulic design to limit the generation of H_2S,
- Sulphate source control technologies such as urine separation or pre-treatment,
- Use of filtration techniques and purification to separate the solids in the sewer so that the organics could be reduced as they are the ones oxidised to H_2S.
- Discharge of sulphides into sewers - in the study of H_2S emission control Zhang (2008) suggests that precipitation of metal sulphides such as ferrous, zinc, copper, nickel and manganese removes dissolved sulphide from the wastewater, thereby decreasing the amount of sulphide available for release to the sewer atmosphere.
- Increasing redox (reduction-oxidation) potential through aeration of the sewage to decrease biochemical oxygen demand. However, this requirement is to be advantageous on pressurized sewer system such as rising main or where there is a change in slope or pipe diameter changes etc.. The disadvantage is that it promotes fire risks and only works best at pressurized points in a sewer pipe where oxygen dissolution is high (Zhang , 2008).
- Addition of nitrates – as cited by Zhang (2008), Heukelekian (1943) observed that in oxygen deficient systems, nitrates were reduced preferentially over sulphates, thus diminishing H_2S formation. This is because in anaerobic conditions the nitrates in the waste water are used as the electron acceptors than the sulphates.

It is apparent that the attack of sewer pipes by sulphuric acid can be reduced to minimal levels through the control of H_2S via chemical and biological technologies that can inhibit the formation and eliminate the H_2S via application of strategies in Figure 2.16.

2.9. Surface coating of sewer pipe concrete

Although surface coatings is not part of the major research for this project, it is important to consider surface coatings of sewer pipes as part of improving acid resistance of sewer pipe concretes. According to Vaidya (2010) there are several methods of surface coatings developed to mitigate microbially induced concrete corrosion in wastewater collection systems and such methods are:

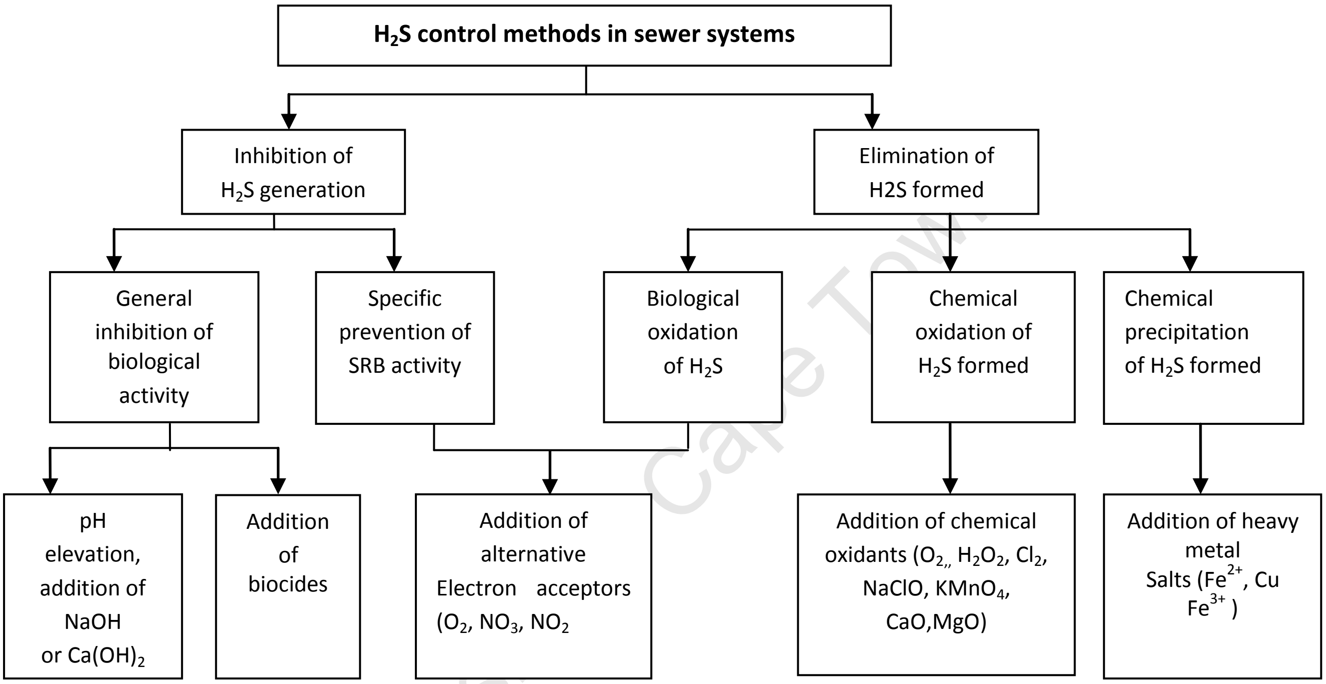


Figure 2.16 Chemical and biological technologies for H_2S emission control in sewer systems (adapted from Zhang *et al*., 2008)

- Spray coatings; however this method is reported from the literature to be unstable due to difficulty in creating proper adhesion between the coating material and the internal surface of the pipe.
- Use of crown sprays process via application of high pH Magnesium Hydroxide Mg $(OH)_2$ to neutralise the acid generated by the *Thiobacillus* bacteria at the crown region, thus elevating the region's alkalinity and deactivating sulphur oxidising bacteria. The application of the Mg $(OH)_2$ is reported to be repeated for every 6-9 months as it is washed away after some time.
- Use of anti-microbial chemicals and biocides, typically applied by mixing it with a concrete or mixing it with the epoxy and sprayed using spraying equipment on the internal surface of the sewer pipes.

- Use of surface coatings by heavy metal oxides Copper oxide (CuO) and silver oxide (AgO). As cited by (Vaidya 2010, Hewayde *et al.,* 2005) did an experiment on heavy metal surface coatings on sewer pipes and bacterial growth in the coated pipes was found to be substantially lower (by up to 99%) than that of the control pipe with the formation of slime layer almost absent in the coated pipes.

2.10. Chapter summary and remarks

Microbially induced concrete corrosion is a process that is affected by many factors such as mixture proportioning, cement content, type of aggregate (calcareous aggregate), porosity of the concrete, concentration of the acid, pH of the acid, temperature and moisture, stability of the corrosion layer formed and concrete types. In the literature review it is considered that there are gaps that need be considered in further research with arising key questions listed below:

- What are the critical parameters needed for predicting the rate of failure of concrete exposed to acid attack, more especially biogenic acid attack?
- Is the use of acid mineral test a good representative of biogenic sulphuric acid attack?
- Are pozzolanic binders (fly ash, condensed silica fume) producing acid resistant concretes?
- Does the use of blended calcium aluminate cement with fly ash and ggbs increases acid resistance as compared to plain mix of CAC concrete?
- Does fly ash- CAC mixes undergo conversion reactions?
- Does a converted CAC concrete have high acid resistance?
- Does a ternary mix of PC-fly ash-silica fume improve acid resistance than respective binary mixes?

2.11. Research approach

Below are several tasks and techniques that had to be done for the development of this project.

- Design concrete mixes and test these mixes for acid resistance at UCT civil engineering laboratory.
- Work regarding the use of Portland cement, fly ash and ggbs had been done previously by Fourie (2007). The results revealed that only silica fume improves acid resistance of concrete while fly ash, ggbs and metakaolin do not produce acid resistant concrete when using dynamic hydrochloric acid test at pH of 1.0. However, the use of blended cements is growing rapidly in construction industry due to the cost savings and environmental protection to limit carbon footprint (Murthi, 2008). This thesis also seeks to advance the use of ternary

mixes. However, fly ash concrete mixed binder system have delayed setting properties and combining these mixes with silica fume can enhance the setting of the concrete, strength development and durability.

- Analysing concrete pipe sections (lids) of various binder aggregates types that have been installed in a 'live sewer' for exposure of biogenic acid attack since 2004 i.e. 7 years.
- However, the focus of this thesis is on the use of blended calcium aluminate cement with fly ash and ggbs at various percent cement replacement to check the optimum percent replacement that can produce acid resistant concrete. It is important to see if the blended mix produces the same acid resistance in biogenic attacks as plain CAC mixes. Acid resistant concrete in this context refers to 1) concrete that does not produce differential corrosion of the hardened cement paste and the dolomite aggregate, 2) less mass loss under acid attack exposure, 3) stifling of the bacteria causing the biogenic acid attack.

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Chapter 3: Materials and Test Methods

3.1. Introduction

The research into biogenic acid attack in the Virginia Experimental Sewer has been on-going for more than 20 years and up to now it is only extreme failure condition at average daily sewage flow of the pipe that has been simulated in the laboratory. However, different combinations of the cements and aggregates have also played a major role in the success of the research to produce competent concrete pipes in aggressive sewers. Calcium aluminate cement/dolomite aggregate concrete is one good performing material; however, it is expensive for use in sewer pipes. The main aim of this chapter is to discuss different materials i.e. blends of CAC and cement extenders (fly ash, ggbs) for use in sewers. The concretes were tested in the accelerated acid solution test, and placed in a 'live sewer' so that the material factor (M_F) of the best performing concrete can be implemented in a life factor method to predict its corrosion rate. Such a concrete mix will then be used in design of sewer pipes while the cost of producing such material is also taken into consideration.

This chapter also discusses the following techniques:

- Selection of raw materials to produce acid resistant concrete; a competent dolomite is needed to produce neutralisation to sulphuric acid attack at the same time as the cement paste.
- Raw materials were prepared i.e. sieve analysis to determine efficient blends of fine aggregates etc.
- Proportioning of mix constituents to prepare 'dry' mix samples similar to that of pipes cast by roller suspension method i.e. low w/c and water content etc.
- Standard test procedures were used to determine physical and chemical properties of concretes.

3.2. Aggregates

The coarse aggregate used was Olifantsfontein dolomite stone 9 -13 mm size and the fine aggregate was dolomite crusher sand also sourced from Olifantsfontein quarry in Gauteng Province. These materials were delivered directly from Kerneos (the company which partially funds the research). The siliceous aggregate (Klipheuwel sand) was sourced from Cape Town. The chemical composition of dolomite aggregates is shown in Table 3.1. Olifantsfontein dolomite has relative density of 2.87 g/cm^3 and and 10 % FACT value of 354 kN as determined by SANS method 5842, 2006 (Fourie 2007). The high 10 % FACT value enables the aggregate to withstand fracture during heavy compaction. The unconsolidated and consolidated bulk densities of the dolomite stone (9 -13 mm) are 1450 kg/m^3 and 1600 kg/m^3 respectively (SANS - 5845, 2006).

Table 3.1 Chemical composition of Olifantsfontein dolomite (Goyns, 2011)

Chemical composition %	**Olifantsfontein dolomite**
CaO	30.90
MgO	21.20
SiO_2	-
Na_2O	-
K_2O	-
TiO_2	-
Fe_2O_3	-
LOI	46.00

The acid insolubilities of Olifantsfontein dolomite stone and dolomite crusher sand are 4.18 % and 6.28 % as determined by acid insolubility test SANS-6242 (Fourie, 2007). This low acid insolubility is a measure of a high neutralisation capacity to counteract sulphuric acid attack in sewer pipes.

3.3. Preparation of raw materials

Sieve analysis (grading) was carried out for the fine aggregates to check the particle size distribution, Hewayde (2007) pointed out that well graded aggregate produces concrete of higher acid resistance than concrete with poorly graded aggregate. This is because in the process of acid attack the tortuosity of ions (H^+) is increased in well graded mixed compared with ungraded ones. Combined fine aggregate i.e. use of two different fine aggregates is now common in advanced mix design processes whereby high strength, durability and workability are critical. Additionally, in sewer pipe concrete design, a high neutralisation capacity is needed and use of dolomite crusher sand meets this requirement. The crusher sand (fineness modulus of 3.61) was blended with a siliceous Klipheuwel with fineness modulus of 2.7. The grading of these fine aggregates is shown in Figure 3.1. The sands were blended in a ratio of 1:1 and the materials were in accordance with SANS - 1083 (2006). Crusher sand has rough surface texture due to the crushing of the parent rock and blending it with siliceous sand that has smooth surface texture was to improve the workability and ease of compaction in a fresh concrete.

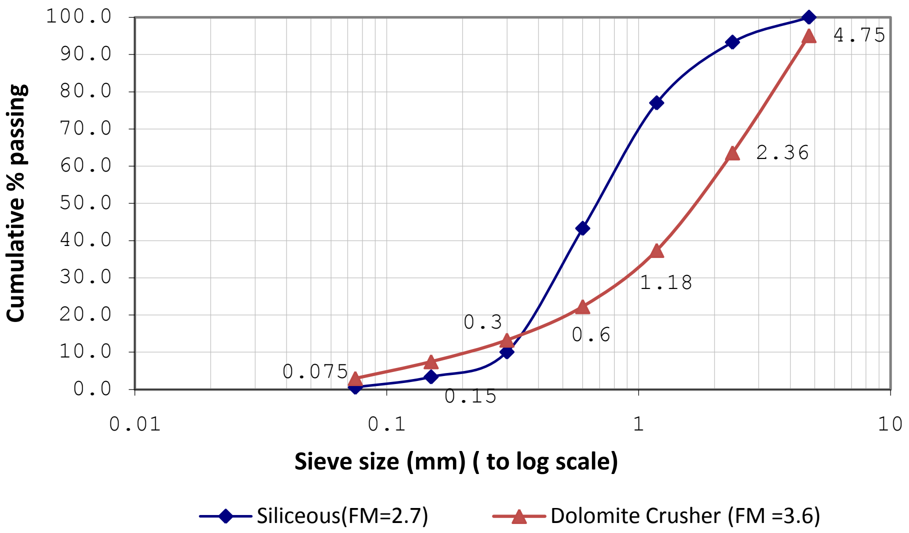

Figure 3.1 Sieve grading analysis of the fine aggregates used

3.1. Cements

Portland cement (PC) is used over a wide range of applications in civil engineering structures. Despite its dominance, special cements such as calcium aluminate cement (CAC) have been developed for applications where Portland cement fails to meet the owner's requirement. CAC has found special application for high early strength (e.g. repairs), performance in highly aggressive environments (sewer pipes) or high temperature applications (refractory). The cost of CAC on the other hand is a barrier, about 4 - 5 times that of Portland cement (Scrivener, 1999) which limits its use in most applications. However, based on the life cycle cost analysis, high initial cost of CACs is justified by a good performance. In this study, CAC is blended with other extenders (fly ash and ggbs) to reduce the cost and see how its performance in aggressive acid environment laboratory tests and exposure to biogenic acid in a 'live sewer' is affected.

3.3.1. Portland cement/fly ash/silica fume mixes

In the 21st century, the cement manucturing regulations all over the world have shifted towards a more sustainable development society with the main focus to minimise carbon emisions (Rehan & Nehdi 2005). Production of cement is a highly energy consuming process with temperatures of about 1400-1500 °C needed to burn limestone or bauxite with significant amount of carbon dioxide released into the atmosphere. In view of the above problem, it is important to recycle materials and use supplementary cementitious materials (SCM) such as fly ash and silica fume in the production of concretes. Other than protection of the environment this will enhance the properties of the concrete, and diversify the application of cement/concrete products into more aggressive environment. Improved sustainability of the cement industry is aligned with reduction in energy related costs because these SCMs are wastes from other manufactures and focusing on market extension of concrete products comprising these binders, it is well recognised in the literature that pozzolans and slag perform better in environments precluding the use of Portland cement alone i.e. sulphate attack and acid attack. The chemical composition of the binders used in this project is given in Tale 3.2.

Table 3.2 Chemical composition of Portland cement (CEM I 42.5 R), fly ash, ggbs and silica fume (Source, Respective manufacturers)

Cement	**Chemical composition by %**													**Source**
	CaO	**MgO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**Mn_2O_3**	**TiO_2**	**SO_3**	**Na_2O**	**P_2O_5**	**K_2O**	**LOI**	**Total**	
CEM1 42.5 R	64.5	0.8	21.2	4.0	3.0	0.1	0.3	2.9	0.1	0.2	0.7	2.87	99.8	PPC[i]
Fly ash	4.1	1.0	54.9	31.3	3.7	0.06	1.67	0.19	0.36	0.49	0.71	0.78	99.3	Ash Resources [2]
(GGBS)	36.4	8.1	37.1	12.8	0.72	0.98	0.59	2.24	0.50	-	1.07	-	99.9	Afrisam [$]
Silica fume	0.68	0.2	96.0	<0.1[ii]	<0.1	-	-	0.25	0.18	-	0.45	1.8	-	Silicon Smelters [3]

[i] Montague Garden [ii] Lower limit detect [$] Vanderbijl Park , [2] Lethabo Plant, Emalahleni Plant

The calcium aluminate cement used in this thesis is sourced from Kerneos in South Africa. Of the various grades of CAC given in Table 2.3 in Chapter 2, this CAC is classified as a low alumina grade with the following chemical composition as given in Table 3.3. The key performance difference of CAC to PC is a high early strength at 24 hours, however the setting time is about the same as that of PC, approximately 3 hours (Bensted, 2002).

Table 3.3 Chemical composition of low alumina calcium aluminate cement sourced from Kerneos South Africa.

Grade	**Chemical composition %**												
Standard low alumina	**CaO**	**Al_2O_3**	**SiO_2**	**Fe_2O_3, FeO**	**Cr_2O_3**	**Mn_2O_3**	**TiO_2**	**MgO**	**SO_3**	**Na_2O**	**K_2O**	**P_2O_5**	**LOI at 950 °C**
	37.6	39.5	4.4	15.1	0.1	0.2	1.8	0.7	0.2	0.1	0.2	0.1	0.2

3.3.2. CAC/fly ash mixes and CAC/ggbs mixes

The CAC/fly ash mixes to date have been mostly used in oil well cementing formulations in Arctic environment where the temperatures encountered are down to – 5 °C (Bensted, 2002). In such environment the hydration of CAC as hydraulic binder releases high heat of hydration that melts permafrost. Hence, the need of blending CAC with fly ash arose so that heat of hydration is lowered. CAC/ggbs is also used in oil well cementing to lower the heat of hydration of the hydraulic binder

(Bensted, 2002) and has also been sucessfully used in durability studies in sulphate and marine environments (Dunster, 2008). The addition of high silica bearing binders such as pozzolans and slag was found in the literature to affect the strength development of CAC concrete (Table 2.4 and 2.5). Therefore, the selected percent cement replacements of CAC/ggbs and CAC/ fly ash in this project were based on the stable hydration products that these systems can produce.

3.4. Basis of mix design

The concrete cylindrical specimens cast and material preparation was to simulate that of the sewer pipes as done during concrete pipe manufacturing. The specimens used for the purpose of this research were thus prepared as relatively stiff and 'dry' mixes heavily compacted (Appendix A.3). The variables were different binders comprising: 1) Portland cement blended with pozzolans (fly ash and silica fume) to make two binary mixes and one ternary mix including a control, 2) calcium aluminate cement blended with fly ash at 85:15, 75:25 and 60: 40 respectively, 3) calcium aluminate cement blended with ggbs at 75:25, 60:40, 50:50 and 40:60 respectively, 4) control group of CAC concrete without any cement extender.

The w/c ratio of 0.36 and water content of 145 ℓ/m^3 were kept constant for all the mixes, and these values are typical for concrete pipe specimens prepared using roller suspension method in pipe manufacturing plants. A trial mix at water content of 160 ℓ/m^3 at w/c of 0.36 was first attempted but was not ideal for heavy compaction, because the mixing water was extracted. A detailed mix design and proportions is shown in Table 3.4. The workability of CAC/ggbs mixes was lower than that of CAC alone and this is because of high levels of $C_{12}A_7$ in CAC cement causing it to act like fast setting cement (Bensted, 2002). CAC concretes were generally thixotropic, that is they appeared to be stiff before they were compacted but quickly fluidify when compacted. However, the workability of CAC/fly ash system was higher than that of CAC alone and this is because of spherical shape of fly ash particles. Ideally cement content above 400 kg/m^3 and w/c ratio of less than 0.40 ensures good placement (Scrivener, 2001). Mix design of these concretes was selected in view of these parameters.

3.5. Casting and preparation of specimens

The Virginia Experimental Sewer is an ongoing project based on the investigation of acid resistance of sewer pipe concretes. It is a 'live' sewer and pipe samples under investigation are cast using a roller suspension method, Figure 3.2. The roller suspension method uses an outer steel form that is rotated in a horizontal position during the pipe making-process. Vibration and compaction are used in combination with centrifuging to consolidate the concrete mix

Table 3.4 Mix design parameters for different concretes used to investigate acid resistance for sewer pipes

Materials and mixes	**Portland Cement Mixes**				**Calcium Aluminate Cement mixes**							
	Control	**Binary**		**Ternary**	**Control**	**CAC blended cements**						
	PC	PC/FA	PC/SF	PC/FA/SF	CAC	CAC/FA	CAC/FA	CAC/FA	CAC/SL	CAC/SL	CAC/SL	CAC/SL
	100	70/30	90/10	72/20/8	100	85/15	75/25	60/40	75/25	60/40	40/60	50/50
Particle density (g/cm^3)	3.14	2.83	2.99	2.82	3.20	3.02	2.99	2.67	3.12	3.07	3.01	3.04
w/c	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36
CAC (kg/m^3)	-	-	-	-	403	342	302	242	302	161	242	201
CEM 1 42.5R (kg/m^3)	403	282	363	290	-	-	-	-	-	-	-	-
GGBS (kg/m^3)	-	-	-	-	-	-			101	242	161	201
Fly ash (kg/m^3)	-	135	-	81	-	60	101	161	-	-	-	-
Silica fume (kg/m$^{3)}$	-	-	40	32	-	-	-	-	-	-	-	-
Dolomite stone (kg/m^3)	1165	1224	1165	1218	1165	1200	1212	1235	1165	1165	1165	1165
Dolomite Crusher sand	442	395	434	397	446	419	411	378	441	439	435	437
Klipheuwel Sand (kg/m^3)	442	395	434	397	446	419	411	378	441	439	435	437
Water (l/m^3)	145	145	145	145	145	145	145	145	145	145	145	145

NB: No superplasticiser used

Table 3.5 Concrete mix ratios to total cement content by mass

Parameter	**Portland Cement Mixes**				**Calcium Aluminate Cement Mixes**							
	Control	Binary		Ternary	Control	CAC blended mixes						
	PC 100	PC/FA 70:30	PC/SF 90:10	PC/FA/SF 72:20:8	CAC 100	CAC: Fly ash			CAC:ggbs			
						85:15	75:25	60:40	75:25	60:40	40:60	50:50
Total constituents (kg/m^3)	2598	2562	2580	2560	2505	2585	2582	2539	2596	2590	2583	2587
% of cement	16	16	16	16	16	16	16	16	16	16	16	16
aggregate/ cement	2.89	3.04	2.89	3.02	2.89	2.93	3.01	3.07	2.89	2.89	2.89	2.89
crusher sand/ cement	1.10	0.98	1.08	0.99	1.11	1.04	1.02	0.94	1.10	1.09	1.08	1.08
Siliceous aggregate/ cement	1.10	0.98	1.08	0.99	1.11	1.04	1.02	0.94	1.10	1.09	1.08	1.08

The mandril also compacts the fresh concrete as it passes between it and the inner wall of the mould. If the concrete mix used in this process is wetter than required, water is extracted from the concrete by the centrifugal forces which develop as the mould is spinning. As the steel mould is rotated, concrete is fed into the form by a conveyor system that is capable of distributing concrete throughout the mould length. Still in the mould, the newly cast pipe is moved to the curing area and steam cured for about 4 hours, thereafter the mould is stripped and the concrete pipe taken to the yard for further air curing before delivery to site.

Figure 3.2 Roller suspension method used for compaction of dry mix concrete for sewer pipes (Goyns, 2011)

In order to determine representative results of both acid resistance and the rate of acid attack of concrete samples in the laboratory, a sample preparation method similar to that of sewer pipes had to be employed. The preparation of ‘labcrete’ cylindrical specimens entailed heavy compaction (Appendix A.3) of freshly mixed concrete into the steel moulds (80 mm diameter × 150 mm) for acid resistance test samples, tensile splitting strength and durability tests samples and (75 mm diameter × 300 mm) mould for compressive strength test samples. This compaction method produces concrete of similar to slightly higher quality to that of sewer pipes manufactured using the roller suspension method (Fourie, 2007).

The compaction was done in four layers in all moulds by a tamping rod and the 10 kg compacting solid cylinder (75 mm × 300 mm). Each layer was compacted 20 times by tamping rod followed by 5 strokes of a 2 kg hammer on the solid cylinder. However, in the 75 mm diameter × 300 mm moulds used for compressive strength, about a quarter of total volume was placed prior to compacting each layer, similar to 80 mm diameter × 150 mm moulds. The steel moulds were stripped after 4 hours and then cured in a hot water bath at 38 °C for a further 10 hours which is roughly equivalent to 4 hours of steam curing when Saul's maturity law is used (Equation 3.1). However, it must be noted that this is based on practicality purposes only because Saul's law of maturity is based on the hydration of normal Portland cement concrete whereas the hydration mechanisms and reactions of calcium aluminate cement concrete are different.

3.5.1. Application of Saul's Maturity Law

Saul's maturity law

$$M(t) = \sum_0^t (T_a - T_o)\Delta t \quad \text{……………………} \quad (3.1)$$

Where :

M(t) = the temperature time factor at age t, or maturity index, degree days or degree hours

Δ t = time interval, days or hours

T_a = average concrete temperature during time interval Δt

T_o = datum temperature, (usually taken as -10 ° C) for OPC

In sewer pipe manufacturing plants such as Rocla, the specimens are left in the moulds to harden for 4 hours and then subjected to steam curing at 50 ° C for a further 4 hours. For simplicity assume the average temperature of heat of hydration in the moulds in the first 4 hours is about 20 ℃ and the steam curing is 50 °C at Δt = 4 hours.

Thus maturity is calculated as follows

M(t) = (20+10) ×4 + (50+10) × 4 = 360 ° C hours

Instead of using steam curing a hot water bath at 38 ° C was used in this research to achieve the same maturity.

Thus:

360 ºC.hours = (38 ° C + 10 ° C) ×Δt

$$\therefore \Delta t = \frac{360\ ℃.hours}{(38+10)℃} = 7.5 \text{ hours}$$

However, for practical purposes 10 hours were used to cure the specimens in a hot water bath at 38℃. The concrete cylinders were then stored in an air conditioned room after 14 hours at a temperature maintained at 22 °C and a relative humidity of 50 % for 28 days before performing all standard tests as discussed below. The specimens were air cured for 28 days because the pipes onsite are air cured for most of their service life, and after 28 days or later, long term properties of concrete can be exhibited. However, to test the efficiency of hand compaction method and the early age properties of the concrete, both tensile splitting and compressive strength tests were performed.

3.6. Standard test methods performed to assess concrete quality for sewer pipe application

Standard tests for compressive strength, tensile splitting, density and durability index (permeability, sorptivity, and porosity) tests were carried out on the concrete samples after 28 days to characterise the concrete properties.

3.6.1. Compressive strength

The compressive strength test was performed according to the principles of standard test (SANS 5863, 2006) on the samples at both early age i.e. after removal of the specimen from water bath (38 ° C) after 14 hours and after 28 days of air curing specimens in air conditioned room at temperature of 22 ° C and relative humidity of 50 % before the test.

3.6.1.1. Significance and use

The compressive strength test is an assessment of a load bearing capacity of a material. It is a common assessment tool of concrete quality to most engineers, and because concrete sewer pipes are supposed to have long service life without compromise. The compressive strength is a measure of load carrying capacity of the pipe and adequate strength is needed for the pipe to withstand loads.

3.6.1.2. Sample preparation

After 28 days of air curing the specimens lost moisture via evaporation and for suitability of the standard test (SANS 5863, 2006), post 28 days of air curing the specimens were pre-saturated for 5 days in water or until there was no further increase in mass when placed in water. A 75 mm diameter × 300 mm cylindrical sample was cut into 3 cylinders of the same height, approximately 100 mm each. Each cylinder was end-ground by a grinder for suitability of the compression test machine such that both ground faces of the cylinder were smooth and parallel. The final height of each sample was approximately 90 mm with height-to-diameter aspect ratio of 1.2.

3.6.2. Tensile splitting test

The tensile splitting test was performed according to principles of standard test (SANS 6253, 2006). The test was done on the cylindrical specimens (80 mm diameter × 150 mm). The average of three specimens was used as the test result. The specimens were tested immediately after removal from water bath at 38 °C after 14 hours as it is done after 4 hours of steam curing in sewer pipe manufacturing. Tensile strength is important for assessing crack control of sewer pipe concrete. This test is also used to assess the quality of the concrete and compaction efficiency.

3.6.2.1. Methodology

Semi-circular steel rods were placed with curved edges touching along the centre line aligned on the longitudinal axis of the concrete cylinder. The load was applied slowly until the rods were held firmly. A compressive load was then applied on the specimen until the specimens failed by splitting (Figure 3.3). The failure load was recorded and converted to tensile splitting strength (MPa).

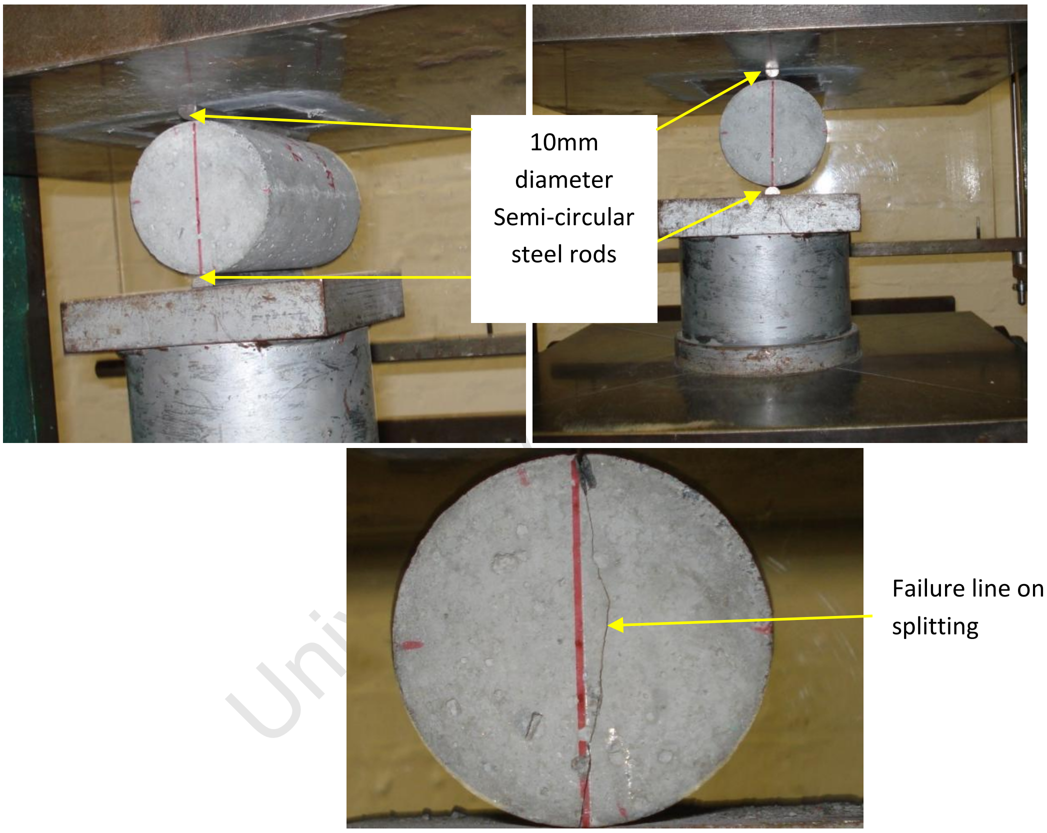

Figure 3.3 Tensile splitting test of 150 mm diameter × 150 mm specimens using compression test machine with specimens failing by splitting approximately along the diametral line

3.6.3. Density

3.6.3.1. Significance and use

Density of the concrete samples was determined according to the standard test (SANS 6251, 2006). Although high density concrete is deemed to have less porosity, density cannot be used to assessing accurate porosity of the concrete specimen. On the other hand density is also used as a basis for proper compaction.

3.6.3.2. Sample preparation

After 28 days of air curing in air conditioned room at temperature of 22 °C and relative humility of 50 %, concrete cylindrical specimens of diameter 80 mm were cut into approximately 30 mm thick discs, and both dry density and saturated density were determined. In determining dry density, the specimens were first dried in a ventilated oven at 100 ° C for 5 days or until there was no further decrease in mass. The cylinders were then immersed in water for 5 days or until there was no change in mass for determination of saturated density.

3.6.4. Durability index tests

Durability index tests (oxygen permeability index, water sorptivity), water absorption and porosity are the key tests used to investigate transport properties of concrete. These tests investigate the ability to allow diffusion of aggressive ions, permeability of gases, and ingress of water. These tests also investigate the moisture absorption potential of the concrete through dependence of the microstructure which in turn is related to the pore structure; all of which assess durability of the concrete structures. However, the question of how to specify durability of sewer pipe concretes in highly aggressive acid environments (pH < 1.0) goes beyond durability indeces and is also not specified in DIN EN-206-1. The durability of these structures is under investigation and this study is part of the investigation. The only tool adopted so far remains a low water/cement ratio and concrete materials that can resist low pH of about 1.0; the most aggressive situation reported for severely corroded sewers (Saucier, 2009).

3.6.4.1. Oxygen permeability index (OPI)

Significance and use

This test method determines the oxygen permeability of 80 mm diameter × 30 mm thick concrete specimens from the rate of pressure decay (initial of 100 kPa) through the sample when placed in a falling head permeater. This gives an indication of concrete quality in terms of impermeability, density, effectiveness of hand compaction method and potential ingress of aggressive acid ions (H^+) during acid attack. The oxygen permeability index (OPI) is calculated as the negative logarithm of Darcy coefficient calculated from the pressure decay rate. OPI values ranges from 9 to 11 with a smaller OPI value indicating a porous concrete material and high OPI value indicating a dense, impermeable concrete material.

Sample preparation and procedure

Although the standard specimen size is 70 mm diameter × 30 mm thickness, special collars were made to accommodate the size of 80 mm diameter specimens cast. The test was performed according to the principles of University of Cape Town Durability Index Procedure Testing Manual 2009. Conditioning of test samples involved prior oven drying of (80 mm diameter × 30 mm) cylindrical discs (average of 4) to a constant mass at temperature of 50 °C for 7 days in a ventilated oven, and a full description of the test can be found from the prescribed manual.

3.6.4.2. Water sorptivity

Significance and use

This test method determines the water sorptivity in $\mathrm{mm}/\sqrt{\mathrm{hr}}$ of concrete (80 mm diameter × 30 mm) in uniaxial direction with the sides of the specimen sealed by tape/epoxy resin. Water sorptivity is the rate of movement of a wetting front through a porous material (Fourie 2007). Water absorption is the main transport mechanism governing the rate of water ingress into unsaturated concrete. It result from capillary forces due to the 'pore structure' (a term normally used in concrete technology meaning total number of pores, pore size distribution and pore geometry (Chandra ,2002)). The test is used for quality control to investigate the rate of water absorption, ingress of aggressive ions and porosity of concrete. Water sorptivity values typically vary between 3 - 15 $\mathrm{mm}/\sqrt{\mathrm{hr}}$. A lower water sorptivity represents a denser concrete, less absorbent material while a higher sorptivity represents a less dense, higher absorbent material. The test was performed according to the principles of University of Cape Town Durability Index Procedure Testing Manual 2009 and full description of the test procedure is found therein.

3.6.4.3. Water absorption and porosity

Significance and use

This is a simple test that investigates the water that can be absorbed in a concrete through the voids and pores. Firstly a concrete specimen is oven dried to remove any water present and then saturated to determine saturated mass. The suction pressure created in a test removes entrapped air, so that water molecules in a saturated specimen can manoeuvre easily under capillary action created when porous material is exposed to water. Water absorption is thus expressed as the % of water absorbed when oven dried porous concrete is placed in a vacuum saturated atmosphere. Voids resulting from honeycombing and poor compaction are not regarded in this test as this is the result of poor concrete practice and not inherent properties of hardened concrete.

Sample preparation and procedure

Conditioning of the test specimens (80 mm diameter × 30 mm thickness) was similar to that of sorptivity test, comprising oven drying at 50 ° C in a ventilated oven to determine a dry mass (m_i). In determining saturated mass (m_{sat}), a suction or negative pressure (- 75 kPa to – 80 kPa) was applied for 3 hours in air tight tank containing the specimens to remove air bubbles in a concrete. The specimens were placed standing on their curved edges to maximise exposure area. A saturated solution of calcium hydroxide was then poured in a tank to a level of 40 mm above the top specimen, and vacuum negative pressure between (- 75 kPa to – 80 kPa) was re –applied for 1 hour 15 min. The vacuum was then released and the specimens were allowed to soak for 18 hours. The saturated mass was then determined and recorded as m_{sat}. Water absorption and porosity of the specimens were determined using.

Water absorption (%) = $((m_{sat} – m_i)/m_{sat}) \times 100$ …………………………………………………………………… (3.3)

Porosity (%) = $((m_{sat} - m_i)/Ad\rho) \times 100$ …………………………………………………………………… (3.4)

Where:

m_{sat} = saturated mass
m_i = Oven dried mass
A = Cross sectional area of a sample
d = Diameter

3.6.5. Acid insolubility

3.6.5.1. Significance and use

Acid insolubility of concrete was determined the same way as that of aggregates (SANS 6242, 2008). The test was performed on all the mixes cast and is used to assess the solubility of the calcareous aggregates in a highly concentrated acid heated to consume all acid soluble portion of the concrete or aggregate. This test method is used as a measure of neutralisation capacity that the aggregate can provide as a sacrificial surface during the sulphuric acid attack of the sewer pipe concrete. However, the test fails to quantify the acid resistance of the sewer pipe concrete in terms of hydrogen ion consumption and rate of acid attack. In this project, the significance of this test is to investigate acid dissolution of different binders for application on sewer pipe concretes either as a liner or as the host pipe.

3.6.5.2. Sample preparation and test procedure

A representative sample of 200 g of concrete to be tested was crushed and ground until it passed through a sieve size of aperture size 600 µm. The sample was reduced further by quartering to obtain a representative portion of 50 g. This portion was ground further until it past through a 150 µm sieve size and was then dried in an oven at a temperature of 100 °C for 2 hours and cooled to room temperature in a desiccator.

Specimens of approximately (10 g) of the powder (mass a) were digested in 2.28 M hydrochloric acid solution and the solution was boiled for 10 min to break down any conglomerated particles. The solution was filtered through Whatman's ashless filter paper with any remains in the beaker washed off by hot water until no cloudiness appeared when tested with 0.1 N of silver nitrate. The residue and the filter paper were placed in a crucible (mass b) and both heated in a kiln at 1000 ° C for an hour. After burning in a kiln, the mass of the crucible and the contents was cooled in a desiccator and (mass c) was determined thereof. The test was repeated with a blank determination for empty crucible (mass d) and (mass e) after burning in a kiln respectively. However, using ashless filter paper implied that (d = e). Acid insolubility (average of four determinations) was calculated from Equation 3.5 below.

$$Acid\ insolubility = \frac{(c-b)-(e-d)}{a} \times 100 \qquad \text{..........} \quad (3.5)$$

Where:

c-b = mass of the residue in grams

e-d = is mass of residue found in blank determination in grams

a = is the mass of the test sample in grams

3.7. Dynamic hydrochloric acid resistance test

3.7.1. Scope

This test method covers the procedure for determining acid resistance of the concrete that is the representative of that actually used in the sewer pipes. The test method determines the neutralisation capacity of the concrete and can quantify the acid resistance via hydrogen ion consumption and mass loss. It simulates the worst-case scenario, which is the attack at the average daily sewage level. However, hydrochloric acid is used not sulphuric acid, because hydrochloric produces soluble salts when reacting with concrete. Thus during the attack, new surfaces are exposed similar to removal of gypsum by continual flow and abrasive suspended solid particles such as fine sand. During titration, the acid solution is also not as quickly clouded as when sulphuric acid is used due to sulphate ions. Full procedure for the test is described in Appendix B. and C for titration method and acid resistance test method respectively.

3.7.2. Significance and use

Although the test does not measure alkalinity directly, when all other parameters are fixed i.e. aggregate, w/c, water content, and cement content, it can measure varying neutralisation capacities for different cementitious materials per concrete mix via hydrogen ion consumption (mg/cm^2).

The microbial induced concrete corrosion (MICC) is dependent on the concentration of the acid, pH and the solubility of the acid. In the sewer pipe atmosphere the pH of corrosion-inducing environment is highly acidic. The test is based on the accelerated conditions that simulate the conditions in the sewer with pH of the HCl solution maintained around 1.0 to assess the resistance of the concrete within 96 hours (or even 48 hours if a clear trend is noticed). Fourie (2007) reports that such aggressive environments are common in South African sewer pipes, maintaining such low pH in testing for acid resistant concrete is helpful to pipe manufacturers to develop concrete mixtures that can be used in the sewer pipes. Thus, the success of the acid immersion tests helps to distinguish which concrete composition can sustain such acidic conditions in a live sewer.

However, the success of the acid resistant concrete in a sewer pipe environment depends on the nature of the mix composition and hydration products of the concrete that influence the growth of the *Thiobacillus* species. Such mixes are CAC, dolomite aggregate, pozzolans and metallic biocides that contain compounds that are toxic towards the growth of the *Thiobacillus* species (acid generating migro-organisms).

3.7.3. Background information to the acid solution test

Although in sewer pipes the main attack is the sulphuric acid, the question of the use of hydrochloric acid in the test method needs mention. Preliminary testing in the development of mineral acid test to simulate corrosion of sewer concrete pipe by Fourie, (2007) showed that sulphuric acid had the following drawbacks:

a) The solution, is rapidly saturated with sulphate ions $(SO_4)^{-2}$ (within less than an hour), and this hinders further attack on concrete specimens

b) The insoluble salt $CaSO_4$ i.e. gypsum as corrosion product formed on the concrete surface protects the concrete from attack. Thus the test failed to simulate the worst –case corrosion at daily sewerage flow.

The development of hydrochloric acid solution test that entails hydrogen ion concentration (aggressivity to concrete), and produces soluble salts when reacting with concrete makes acid solutions last longer between solution renewals. As the concrete surface is attacked, the dissolution of soluble portions of the concrete takes place and insoluble portions of the concrete fall out. Thus the test simulates the worst-case scenario attack that happens at average daily sewage flow of sewer pipes. The test is highly reproducible, because as the acid attacks the concrete the soluble salt i.e. calcium chloride becomes part of the solution. If the solutions renewals, pH monitoring and brushing are kept constant throughout the test the concrete is exposed for attack for the duration of the test. In the invention of the test, the standard deviation was between 0.1 and 0.9 % and 0.07 to 1.74 mg/cm^2 for mass loss and hydrogen ion consumption respectively (Fourie 2007). This is low and hence once off testing of concrete mixes gives confidence as used in this thesis.

3.7.4. Effectiveness of dynamic hydrochloric acid resistance test

Concrete made of siliceous aggregates is more prone to acid attack than the calcareous aggregate because the acid only attacks the soluble binder and the siliceous aggregate protrude and later fall out. The PC /DOL concrete socket sourced in Virginia Experimental Sewer (Figure 3.4 a) has corroded less after 14 years in service with roughly uniform corrosion, wherease in a PC/SIL pipe in Figure 3.4 b), the binder had been completely corroded and washed away. Thus, under constant applied load, the aggregates loose support in a concrete matrix thus adversely lowering structural integrity of the pipe. The top section of the PC/SIL pipe probably fell and was washed away and was never found (Figure 3.4 b). Thus looking at the samples that have been tested in the laboratory by Fourie (2007) in Figure 3.5, it is obvious that the test can simulate this extreme failure pattern hence making it accurate for prediction of corrosion rate as a function of both acid dissolution and mass loss. Therefore the standard test for hydrochloric acid resistance is only used for dolomite aggregate concrete.

3.7.5. General comments and limitations

Although the test can accurately determine acid resistance of a concrete it fails to determine the acid resistance of biogenic sulphuric acid attack generated by the *Thiobacillus* species in sewer pipes at the crown of the pipe.

The dynamic hydrochloric acid solution test is only aimed at determining acid resistance of cylindrical concrete specimens by virtue of hydrogen ion consumption (mg/cm^2) and mass loss (%). It incorporates the cleansing and solution renewals to simulate the abrasion effect of the running sewer water and exposing concrete specimen to constant aggressive acid attack (pH =1.0), as in the average daily sewerage flow of the sewer pipe.

a) OPC/ Dolomite socket in Virginia Experimental Sewer after 14 years of concrete pipe sewer in service (photo by Goyns, 2011).

b) OPC/Siliceous socket Virginia Experimental Sewer after 14 years of concrete pipe in service; with the top missing (photo by Goyns, 2011).

Figure 3.4 The effectiveness of dolomite aggregate to provide neutralisation capacity in an acid attack of concrete.

a) Dolomite aggregate concrete

b) Siliceous aggregate concrete

Figure 3.5 The effectiveness of dynamic hydrochloric test method to simulate extreme corrosion on the average daily sewage flow of the pipe (Fourie, 2007)

The test involves back titration method - addition of a known volume of titrant or sodium hydroxide to the unknown concentration of the acid solution in which the concrete had been immersed to determine concentration of the acid solution at neutralisation point (Appendix B). However, the method is accurate for Portland cement concrete and there is minimal precipitation of concrete ions occurring if one assumes that the sodium hydroxide only reacts with excess acid not reacted with cementitious material Equation 3.6.

$$3H^{+} + 3NaOH \rightarrow 3Na^{+} + 3H_2O \quad \text{……………………………}(3.6)$$

The standard test recommends that the solution renewal be done after 24 hours when testing one specimen, 12 hours for two specimens, and 8 hours for three specimens when testing in one compartment (Fourie 2007). However, this does not apply for concretes with high alumina contents as with blends containing slag and fly ash, because during titration the aluminium ions (Al^{3+}) tend to form the precipitate $Al(OH)_3$ (Equation 3.7). It was discovered that solution renewals can be done as soon after about 12 hours for one specimen , alternatively, Dhir (1999) proposes the following:

- Addition of sodium floride (NaF) to the acid solution before adding a titrant, this combines with the aluminium ions released and stops the formation of $Al(OH)_3$, the calculation of the hydrogen consumption (mg/cm^2) then becomes accurate in which no precipitate forms Equation 3.8.

$$Al^{3+} + 3NaOH \rightarrow Al(OH)_3 + 3Na^{+} \quad \text{……………………………}(3.7)$$

$$3H^{+} + 3NaOH + 3NaF + Al^{3+} \rightarrow AlF_3 + 3Na^{+} + 3H_2O \quad \text{……………………………}(3.8)$$

3.8. Remarks and chapter summary

The experimental work discussed in this chapter forms part of a larger programme of investigation of acid resistance of sewer pipe concrete. The current study investigates the attack of various concrete types i.e. calcium aluminate cement with blended extenders (fly ash and slag) and Portland cement with blended with (fly ash and silica fume) in concentrated acid solution (pH= 1.0). The chapter discussed in detail the requirements for preparation of raw materials i.e. grading of aggregates in the laboratory, mix proportioning of a dry mix that is low w/c (<0.36) ratio and low water content approximately 145 m^3/l. This was to enable the specimens to be representative of those prepared by roller suspension method by sewer pipe manufacturers. Such mixes are designed so that when heavily compacted the wet concrete does not extract water.

Blended calcium aluminate cement concrete with the extenders is not a common concrete practice except in few special applications such as oil well cementing and in sulphate marine environments.

Thus, for the purpose of this study it was crucial to characterise concrete properties via, transport and durability properties (OPI, sorptivity and porosity), mechanical properties (compressive, tensile strength) and chemical properties (acid resistance, acid insolubility). Standard test procedure and preparation of specimens were mentioned and discussed if the specimens were not conforming to standards. However, most of the test methods are discussed in the Appendix. A back titration method was used to determine the concentration of the acid solution after every 4 hours of testing concrete specimen in hydrochloric acid solution test. The use of one specimen is due to high reproducibility as determined in its invention with standard deviation between 0.1 and 0.9 % and (0.07 to 1.74 mg/cm^2) for mass loss and hydrogen ion consumption respectively.

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Chapter 4: Results and Discussion

4.1. Introduction

The aim of this chapter is to present the results of concrete mixes cast in a laboratory (Table 3.4) for all standard tests performed. The main aim of this chapter is to assess the acid resistance of the sewer pipe concrete in the acid solution test. There has been common use of supplementary cementitious materials (i.e. fly ash, silica fume and ggbs) in concrete construction for cost savings, environmental protection and energy savings. The physical and chemical properties of the concretes comprising these binders are of paramount importance in acid resistance of sewer pipe concrete as will be discussed in the following sections.

There are three groups of concretes that are analysed for each standard test method. These are: 1) Portland cement concrete blended with pozzolans to make two binary mixes and one ternary mix, 2) Calcium aluminate cement concrete blended with fly ash. 3) Calcium aluminate cement concrete blended with ggbs.

4.2. Compressive strength

The aim of this investigation was to assess the success of hand compaction method on the concrete mixes because this method gives the results similar or slightly higher than that of pipes prepared using roller suspension method (Fourie, 2007). Compressive strength also assesses the maximum stress that the concrete can take before failure. The compressive strength was tested on 75 mm diameter × 90 mm length cylinders, using an average of 3 specimens for all the concretes. The results are at early age i.e. after removal of the specimen from hot water bath (38 ° C) after 14 hours, and after 28 days of air curing. Early age strength is particularly useful to assess damage or fracture potential of the newly cast pipe material.

4.2.1. Blended Portland cement concrete with cement extenders

The compressive strengths of Portland cement concrete (PC) using CEM1 42.5 R and blended PC with cement extenders are shown in Figure 4.1. The standard deviation and coefficient of variation of these results are shown in Table 4.1. The compressive strength of plain PC concrete at early age (14 hours) is higher than that of all the blended cement concretes due to rapid strength development and higher heat of hydration from hydraulic activity of the cement (Swamy, 1986, Chandra, 2002). The use of fly ash is limited in pre-cast concrete plants especially concrete pipes where rapid turnover is needed (Fourie, 2007). This is due to slow rate of hydration of fly ash that leads to slow strength development (Figure 4.1).

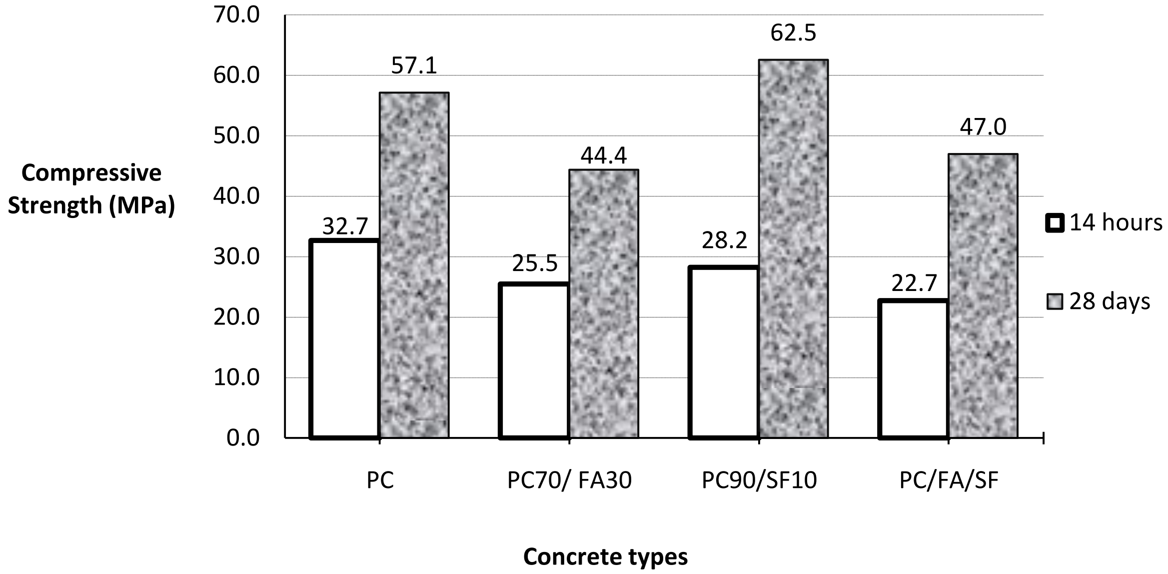

Figure 4.1 Compressive strength test results (MPa) average of three specimens of unitary, binary and ternary Portland cement concrete (75 mm diameter × 90 mm with aspect ratio of 1.2)

Table 4.1 Statistical variables for compressive strength of blended Portland cement concrete

	Concrete mixes							
	PC 100		**PC 70/FA 30**		**PC90/SF10**		**PC72/FA20/SF8**	
	14 hours	28 days	14 hours	28 days	14 hours	28 days	14 hours	28 days
Average (MPa)	32.7	51.1	25.5	44.4	28.2	62.5	22.7	47.0
Std Dev	4.8	4.7	3.4	5.1	3.4	3.2	0.5	4.0
COV (%)	14.8	8.2	13.2	11.5	12.0	5.1	2.1	8.5

Unlike fly ash, the reaction involving silica fume is rapid and no long curing period is necessary before desired strength and impermeability is achieved. Thus, a ternary blend of both fly ash and silica fume in Portland cement can play a vital role in improving early age strength (Murthi, 2008). However, in this research a ternary mix of PC, fly ash and silica fume after 14 hours does not outperform fly ash mix in terms of strength development but does after 28 days because strength development of silica fume is noticeable within 3 to 28 days (Swamy, 1986. The high coefficient of variation at early age compared with 28 days shows that curing is important for microstructure and strength of concrete.

Generally silica fume concrete has higher compressive strength than fly ash concrete due to curing sensitivity and slow strength development of fly ash. The beneficial effects of pozzolanic reactions on strength are noticeable after 28 days (Swamy, 1986). Sewer pipe concretes are air cured and this shows that the application of 30 % fly ash mix is limited.

After 28 days a 10 % silica fume concrete mix had 10 % higher compressive strength than PC concrete, and a ternary mix had 17 % less compressive strength, with the reduced strength attributed to the curing sensitivity of fly ash. Superior compressive strength of silica fume concrete was attributed to high pozzolanic reactivity of silica fume and properties of the hardened cement paste formed thereof (Swamy, 1986, Chandra, 2002).

4.2.2. Calcium Aluminate Cement /fly ash concrete

The compressive strengths of a plain CAC concrete and CAC blended with fly ash at 85:15, 75:25, 60:40 respectively are shown in Figure 4.2. One other plain CAC concrete mix was cured for 7 days in a water bath at 38 °C, rather than the 10 hours like all specimens. This was done to investigate the effect of conversion i.e. reduction in strength due to ongoing reactions of metastable hydrates. This concrete mix attained a compressive strength of 37.2 MPa (Figure 4.2) after 7 days shown in the literature (Figure 2.12) as the time for full conversion. Standard deviation and coefficient of variation of the results are shown in Table 4.2. Both fully converted and unconverted plain CAC concretes were tested for acid resistance after 28 days. The unconverted specimens are those cured in similar conditions to the rest of the specimens i.e. 10 hours in water bath (38 °C).

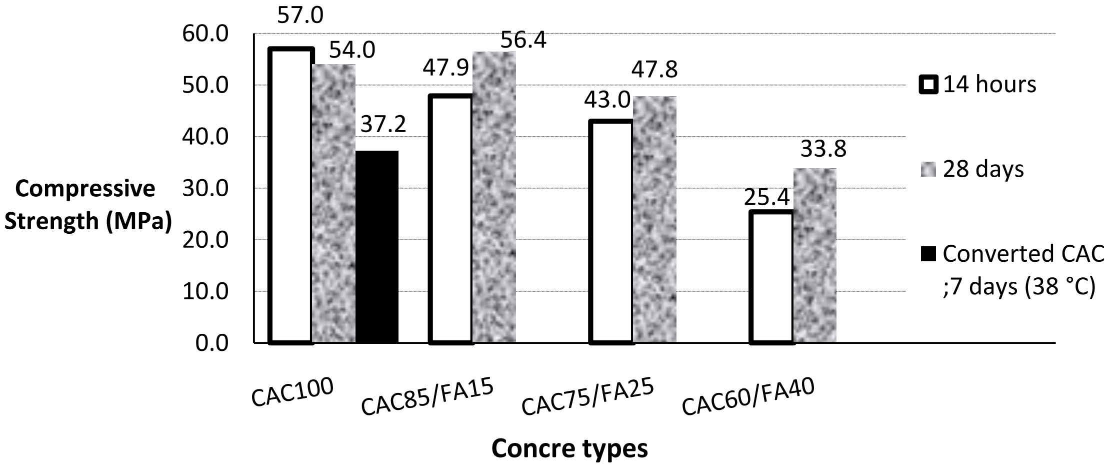

Figure 4.2 Compressive strength test results of CAC – fly ash blended concrete average of three specimens (75 mm diameter × 90 mm with aspect ratio of 1.20).

Table 4.2 Statistical variables for compressive strength of CAC- fly ash concrete

	Concrete mixes								
		CAC100		CAC85:FA15		CAC75:FA25		CAC60l:FA40	
	14 hours	7 days (Converted	28 days	14 hours	28 days	14 hours	28 days	14 hours	28 days
Average (MPa)	57.0	37.2	54.0	43.0	56.4	43.0	47.8	27.8	38.6
Std Dev	1.8	1.4	3.4	3.2	1.0	1.4	1.6	1.6	1.8
COV (%)	3.2	3.7	6.3	7.4	1.7	3.2	3.4	5.7	4.6

Discusion

The lower compressive strength of 54.0 MPa for plain CAC concrete after 28 days was less than that of 57.0 MPa at 14 hours due to conversion reactions of CAC. Conversion of CAC is a mechanism in which hydration of metastable products release some water that results in a higher porosity at a given degree of hydration, hence reducing the compressive strength (Concrete Society, 1997). The released water is made available for further reaction of remaining anhydrous material (Figure 4.4) (Scrivener *et al.*, 1999). On the other hand, a fully converted concrete with compressive strength of 37 MPa lost about 35 % of the compressive strength from unconverted concrete with compressive strength of 57 MPa. This is critical in design and one can wonder if the acid resistance of the converted CAC concrete is still the same as that of unconverted one (see Section 4.8).

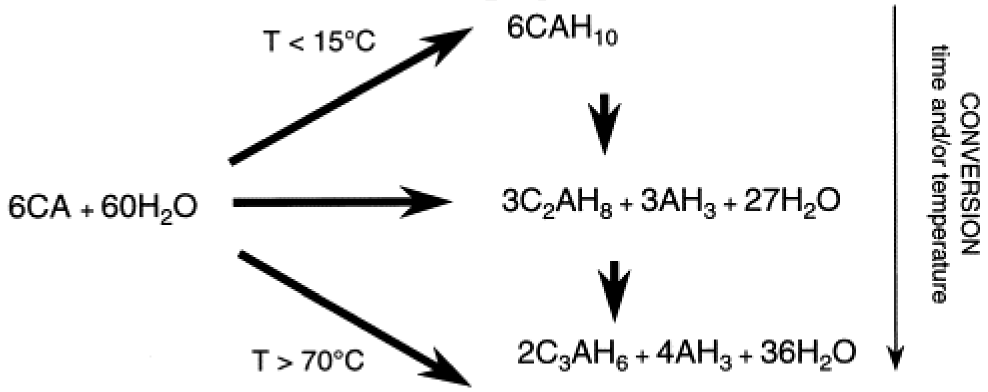

Figure 4.3 Hydration reactions of monocalcium aluminate as the main hydraulic constituent of calcium aluminate cement (Scrivener *et al.*, 1999).

The compressive strength of plain CAC concrete was higher than that of blended CAC/fly ash concretes. Increasing fly ash content lowers the compressive strengths considerably. An increase in content of fly ash increases dicalcium aluminate silicate phase (C_2AS) which has very low hydraulicity and causes a significant reduction in hardening properties of CAC concrete (Robson, 1962). It is also noticed from the results that after 28 days of air curing, there is generally no conversion for blended

CAC concretes. This behaviour is explained in terms of stable hydration product gehlenite hydrate (or stratlingite) C_2ASH_8 which also has slow strength development (Fernández, 2008). The SCMs release silica i.e. high silica content readily makes silica available in a reaction with C_2AS to form C_2ASH_8 (Equation 4.1) (Majumdar, 1990) as cited by (Hidalgo *et al*, 2009). Stratlingite is common in old CAC structures, and is also found in abundance in CAC concrete blended with fly ash indicating that conversion is not delayed but is eliminated in the blended concretes.

$C_2AS + 8S \rightarrow C_2ASH$………. (4.1)

4.2.3. Calcium Aluminate Cement /ggbs concrete

The compressive strengths of a plain CAC concrete and blended CAC with ggbs at 75:25, 60:40, 50:50 and 40:60 respectively are shown in Figure 4.3, statistical parameters are also shown in Table 4.3. A high coefficient of variation of 24.7 % for 75 % CAC: 25 % SL mixture at 14 hours is an outlier; however there is similar trend for all mixes in terms of strength development.

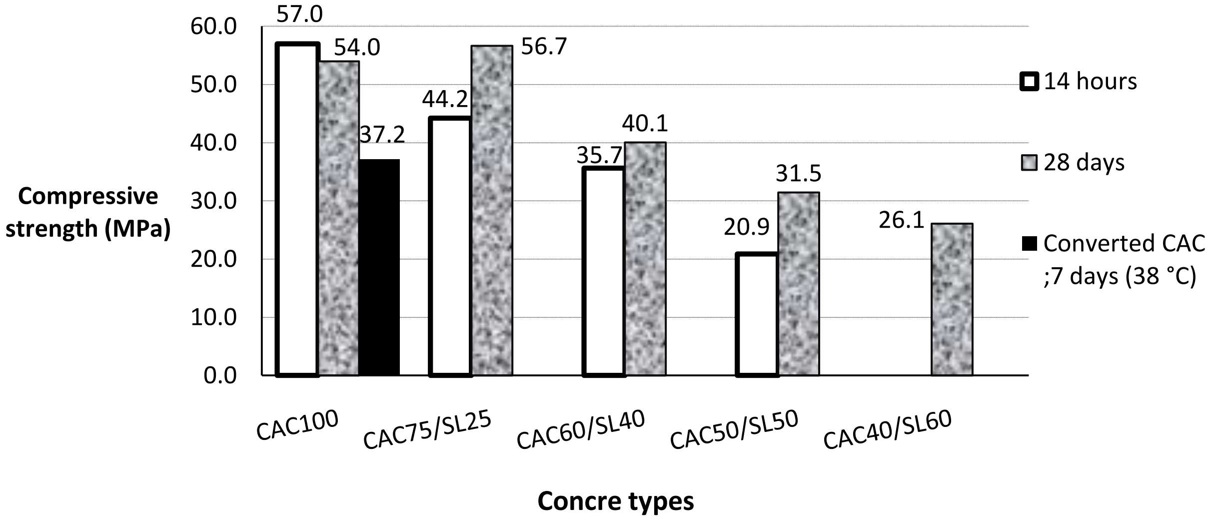

Figure 4.4 Compressive strength test results of CAC – ggbs blended concrete average of three specimens (75 mm × 90 mm aspect ratio of 1.2).

Discusion

Similar to CAC/fly ash concretes, the compressive strength of plain CAC concrete was higher than that of blended CAC/ggbs concretes. Increasing ggbs content lowers the compressive strengths as well because of the presence of stratlingite in CAC/ggbs system (Majumdar, 1992).

4.2.4. General Discussion

A plain CAC concrete achieves in 14 hours the strength that a plain PC achieved in 28 days, the key difference in attaining these values lies in the nature of the active phases that lead to setting and hardening properties of each type of cement (Scrivener, 1999). On hydration, Portland cement produces amorphous calcium silicate hydrates (C-S-H) and crystalline calcium hydroxide (CH)

(Scrivener, 1999, Bensted, 2002). In contrast, CACs produce calcium aluminate hydrates. The later formation reaction is rapid and high proportion of mixing water is needed (Robson, 1962).

Table 4.3 Statistical variables for compressive strength of CAC- ggbs concrete

	Concrete mixes										
	CAC 100			**CAC75/SL25**		**CAC60/SL40**		**CAC50/SL50**		**CAC40/SL60**	
	14 hours	7 days (Converted	28 days	14 hours	28 days	14 hours	28 days	14 hours	28 days	14 hours	28 days
	57.0	37.2	54.0	44.2	56.7	35.7	40.1	20.9	31.5	-	26.1
Std Dev	1.8	1.4	3.4	10.9	1.8	4.6	4.6	1.3	1.5	-	2.8
COV (%)	3.2	3.7	6.3	24.7	3.3	13.0	11.5	6.3	5.6	-	9.0

A typical sewer pipe concrete has compressive strength in the range 58 – 80 MPa (Fourie, 2007), generally the compressive strength of blended CAC concretes are less than this. Low early-strength on the other hand for blended Portland cement concrete with cement extenders can conceivably lead to problems such as cracking and breakage on de-moulding of the pipes directly after steam curing.

Although concrete pipes are steam cured for 4 hours in pipe manufacturering, the conversion reaction is still not yet complete and this may cause a problem because the pipe may be designed for higher strengths than it can actually carry over its service life. It was for the same reason that calcium aluminate cement was banned for use in structural applications in the United Kingdom (Concrete Society, 1997). Theferore engineers need be aware that the use of plain CAC can only be used as a lining material in sewer pipes because this conversion can result in a pipe failure if used as a host pipe due to reduced structural integrity. Hence, preliminary measures such as exposing control specimens to a high temperature (38 ° C), at 100% relative humidity in which the maximum conversion and stable strength occurs at about 7 days should be used to achieve that strength for design.

4.3. Tensile splitting strength

4.3.1. Blended Portland cement concrete

The tensile splitting strengths of blended PC concrete with cement extenders performed at 14 hours are shown Figure 4.5. The standard deviation and coefficient of variation (COV) are also presented in Table 4.4. The high COV values are discussed in the general comments in Section 4.3.4.

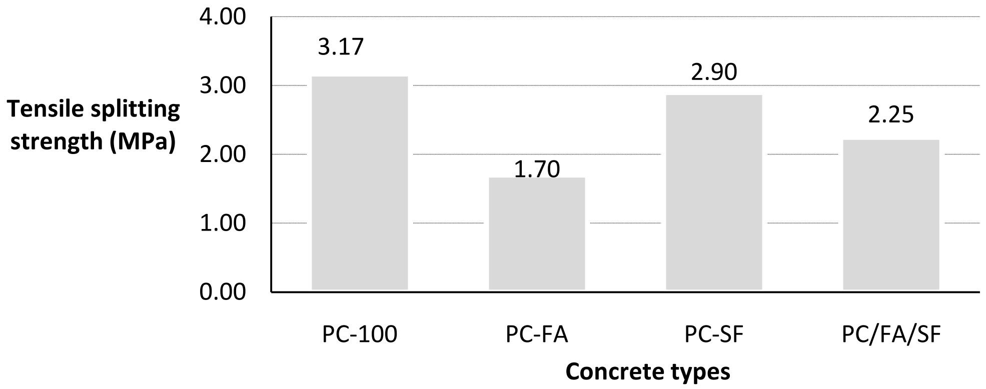

Figure 4.5 14 hour tensile splitting strength results (MPa) of Portland cement concrete blended with cement extenders, average of 3 specimens of cylindrical samples (80 mm diameter × 150 mm).

Table 4.4 Statistical variables for tensile splitting strength at early age (14 hours)

	Concrete mixes			
	PC100	**PC70:FA30**	**PC90:SF10**	**PC-FA-SF**
Average	3.17	1.70	2.90	2.25
Std Dev	0.86	0.49	0.94	0.52
COV (%)	27.2	28.6	32.5	23.3

Discussion

A plain PC concrete had tensile splitting strength of 3.17 MPa, a binary mix of fly ash and Portland cement concrete had low tensile splitting strength of 1.70 MPa similar to that of (Fourie, 2007). A low strength for fly ash concrete makes it difficult for application in the precast plants such as sewer pipe manufacturing where rapid turnover is needed. Silica fume plays an important role in increasing early age strength of concrete, thus (8 %) of silica fume was added to fly ash mix to make a ternary mix that had higher tensile strength of 2.25 MPa than just binary mix of Portland cement and fly ash. However, 14 hours after casting, ternary mix specimens were not yet hardened sufficiently and had to be handled with care as some of the specimens broke when stripping the moulds before immersion in a water bath at 38° C. This is because; at such early age silica fume had not yet developed strength as well and this condition was probably exacerbated by the presence of fly ash due to its effect to lower heat of hydration (Swamy, 1986).

On the other hand a high tensile strength at early age for Portland cement concrete compared with blended cement concrete is common in concrete technology and is related to longer setting time and slow strength development of SCMs (Murthi, 2008).

4.3.2. Calcium Aluminate Cement /fly ash concrete

Tensile splitting strengths performed after 14 hours for calcium aluminate cement /fly ash concretes are shown in Figure 4.6. Standard deviation and coefficient of variation are shown in shown in Table 4.5.

Discussion

The effect of fly ash on calcium aluminate cement concrete is well illustrated in Figure 4.6, in which increasing fly ash content in CAC/fly ash blends has a negative effect on tensile strength of the concrete at early age. The scope of this research does not cover detailed analysis of hydration mechanisms of the CAC/fly ash system in both early and long term age. This behaviour can be explained in terms of the hydration products formed i.e. gehlenite hydrate (or stratlingite) C_2ASH_8 which has a slow strength development (Fernández, 2008).

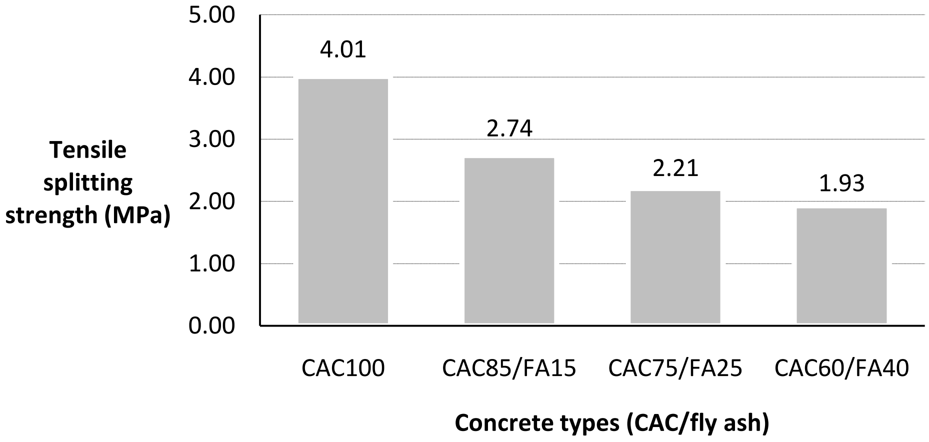

Figure 4.6 Tensile splitting strength results (MPa) of blended CAC/fly ash mixes at early age (14 hours)

Table 4.5 Statistical variables for tensile splitting strength CAC/fly ash concrete blend after 14 hours

	Concrete mixes			
	CAC100	**CAC85:FA15**	**CAC75:FA25**	**CAC60:FA60**
Average	4.01	2.74	2.21	1.93
Std Dev	0.53	0.41	0.39	0.49
COV (%)	13.2	14.8	17.7	25.6

4.3.3. Calcium Aluminate Cement /ggbs concrete

Tensile splitting strengths performed after 14 hours of CAC/ggbs concrete is illustrated in Figure 4.7. In all the mixes, an increase in the content of slag results in a reduction in tensile splitting strengths of the concrete. Standard deviation and coefficient of variation are also shown in Table 4.6.

Discussion

Similar to fly ash, slag has a negative effect on the strength development of CAC concrete. This is ascribed to the composition of hydration products, i.e. a stratlingite (C_2ASH_8) which is a stable chemical compound that is formed during hydration of blended CAC with silica bearing additives (Hidalgo, 2009). Its content increases with the content of C_2AS - a phase in CACs that is responsible for slow strength development. However, the blends show a continuous strength gain up to 2 years (Scrivener, 1998).

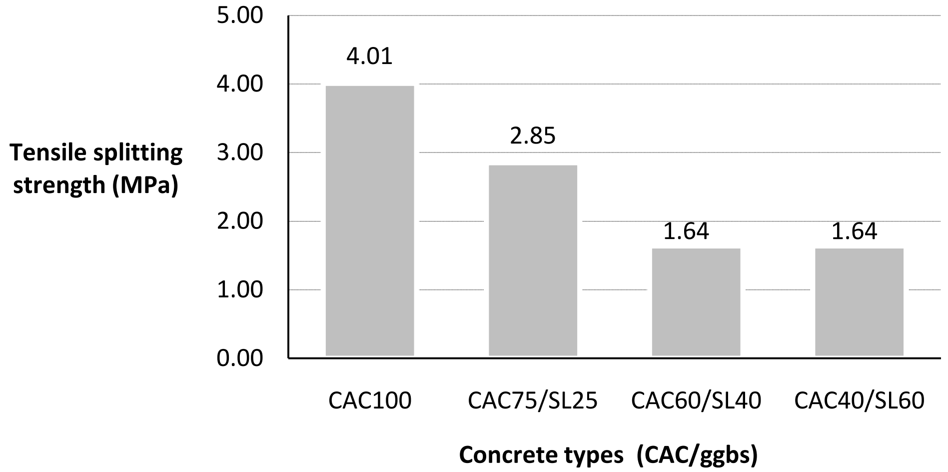

Figure 4.7 Tensile splitting strength results (MPa) of blended CAC /ggbs mixes at early age (14 hours)

Table 4.6 Statistical variables for tensile splitting strength of CAC/ggbs concrete blend after 14 hours

	Concrete mixes			
	CAC100	**CAC75:SL25**	**CAC60:SL40**	**CAC40:SL60**
Average	4.01	2.85	1.64	1.61
Std Dev	0.53	0.40	0.14	0.43
COV (%)	13.2	14.0	8.5	26.4

4.3.4. General comments

Tensile splitting strength of all blended calcium aluminate cement concrete is lowered significantly with an increase in slag and fly ash content. Concrete is weak in tension, and the values of tensile splitting strength investigated in this thesis range from 1.6 – 4.0 MPa. In general, there is a high coefficient of variation for tensile splitting strengths for all the concretes is due to the following:

- ❖ The simplification of the method comprising:
    - ➢ The theory for calculating the tensile strength assumes the concrete is a homogeneous material whereas it is a heterogeneous comprising; aggregate, cement

paste and interfacial transition zone all of which affect the tensile strength of the concrete.

- The theory is also assumed to be linear,
- The load is not applied along a line but a strip,

- All the above factors; either directly or indirectly lead to a specific failure pattern that does not necessarily split the concrete specimen into a perfect semi-cylinder (Figure 4.8).

Generally speaking, tensile splitting strength of concrete has a high inherent variability and many agencies and concrete laboratories rely on compressive strength tests using established correlations to estimate crack potential of a concrete.

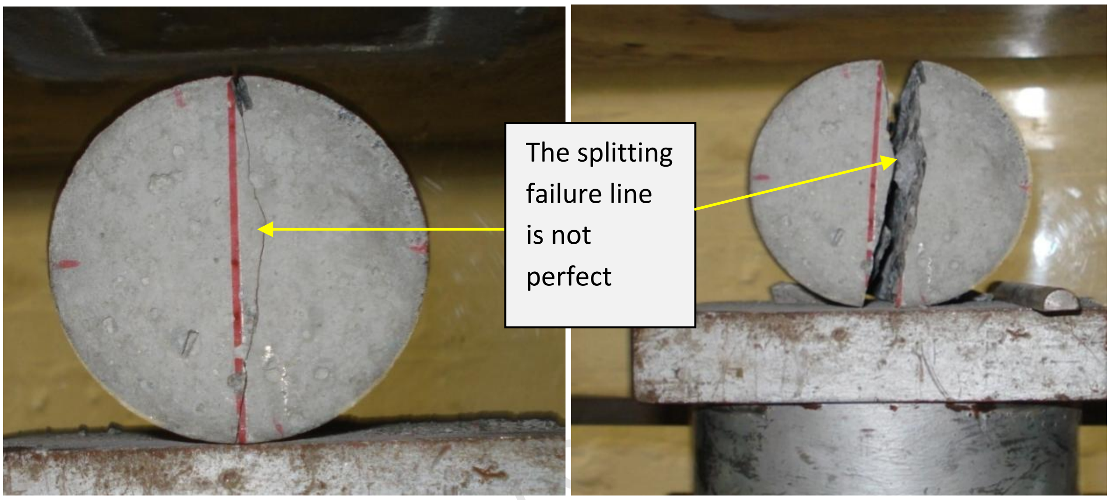
The splitting failure line is not perfect

Figure 4.8 Imperfect failure line of a tensile splitting test.

4.4. Density

4.4.1. Blended Portland cement concrete

The results of oven dried and saturated densities of specimens determined after 28 days of air curing the specimens are presented in Table 4.7, statistical parameters are also shown

Table 4.7 Oven dried and saturated density (g/cm^3) Portland cement concrete blended with cement extenders (average of four specimens) determined after 28 days of air curing.

	Plain PC		**PC70:FA30**		**PC90:SF10**		**PC72:FA20:SF8**	
	Dried	Sat.	Dried	Sat.	Dried	Sat.	Dried	Sat.
Average	2.575	2.622	2.390	2.473	2.464	2.498	2.435	2.510
Std Dev	0.041	0.023	0.037	0.029	0.062	0.051	0.039	0.025
COV (%)	1.60	0.88	1.57	1.18	2.50	2.10	1.59	1.00

Discussion

The difference in densities of the PC concrete and that of blended PC with pozzolans is due to the difference in particle density of the Portland cement of 3.14 g/cm^3, compared with 2.30 g/cm^3 for FA and 2.10 g/cm^3 for silica fume. The blended particle density is then 2.83 g/cm^3, 2.99 g/cm^3 and 2.82 g/cm^3 for 30 % fly ash, 10 % silica fume and ternary mix respectively. The difference in density of concretes can also be explained in terms of the densities of the hydrates, especially calcium silicate hydrate (C-S-H) which is a main strength-giving compound of hydrated cementitious materials with density varying between 1.9 - 2.1 g/cm^3 (Gartner *et al.,* 2002). The content of C-S-H is increased by pozzolanic reactions of fly ash and silica fume, but since its density is between 1.9 - 2.1 g/cm^3 and is smaller than the overall density of the raw materials its effect is not so obvious on the hydrated concrete material. According to SANS 676, (2003), concrete pipe materials shall be selected to achieve maximum density and higher oven dried density as an indication of how dense the solid particles of the concrete are.

4.4.2. Calcium Aluminate Cement /fly ash concrete

The results of densities of CAC/fly ash mixes for both oven dried and saturated specimens are presented in Table 4.8.

Discussion

The density of plain CAC is found to be higher than that of mixes blended with fly ash, this can also be attributed to high particle density of 3.20 g/cm^3 of CAC which is lowered when CAC is blended with fly ash of low particle density of 2.3 g/cm^3. According to SANS 676, 2003 concrete pipe materials shall be selected as to achieve maximum density with minimum porosity.

4.4.3. Calcium Aluminate Cement/ ggbs concrete

The results of densities of CAC/ggbs mixes for both oven dried and saturated are presented in Table 4.9. The densities of CAC/ggbs concrete mixes were found to be in a typical range of 2.40 -2.6 g/cm^3 of pipe materials prepared using either hand compaction.

Discussion

There is a common trend noticed on the values of densities with decrease of CAC content or increase of ggbs content. The difference in densities is explained in terms of varying particle densities of the raw cements before hydration, with plain CAC having 3.20 g/cm^3 and ggbs 2.90 g/cm^3, since other factors (aggregate and w/c ratio) were kept constant. The second reason is inferred from nature of hydration products present in both CAC/fly ash and CAC/ggbs mixes i.e. the presence of a di-calcium aluminate silicate phase (C_2AS) in these systems which hydrates slowly to form stratlingite (Equation

4.1) that dominates as the stable, long-term strength - giving compound with its density of about 1.90 g/cm^3 (Bensted *et al.,* 2002). In addition, this hydrate has lower density compared to the density of raw cements, thus they take precedence in determining the overall density of hydrated concrete material.

Table 4.8 Oven dried and saturated density (g/cm^3) of calcium aluminate /fly ash mix (average of four specimens) after 28 days of air curing

	Plain CAC		**CAC85:FA15**		**CAC75:FA25**		**CAC60:FA40**	
	Dried	Sat.	Dried	Sat.	Dried	Sat.	Dried	Sat.
Average	2.604	2.662	2.533	2.603	2.559	2.628	2.555	2.633
Std Dev	0.038	0.040	0.044	0.037	0.048	0.047	0.042	0.041
COV (%)	1.48	1.49	1.73	1.41	1.86	1.80	1.63	1.55

Table 4.9 Oven dried and saturated density (g/cm^3) of calcium aluminate /ggbs mix (average of four specimens) after 28 days of air curing

	100 % CAC		**CAC75:SL25**		**CAC60:SL40**		**CAC50:SL50**		**CAC40:SL60**	
	Dried	Sat.	Dried	Sat.	Dried	Sat.	Dried	Sat.	Dried	Sat.
Average	2.604	2.662	2.657	2.756	2.551	2.615	2.504	2.552	2.416	2.575
Std Dev	0.038	0.040	0.031	0.023	0.023	0.030	0.087	0.062	0.117	0.074
COV (%)	1.48	1.49	1.16	0.85	0.89	1.16	3.48	2.45	4.86	2.86

4.4.4. General discussion

Generally, the density of the CAC concretes is higher than that of Portland cement concrete with or without cement extenders, mainly because of high content of iron compouds (Fe $^{3+}$/Fe $^{2+}$) present in CAC. The chemical composition is shown in Tables 3.2 and 3.3 of PC and CAC respectively. The specific gravity of iron compounds in CAC are in the range of 3.70 to 4.9 (Robson, 1962), the average aluminates and silicates present in CAC have specific gravities just under 3.9 (Bensted, 2002). Thus CAC iron compound primarily influence density of CAC concrete.

4.5. Oxygen Permeability Index (OPI)

4.5.1. Blended Portland cement concrete

The oxygen permeability index as a measure of permeability and density determined after 28 days of air curing is shown in Table 4.10, with coefficient of variation (COV) of the Darcy coefficient (k).

Table 4.10 Darcy (k), Oxygen permeability index (log scale) of blended Portland cement concrete with cement extenders, (average of four specimens) determined after 28 days of air curing

	Portland cement concrete mixes			
	Plain PC	**PC70:FA30**	**PC90:SF10**	**PC72:FA20:SF8**
k (m/s	2.85×10^{-11}	2.84×10^{-11}	1.17×10^{-11}	1.11×10^{-11}
OPI (log scale)	10.55	10.55	10.93	10.95
COV (%)	3.9	5.1	7.6	5.1

NB: The coefficient of variation is calculated for k values

Discussion

The oxygen permeability index of a ternary mix (PC, fly ash, silica fume) and that of 10 % silica fume concrete is high showing substantially less permeable concretes. This is because of refined microstructure as a result of pozzolanic reaction of silica fume and free lime in both the bulk paste and in interfacial transition zone (ITZ) during hydration mechanisms to produce more calcium silicate hydrate (Chandra, 2002), (Goyal *et al.,* 2009). However, the oxygen permeability of fly ash mix and that of PC concrete are the same at 10.55 probably due to similar 'pore structure' - a term normally used in concrete technology to refer to: pore size, pore distribution and shape of the pores (Chandra, 2002).

4.5.2. Calcium Aluminate Cement /fly ash concrete

The oxygen permeability index of the blended CAC/fly ash concrete is presented in Table 4.11.

Discussion

The oxygen permeability of the plain CAC concrete and blended CAC/fly ash concretes is found to be the same probably due to similar hydration products and/or pore structure.

Table 4.11 Oxygen permeability index (log scale) of blended Calcium Aluminate Cement/fly ash concrete, (average of four specimens) determined after 28 days of air curing.

	Plain CAC	**CAC85:FA15**	**CAC75:FA25**	**CAC60:FA40**
K (m/s	1.28×10^{-10}	1.25×10^{-10}	1.29×10^{-10}	1.25×10^{-10}
OPI (log scale)	9.89	9.90	9.89	9.90
COV (%)	3.8	4.5	4.2	2.6

NB: The coefficient of variation is calculated for k values

4.5.3. Calcium Aluminate Cement/ ggbs concrete

The oxygen permeability index of CAC/ggbs concrete blends is shown in Table 4.12.

Discussion

The oxygen permeability index of CAC/ggbs concrete is different to that of plain CAC concrete, ggbs does not necessarily increase the impermeability of CAC concrete and generally there is no correlation between compressive strength and OPI of blended CAC with cement extenders as shown in Figure 4.9.

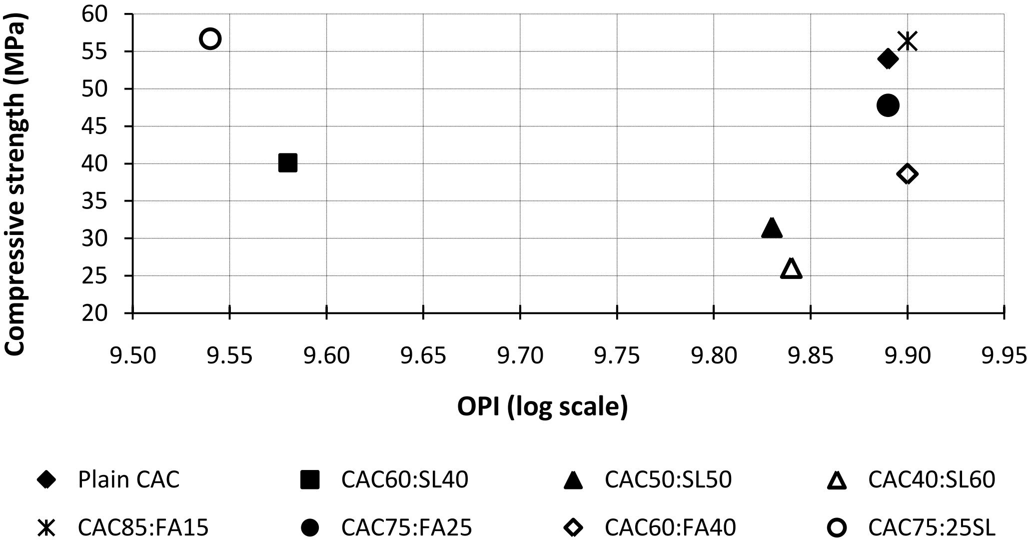

Figure 4.9 The relationship of OPI and compressive strength of blended CAC concrete with fly ash and ggbs

4.5.4. General discussion

Similar to CAC/fly ash mixes, the OPI values of CAC/ggbs may be considered relatively low, possibly attributed to: 1) relative courseness of CAC with specific surface area of about (338 m^2/kg Blaine) which is not as finely ground as Portland cement (CEM I 42.5R). Thus a hydrated paste may provide continuous permeability, larger pores or pronounced pore structure. 2) different basic microstructure and pore structure of CAC compared to PC concretes. It is not because of increased porosity as a result of conversion because these concretes were not fully converted at the time of testing and the porosity of CAC concrete is actually less than that of OPC concrete, this will be discussed in detail in the following Section.

Table 4.12 Oxygen permeability index (log scale) of blended Calcium Aluminate Cement/ggbs Concrete, (average of four specimens) determined after 28 days of air curing.

	100 % CAC	**CAC75:SL25**	**CAC60:SL40**	**CAC50:SL50**	**CAC40:SL60**
k (m/s)	1.28×10^{-10}	2.92×10^{-10}	2.67×10^{-10}	1.48×10^{-10}	1.45×10^{-10}
OPI (log scale)	9.89	9.54	9.58	9.83	9.84
COV (%)	3.8	2.8	4.5	5.8	4.8

NB: The coefficient of variation is calculated for k values

4.6. Sorptivity and porosity

4.6.1. Blended Portland cement concrete

Water absorption indicates concrete potential to absorb aggressive acid ions (H^+) after capillary movement has taken place when concrete is saturated with the ions. However, the high COV for concrete with extenders is probably affected much by curing since the samples were air cured for 28 days prior to testing. Water sorptivity and porosity values for blended Portland cement concretes are shown in Table 4.13. The water absorption values (%) calculated from the sorptivity test using oven dried mass and vacuum saturated mass are also reported in Table 4.14.

Table 4.13 Water Sorptivity ($\text{mm}/\sqrt{\text{hr}}$) and porosity (%) of blended Portland cement concrete, (average of four specimens determined after 28 days of air curing.

	100 % PC		**PC70:FA30**		**PC90:SF10**		**PC72:FA20:SF8**	
	Sorptivity	**Porosity**	**Sorptivity**	**Porosity**	**Sorptivity**	**Porosity**	**Sorptivity**	**Porosity**
	$\text{mm}/\sqrt{\text{hr}}$	(%)	$\text{mm}/\sqrt{\text{hr}}$	(%)	$\text{mm}/\sqrt{\text{hr}}$	(%)	$\text{mm}/\sqrt{\text{hr}}$	(%)
Average	6.1	7.4	6.4	8.8	3.2	7.0	3.7	8.3
Std Dev	0.5	0.32	1.1	0.4	0.4	0.5	0.5	0.4
COV (%)	7.8	4.36	16.5	4.4	11.1	7.1	14.5	4.7

Discussion

The sorptivity test and water absorption test evaluate concrete characteristics by virtue of mass transfer of the fluids or ions that enter the concrete via either by adsorption, surface diffusion, and bulk flow depending on the surface pressure of the concrete surface (Hearn, 1994). Material characteristics that control the above transport processes are; 1) pore structure which involves:

(pore size, pore distribution, and the shape of the pores), 2) interfacial transition zone (ITZ), grading of the aggregates (Hearn *et al.,* 1994).

Table 4.14 Water absorption (%) of Portland cement concrete blended with cement extenders, (average of four specimens) determined after 28 days of air curing

	100 % PC	**PC70:FA30**	**PC90:SF10**	**PC72:FA20:SF8**
Water Absorption (%)	3.08	4.67	2.79	3.35
Std Dev	0.34	0.14	0.18	0.19
COV (%)	11.14	3.10	6.60	5.55

10 % silica fume concrete has lowest sorptivity and absorption of 3.2 mm/√hr and 2.79 % respectively because of inferred property of refined pore structure due to its fine filler effect that densify the ITZ, in addition more calcium silicate formed from the pozzolanic reaction provides more binding (Chandra, 2002, Alexander, 2011). A ternary mix on the other hand has slightly higher sorptivity and water absorption of 3.7 mm/√hr and 3.35 % respectively. In general, it is noticed that blended PC concrete with cement extenders have lower sorptivity values than plain PC concrete due to addition of the calcium silicate from pozzolanic reaction (Equation 4.2). The pozzolans improves workability of wet concrete and ease of compaction thus providing dense packing. These features geneally increase impermeability of concrete. However whether the use of pozzolans in concrete can effectively reduce permeability would in the end depend on curing history. Initial accelerated curing such as in precast structural concrete (sewer pipes), has shown to result in lower permeability of fly ash concrete compared to rapid – hardening portland cement (Swamy, 1986).

$3Ca(OH)_2 + 2SiO_2 \rightarrow 3CaO.2SiO_2.3H_2$ ……………………………………………………………………………………(4.2)

The porosity of 10 % silica fume concrete mix was found to be less than that of plain PC concrete and that of ternary mixes. This is because of the fine filler effect of the fine silica fume that provides refinement of the microstructure (Chandra, 2002, Fourie, 2007 and Goyal *et al.,* 2009). A ternary mix on the other hand has fly ash and hydration of fly ash mixes is said to be affected by air curing as the specimen were air cured for 28 days before perfoming the test. However the porosity for all mixes are less than 10 % a maximum for concretes to be used in sewer pipes (Fourie, 2007), this is an indication that the concrete is well compacted.

4.6.2. Calcium Aluminate Cement /fly ash concrete

Water sorptivity and porosity values are shown in Table 4.15, and water absorption in Table 4.16.

Table 4.15 Water Sorptivity (mm/$\sqrt{\mathrm{hr}}$) and porosity (%) of blended Calcium Aluminate Cement/fly ash concrete, (average of four specimens) determined after 28 days of air curing.

	Plain CAC		**CAC85:FA15**		**CAC75:FA25**		**CAC60:FA40**	
	Sorptivity	**Porosity**	**Sorptivity**	**Porosity**	**Sorptivity**	**Porosity**	**Sorptivity**	**Porosity**
	mm/$\sqrt{\mathrm{hr}}$	(%)	mm/$\sqrt{\mathrm{hr}}$	(%)	mm/$\sqrt{\mathrm{hr}}$	(%)	mm/$\sqrt{\mathrm{hr}}$	(%)
Average	13.2	7.6	14.4	7.3	11.7	7.7	13.0	8.0
Std Dev	0.8	0.9	1.2	0.3	1.0	0.5	0.6	0.6
COV (%)	5.8	11.4	8.3	4.3	8.4	6.4	4.7	7.4

Table 4.16 Water absorption (%) of blended Calcium Aluminate Cement/fly ash concrete (average of four specimens).

	Plain CAC	**CAC85:FA15**	**CAC75:FA25**	**CAC60:FA40**
Water Absorption (%)	3.94	2.87	3.15	3.17
Std Dev	0.30	0.13	0.28	0.29
COV (%)	7.6	4.6	8.8	9.3

Discussion

The addition of fly ash in CAC concrete does not seem to decrease water sorptivity. The porosity of the concrete on the other hand is found to be independent of the fly ash content used to replace calcium aluminate cement, this might be because of the complex hydration products and pore structure of the system.

In general, the water sorptivity of CAC concretes is higher than that of Portland cement concretes and addition of fly ash and ggbs does not decrease the sorptivity of CAC concretes. However, there are exceptions with 25 % ggbs and 50 % ggbs replacement performing better. It is noticed that water absorption values of all CAC concretes are still low because of their low porosities as shown in Table 4.16 and 4.18.

4.6.3. Calcium Aluminate Cement/ ggbs concrete

Water sorptivity and porosity values are shown in Table 4.17, and water absorption in Table 4.18.

Table 4.17 Water Sorptivity ($\text{mm}/\sqrt{\text{hr}}$) and porosity (%) of blended Calcium Aluminate Cement/ggbs concrete (average of four specimens).

	Plain CAC		CAC75:SL25		CAC60:SL40		CAC50:SL50		CAC40:SL60	
	Sorptivity	**Porosity**	**Sorptivity**	**Porosity**	**Sorptivity**	**Porosity**	**Sorptivity**	**Porosity**	**Sorptivity**	**Porosity**
	$\text{mm}/\sqrt{\text{hr}}$	(%)	$\text{mm}/\sqrt{\text{hr}}$	(%)	$\text{mm}/\sqrt{\text{hr}}$	(%)	$\text{mm}/\sqrt{\text{hr}}$	(%)	$\text{mm}/\sqrt{\text{hr}}$	(%)
Average	13.2	7.6	9.5	8.2	10.5	8.3	9.5	6.9	11.7	8.6
Std Dev	0.8	0.9	0.7	0.5			0.7	0.07	1.8	0.3
COV (%)	5.8	11.4	7.2	5.4	10.7	10.8	7.5	5.2	15.7	0.8

Table 4.18 Water absorption (%) of blended Calcium Aluminate Cement/ggbs concrete (average of four specimens).

	Plain CAC	CAC75:SL25	CAC60:SL40	CAC50:SL50	CAC40:SL60
Water Absorption (%)	3.94	3.30	3.32	3.65	4.16
Std Dev	0.30	0.14	0.38	0.17	0.42
COV (%)	7.6	4.1	11.3	4.8	10.2

Discussion

Generally, the use of ggbs is found to increase the porosity, this might be because of: 1) basic microstructure and, 2) poor workability of wet CAC/ggbs that was stiff and hard to compact as compared to CAC/fly ash mixes that were more workable than CAC concrete alone. However the porosities are acceptable for concrete to be used in sewer pipes i.e. less than required 10 % (Fourie, 2007).

The porosity of CAC concretes is generally found to be less than that of Portland cement concretes. This is because, during hydration reaction CACs use a higher proportion of mixing water for its high early strength development than PC concrete which reduce the free water that forms the voids (Robson, 1962). However, one must note that the low porosity was not the result of any conversion at the time of testing the specimens, as the specimens were only placed in water bath (38 °C) for 10 hours and thereafter air cured whereas full conversion happens at about 7 days in water bath at 38 °C (Scrivener, 2003).

A hydrated CAC tends to lose part of combined water more readily than Portland cement (Robson, 1962). Therefore on oven drying the specimens the combined water could be eliminated. Vacuum saturating the specimen may consume free water and determining porosity for concretes made up of different cements in this way somehow may not provide very accurate comparison. Hence, methods such as mercury intrusion porosimetry (MIP) can be recommended for such applications and this goes beyond the scope of current research. However, this effect may be acute at higher w/c ratio concretes whereby complete hydration occurs quickly and it does not really hold at low w/c ratio < 0.36 similar to that of concrete used in sewer pipes and those used in this project.

4.7. Acid insolubility

4.7.1. Blended Portland cement concrete

The acid insolubility of the concrete specimens as determined by SANS 6242 (2008) was used to assess dissolution potential of a dolomite- based Portland cement concrete in a highly concentrated boiled acid solution. The results are presented in Table 4.19.

Table 4.19 Acid insolubility (%) of blended Portland cement concrete blended with cement extenders (SANS 6242, 2008) (average of four specimens).

	100 % PC	**PC70:FA30**	**PC90:SF10**	**PC72:FA20:SF8**
Acid Insolubility (%)	19.9	23.5	27.1	30.8
Std Dev	0.7	0.4	0.5	0.1
COV (%)	3.4	1.7	1.7	0.5

Discussion

All the mixes cast in this project have the same w/c and siliceous filler aggregate content. Thus the difference in values of acid insolubility dictates difference in mineral composition of the hydration products. The mineral additives consumed the free lime in a pozzolanic reaction to give more calcium silicate that probably has higher insolubility than portlandite (Goyal *et al.*, 2009). Therefore, it is noticed that acid insolubility is a function of silica content per cement extender that reacts in a pozzolanic reaction to reduce free lime and is higher for silica fume (96.0 %) than in fly ash (54.9 %).

4.7.2. Calcium Aluminate Cement /fly ash concrete

The results of acid insolubility (average of four specimens) for blended CAC/Fly ash concrete are presented in Table 4.20 .

Discussion

The acid insolubility of the CAC concretes increased as the content of fly ash was increased. This behaviour is due to high silica content of fly ash (54.9%) and hence Si/Al ratio leading to an increase in content of hydration product (C_2ASH_8) stratlingite (silica bearing compound with significant acid insolubility) that tends to dominate if fly ash content is increased. The amount of stratlingite formed is dependent on the ability of an additive to release silica (Hidalgo *et al.*, 2009).

Table 4.20 Acid insolubility (%) of blended Calcium Aluminate Cement/fly ash concrete as determined by SANS-6242 (2008) (average of four specimens).

	Plain CAC	**Converted plain CAC**	**CAC85:FA15**	**CAC75:FA25**	**CAC60:FA40**
Acid Insolubility (%)	18.0	15.3	19.0	20.4	22.8
Std Dev	0.6	0.3	0.4	0.3	0.3
COV (%)	3.2	2.3	2.3	1.2	1.2

The second reason is the reduction of a base i.e. alumina gel Al $(OH)_3$ (gibbsite) as fly ash content increases as shown in Chapter 2 in Table 2.6. Converted CAC concrete also exhibits less acid insolubility than unconverted CAC concrete with 15.3 % and 18.0 % acid insolubility respectively. Considering conversion reactions in Equations 4.3 and 4.4, the high acid solubility of converted CAC concrete is due to high content of alumina gel i.e. AH_3 that is acid soluble.

$3CAH_{10} \rightarrow C_3AH_6 + 2AH_3 + 18\ H$ ………………………………………………………………………………………… (4.3)

$3C_2AH_8 \rightarrow 2C_2AH_6 + AH_3 + 9\ H$ …………………………………………………………………………………………. (4.4)

According to SANS 676, (2003) sewer pipe concrete material intended to be resistant to chemical attack shall have an acceptably low content of insoluble material in hydrochloric acid and should not exceed 25 % (m/m). The CAC/fly ash concrete blends meet the criteria hence the mixes are candidates for use in sewer pipe application.

4.7.3. Calcium Aluminate Cement/ ggbs concrete

The acid insolubility of CAC/ggbs concrete blend is shown in Table 4.21.

Table 4.21 Acid insolubility (%) of blended Calcium Aluminate Cement/ggbs concrete as determined by SANS-6242 (2008) (average of four specimens).

	Plain CAC	**CAC75:SL25**	**CAC60:SL40**	**CAC50:SL50**	**CAC40:SL60**
Acid Insolubility (%)	18.0	17.2	18.2	22.0	20.5
Std Dev	0.57	0.16	0.63	0.44	0.63
COV (%)	3.2	0.9	3.4	2.0	3.1

Discussion

A similar pattern as in CAC/fly ash concrete mixes is noticed with acid insolubility of CAC/ggbs concrete. This is because ggbs also has a significant percentage of silica (37.1 %) which is less than in fly ash (54.9 %) and is responsible for the formation of stratlingite as well (Majumdar, 1992). However, lower values of acid insolubility for CAC/ggbs concretes probably relates to less capacity of slag to release silica as formation of stratlingite is proportional to content of silica available in calcium aluminate hydrates (Hidalgo *et al.,* 2009). The low values of acid insolubility indicate high neutralisation capacity of the concrete and so CAC/ggbs blend can also be a good candidate for use in biogenic sulphuric acid of sewer pipes whereby aluminium hydroxide is needed to stifle the bacterial growth and provide neutralisation capacity (Section 4.9).

4.8. Dynamic hydrochloric acid resistance test

4.8.1. Introduction

Acid resistance of the concrete was evaluated using hydrogen ion consumption as a measure of how hydrochloric acid donates the proton (H^+) to the concrete and how the concrete accepts the proton in the reaction. Mass loss on the other hand is used to indicate the rate of acid attack incorporating both acid dissolution and fall out of acid insoluble particles.

4.8.2. Blended Portland cement concrete

The performance of blended Portland cement concrete comprising fly ash and silica fume in a dynamic hydrochloric acid solution maintained at pH = 1.0 is shown in Figures 4.10 and 4.11 for mass loss and hydrogen ion consumption respectively. After 48 hours, the mass loss of 16.05 % and the hydrogen ion consumption of 17.79 g/cm^2 for plain Portland cement concrete was higher than that of concrete blended with mineral additives; 30 % fly ash concrete (PC/FA) achieved mass loss and hydrogen ion consumption of 17.72 % and 13.47 g/cm^2 respectively, 10 % silica fume concrete (PC/SF) achieved mass loss and hydrogen ion consumption of 13.43 % and 8.79 g/cm^2 respectively. A ternary mix with 72 % Portland cement: 20 % fly ash (PC/FA/SF) achieved a mass loss and hydrogen ion consumption of 15.28 % and 10.36 g/cm^2 respectively.

Discussion

Plain Portland cement concrete is found to have higher hydrogen ion consumption than the binary and ternary mixes. This is because of the ability of the hydration product of PC i.e portlandite $Ca(OH)_2$ that is readily reactive with the hydrochloric acid and as a strong base it completely dissociates when reacting with strong acid (Equation 4.5). However other hydration products such as calcium silicates (main strength giving compound of cement paste), calcium aluminates and calcium alumino-ferrites are less reactive (Alexander, 2011). 30 % fly ash concrete has high mass loss and this is probably due to fall out of acid insoluble particles as reflected by acid digestion test SANS (6242-2008) with acid insolubility of 23.52 % as compared to 19.94 % of OPC concrete for the same w/c ratio and siliceous aggregate content.

$Ca\,(OH)_{2\,(S)} + 2H^{+}\,(aq) \rightarrow Ca^{2+}{}_{(aq)} + 2H_2O_{\,(aq)}$ ………………………………………………………………………………… (4.5)

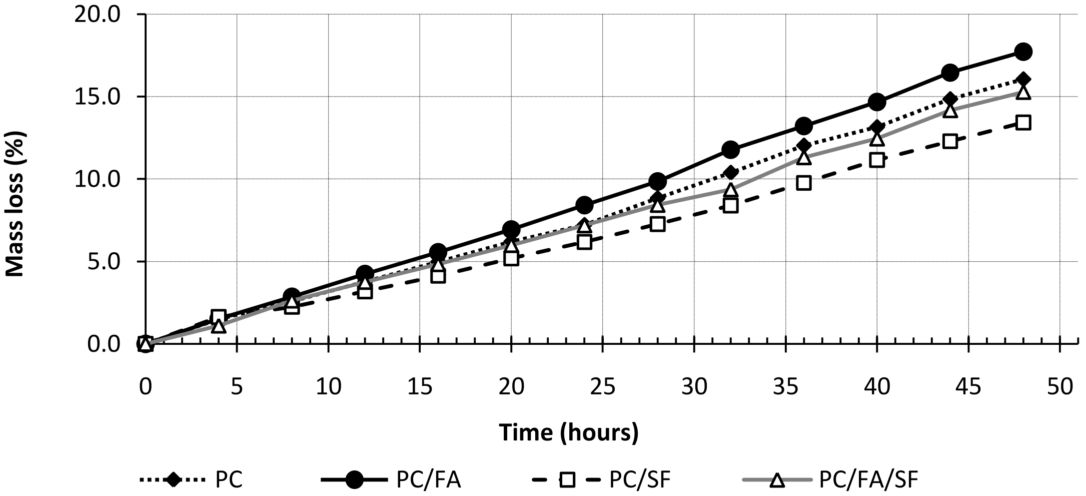

Figure 4.10 Mass loss of blended Portland cement concrete comprising Olifantsfontein dolomite aggregate in hydrochloric acid solution at pH adjusted to 1.0 every four hours.

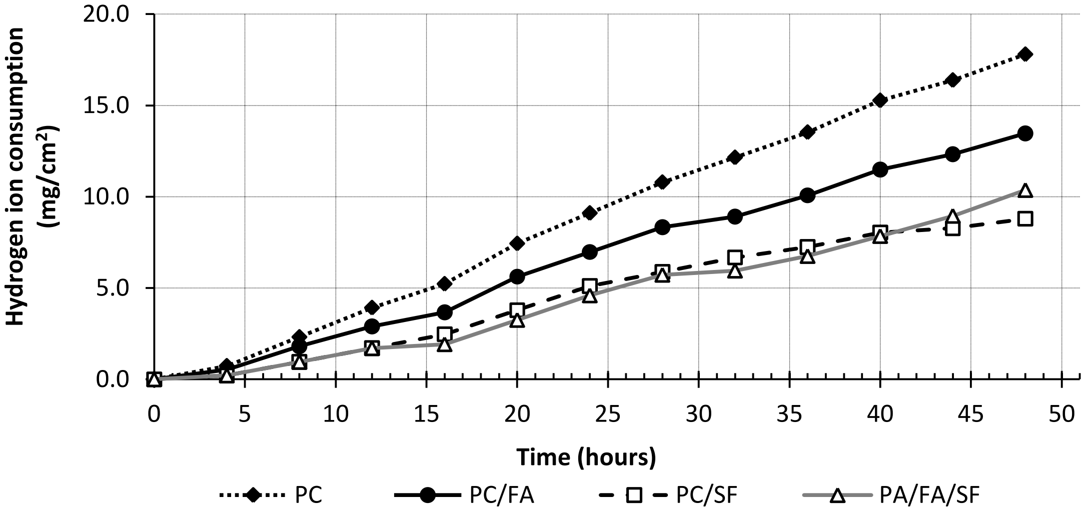

Figure 4.11 Hydrogen ion consumption of blended Portland cement concrete comprising Olifantsfontein dolomite aggregate in hydrochloric acid solution with pH adjusted to 1.0 every four hours.

The ratio of mass loss to hydrogen ion consumption as shown in Figure 4.12 for PC/FA concrete was constant at about 1.3 closer to 1.5 for silica fume concretes which has higher acid insolubility of 27.1

%, a plain PC concrete had a ratio less than unity at about 0.9. This means that mass loss for blended concretes is mainly a function of acid insoluble particles and mass loss for plain PC is mainly a function of acid dissolution.

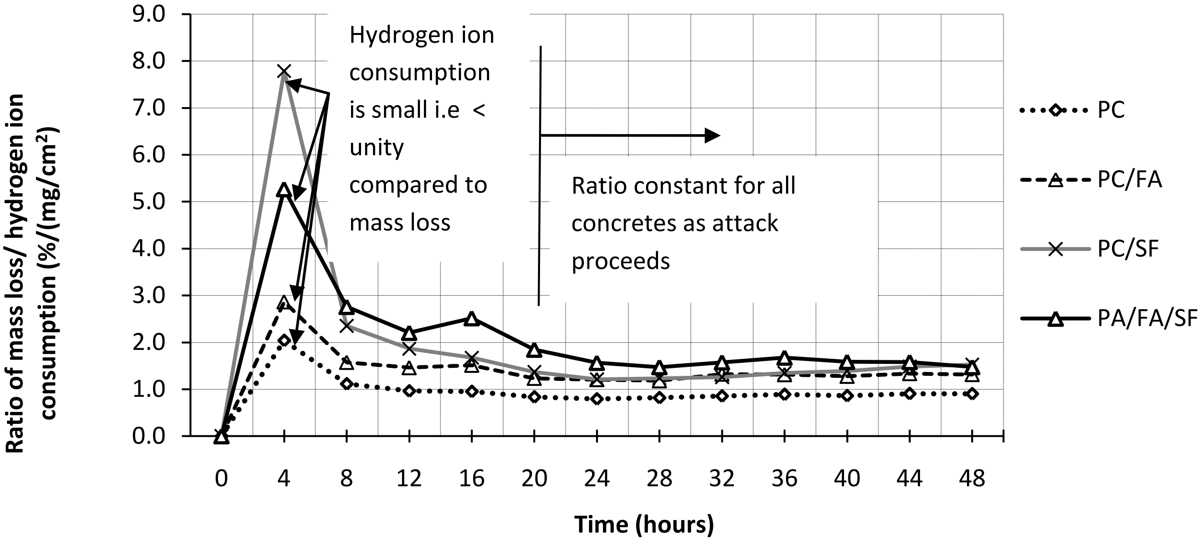

Figure 4.12 Ratio of mass loss to hydrogen ion consumption in an acid resistance test for blended PC concretes

The 10 % silica fume and ternary mix concretes are found to perform well in acid resistance test (pH =1.0) with approximately similar and lowest hydrogen ion consumption. The high performance can also be attributed to reduction in calcium hydroxide content of the cement paste, which decreases linearly with the amount of silica fume added as a result of pozzolanic reaction (Swamy ,1986). This effect is illustrated in Figure 4.13. Better perfomance of PC concrete blended with silica fume is also attributed to high impermeability, as shown in Section 4.5.1 by OPI values with this property inferred to refinement of the microstructure and fine filler effect of silica fume (Chandra, 2002).

The physical and chemical interaction of mix contituents are important and are reflected in acid resistance test (Alexander, 2011). For example, the rate of aggregate dissolution in relation to binder dissolution is a factor, leading to fall out of acid insoluble particles including the aggregates. and acid insolubility test – (SANS ,6242) does not reflect these features. It is noticed that 10 % silica fume has the lowest mass loss of 15.05 %, although this does not differ much to mass loss of 16.93 % for ternary mix. This can be explained by strong bond between binder to aggregrate and inferred absence of interfacial transision zone (ITZ) (Fourie, 2007). The pozzolanic reaction with fly ash consumes portlandite to give more calcium silicate and improved acid resistance, since calcium silicate is less soluble than portlandite. Chandra (2002) confirms that addition of fly ash to PC has no effect to ITZ.

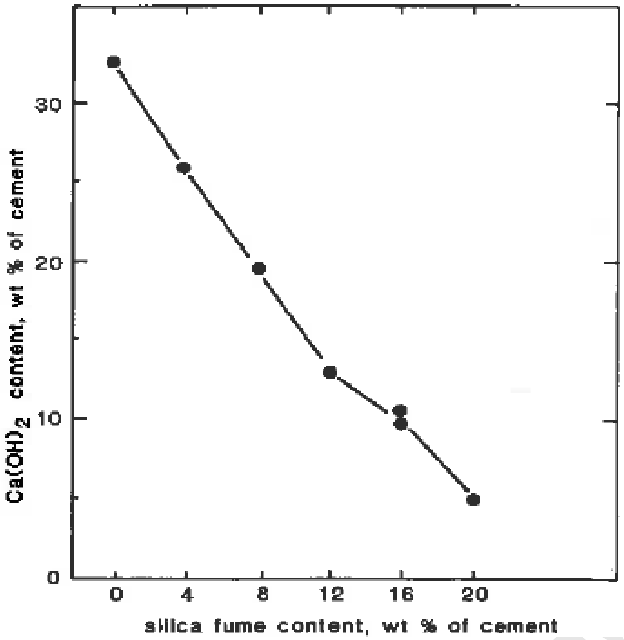

Figure 4.13 Influence of cement replacement by silica fume on the calcium hydroxide content of cement paste (Swamy, 1986)

During acid – concrete interaction, dissolution and fall out of acid insoluble particles occures simulyaneoulsy because mass loss is a function of these factors with the latter being higher as reflected by acid digestion test at 27.12 % for 10 % silica fume mix, and 30.80 % for ternary mix.

It clear that the corrosion resistance of concrete due to acid attack is affected by mineral additives such as fly ash and silica fume since these materials modify the chemical composition and pore system of the hardened paste as well the composition and permeability of the corroded layer (Dorner 2002). Porosity, permeability, and sorptivity of 'labcrete' are used for design. However, once corrosion has occurred transport properties of the corroded layer are different, and the choice of materials then becomes important. It is the nature of the hydration products rather than the porosity of the hardened paste that specifies the corrosion resistance Shi and Stegemann (2000) as cited by Dorner, (2002).

Typical measurements on sewer pipe concrete materials prepared using either hand compaction or roller suspension method are: porosity (8 - 10 %), OPI values between (10 -11) and water sorptivity (4 - 6 $mm/\sqrt{hr}$) (Fourie, 2007). It is noticed that all the properties of the concretes conform to this requirement with sorptivity values for PC and PC/FA concretes on the borderline (Table 4.22). However, there is one most important factor that must be put into consideration here. PC concrete has acceptable transport properties because of portlandite that forms during cement hydration.

However, when attacked by the acid it is the $Ca(OH)_2$ that is affected most and hence the transport properties after corrosion are more likely to be different and determined predominantly by the products of corrosion.

There are two factors noted. 1) With visible evidence on silica fume concretes (PC/SF and PC/FA/SF), improved transport properties with cement extenders make concrete more acid resistant, 2) Products of pozzolanic reaction that are less soluble than portlandite make concrete blended with cement extenders more acid resistant. However, the effect of neutralisation is important and for concretes with longer service live the reduced alkalinity may be a problem.

Table 4.22 Transport properties of modified Portland cement concrete (Section 4.5.1 and 4.6.1)

Transport phenomenon in concrete	**Blended Portland Cement concrete**			
	PC	PC/FA	PC/SF	PC/FA/SF
Permeability (OPI) log scale	10.55	10.55	10.93	10.96
Sorptivity mm/hr $^{0.5}$	6.1	6.4	3.2	3.7
Porosity (%)	7.77	8.75	6.95	8.25

Visual observation of the samples in Figure 4.14 reveals that the concrete mixes with silica fume, i.e. 10 % silica fume mix and ternary mixes have cement paste that is more acid resistant than Olifantsfontein dolomite aggregate such that there is pitting created on the aggregate while the cement paste resists the acid attack.

4.8.3. Calcium Aluminate Cement /fly ash concrete

After 48 hours of testing the specimens in a dynamic hydrochloric acid resistance test, a 60 % CAC: 40 % Fly ash mix had mass loss and hydrogen ion consumption of 32.82 % and 15.23 mg/cm^2 respectively as illustrated by Figure 4.15 and Figure 4.17. A 75 % CAC: 25 % fly ash mix had mass loss and hydrogen ion consumption of 29.37 % and 15.87 mg/cm^2 respectively. Plain CAC concrete cured under the same conditions as the rest of the concretes at 38 °C in water bath for 10 hours and tested after 28 days of air curing in a conditioned room temperature at 22°C and relative humidity (RH) of 50 %, had mass loss of 31.67 % and hydrogen 20.98 mg/cm^2 respectively.

Due to likelihood of plain CAC concrete to undergo conversion reactions, extended curing was done on one of the plain CAC specimens for about 7 days, reported by (Robson, 1962) to be the time for full conversion at temperature of 38 °C and 100 % RH.

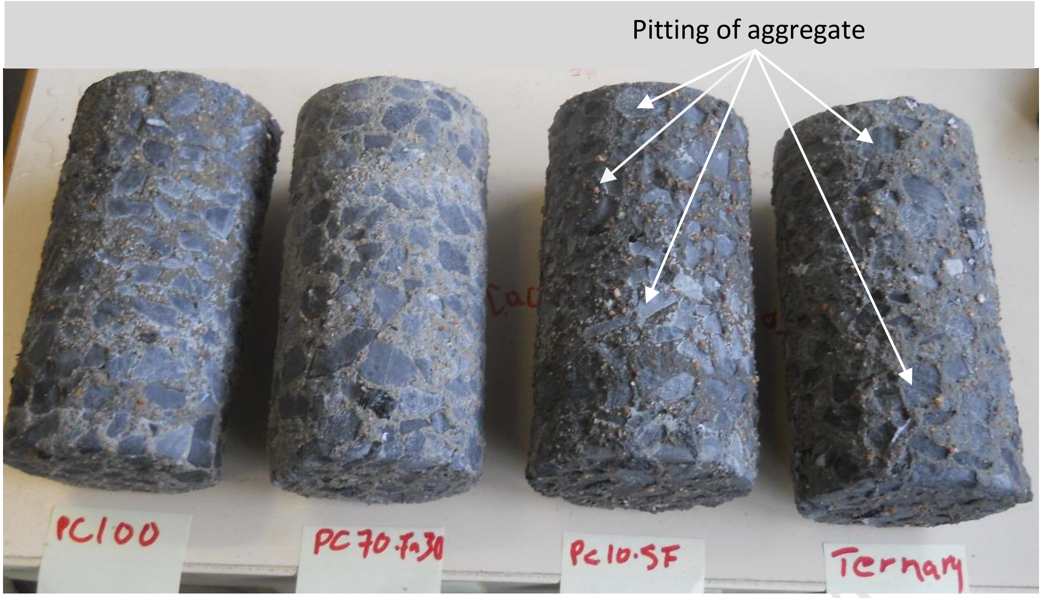

Figure 4.14 Visual inspection of the modified Portland cement concrete in a dynamic hydrochloric acid solution with at pH adjusted to 1.0 at four hourly intervals.

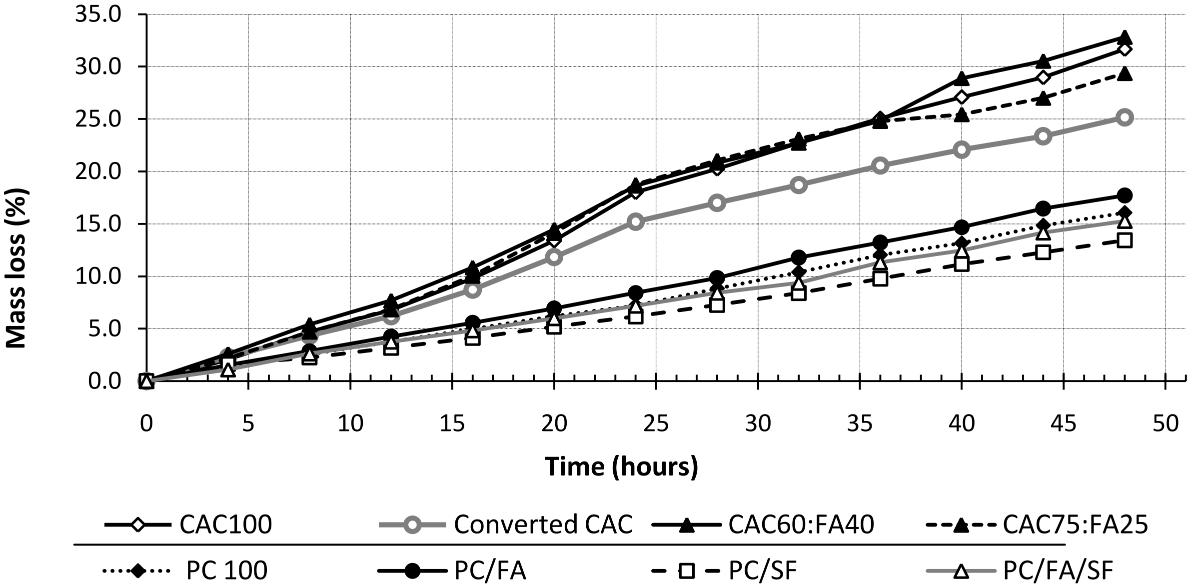

Figure 4.15 Mass loss with time of CAC – fly ash blended systems of Olifantsfontein dolomite aggregate in hydrochloric acid solution at pH adjusted to 1.0 every four hours.

This concrete is referred to as 'converted CAC' concrete in Figure 4.15 and Figure 4.17 respectively. After 48 hours in acid resistance test, this concrete attained 25.16 % and 13.77 g/cm^2 mass loss and hydrogen ion consumption respectively. Visual inspection of the samples in Figure 4.16 shows that blended mixes with fly ash and unconverted CAC concrete have non-uniform attack with cement paste being attacked more thus leaving aggregate standing proud.

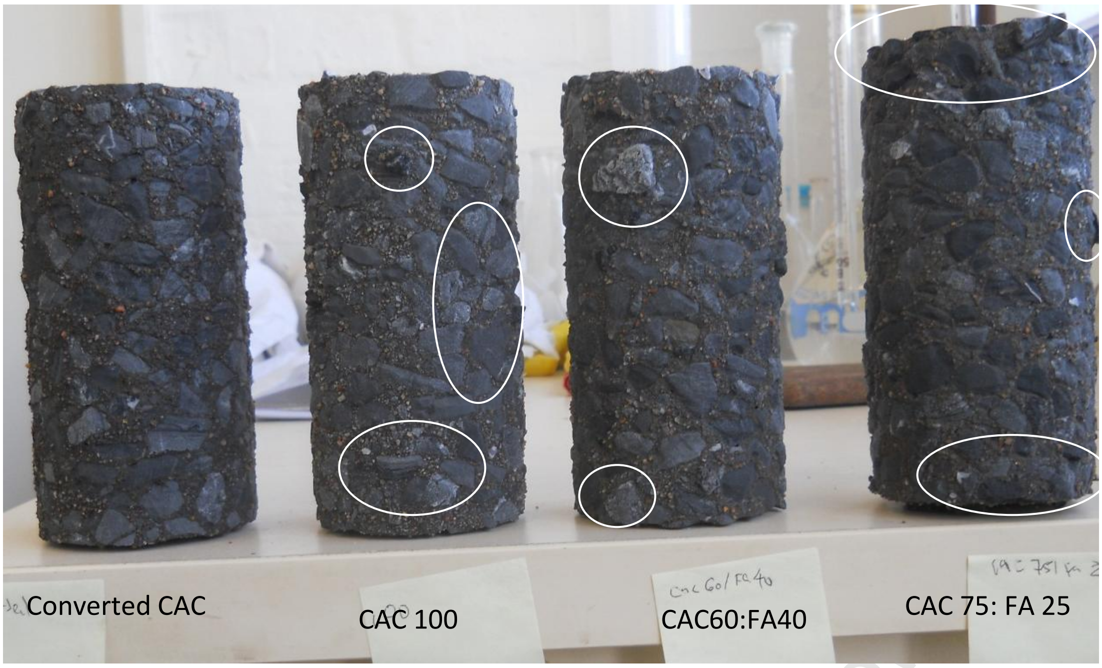

Figure 4.16 Visual observation of the CAC/fly ash concretes in a dynamic hydrochloric acid solution with at pH adjusted to 1.0 at four hourly intervals after 48 hours.

Circles are locations of extreme protruding aggregates

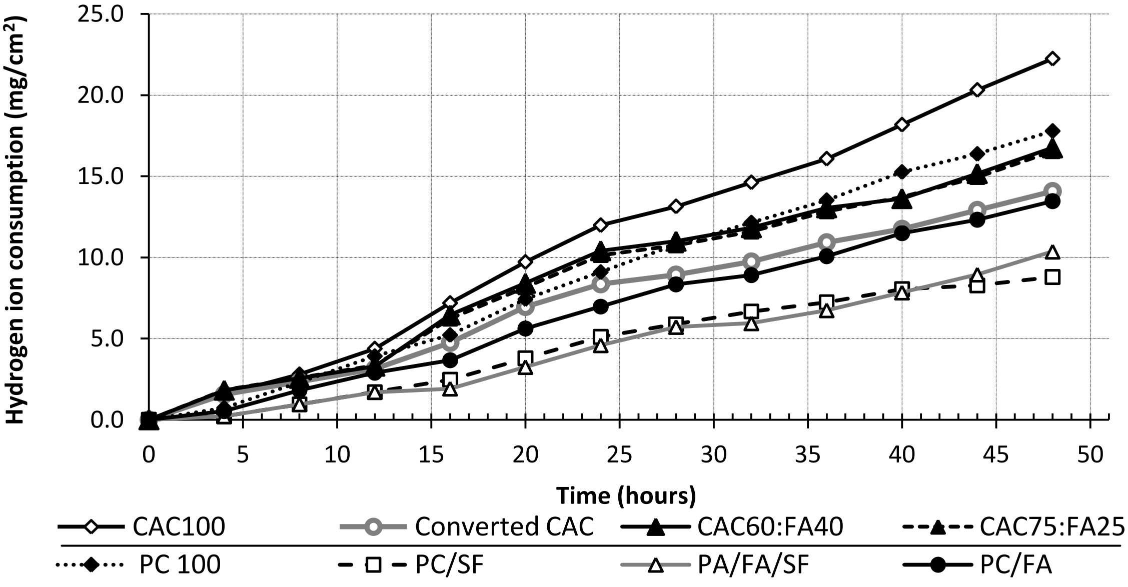

Figure 4.17 Hydrogen ion consumption of CAC – fly ash blended systems of Olifantsfontein dolomite aggregate in hydrochloric acid solution at pH adjusted to 1.0 every four hours.

By contrast, converted CAC was more uniformly attacked. Although converted CAC shows a better performance in acid resistance test, there are two main challenges in terms of practical use of converted CAC in sewer pipes. 1) It is costly to steam cure the concrete for 24 hours i.e. time required for full conversion, and this reduce the turnover required in precast plant such as sewer pipes. 2) the high cost of CAC is not reduced.

Discussion

One most interesting result in this research is that, extended curing at high temperatures (38 °C) is very crucial in development of engineering properties of CAC concrete due to formation of stable hydration products (Hidalgo, 2009). Although the supplementary cementitious materials (SCMs) such as fly ash and ggbs may save the overall material cost and improve acid resistance of some concretes, it is clear that the acid resistance of a converted CAC concrete is higher than that of unconverted CAC concrete and that of blended CAC/FA system. This is probably because of stable hydration products unhampered by mineral additives. The failure mechanism of these concretes demonstrates that the cement paste of CAC/fly ash mixes and plain CAC not fully cured was not uniform as their cement paste was attacked more than the aggregate hence leaving the aggregates exposed. Thus, exacerbating the attack as the embedment of the aggregates in matrix of cement paste was lost.

A plain CAC concrete cured in the same way as the blended fly ash mixes has lower acid resistance than the blended concretes. This is because of high alumina gel i.e. $Al(OH)_3$ in pure CAC (Table 2.6) that is readily reactive with the acid. High fly ash content in a CAC concrete lowers the neutralisation capacity because of an increase in insolubility i.e. the acid insolubility as determined by SANS, 6242 increases from 18.01 % for plain CAC concrete to 22. 78 % for 40 % fly ash blend. $Al(OH)_3$ is the most important parameter known to stiffle the *Thiobacillus* colonies through provision of bacteriostatic effect (Alexander, 2011). A high content of fly ash in a CAC/FA system may not be desirable in a 'live sewer' as the alumina gel or gibbsite content $Al(OH)_3$ decreases when CAC is blended with silica bearing additives such as fly ash (Hidalgo, 2009). Thus, based on the cost of CAC and neutralisation capacity, optimisation then becomes important. It's a fair assumption to take a 25 % fly ash replacement as the optimum in mix design if other factors such as strength reduction are taken into account. The increase of fly ash content lowers CAC strength, as discussed in Section 4.2 and 4.3 . Aditionally, similar pattern for the graphs of mass loss and hydrogen ion consumption for plain CAC concretes (converted and unconverted) indicate that the materials reacted with the acid is reflected by the mass loss.

4.8.4. Calcium Aluminate Cement/ ggbs concrete

Mass loss (%) and hydrogen ion consumption (mg/cm^2) of CAC/ggbs concrete mixes are presented in Figures 4.18 and 4.20 respectively. A plain CAC concrete had mass loss of 31.67 % and hydrogen

20.98 mg/cm^2 respectively after 48 hours. A 75 % CAC: 25 % ggbs concrete mix had 33.52 % and 17.43 mg/cm^2 mass loss and hydrogen ion consumption respectively. A 60 % CAC: 40 % ggbs mix had 30.84 % mass loss and 16.36 mg/cm^2 hydrogen ion consumption. A 50 % CAC: 50 % ggbs had mass loss of 32.45 % and 16.42 mg/cm^2 of hydrogen ion consumption. Lastly a 40 % CAC: 60 % ggbs concrete mix had highest mass loss of 39.56 % and lowest hydrogen ion consumption of 9.68 mg/cm^2.

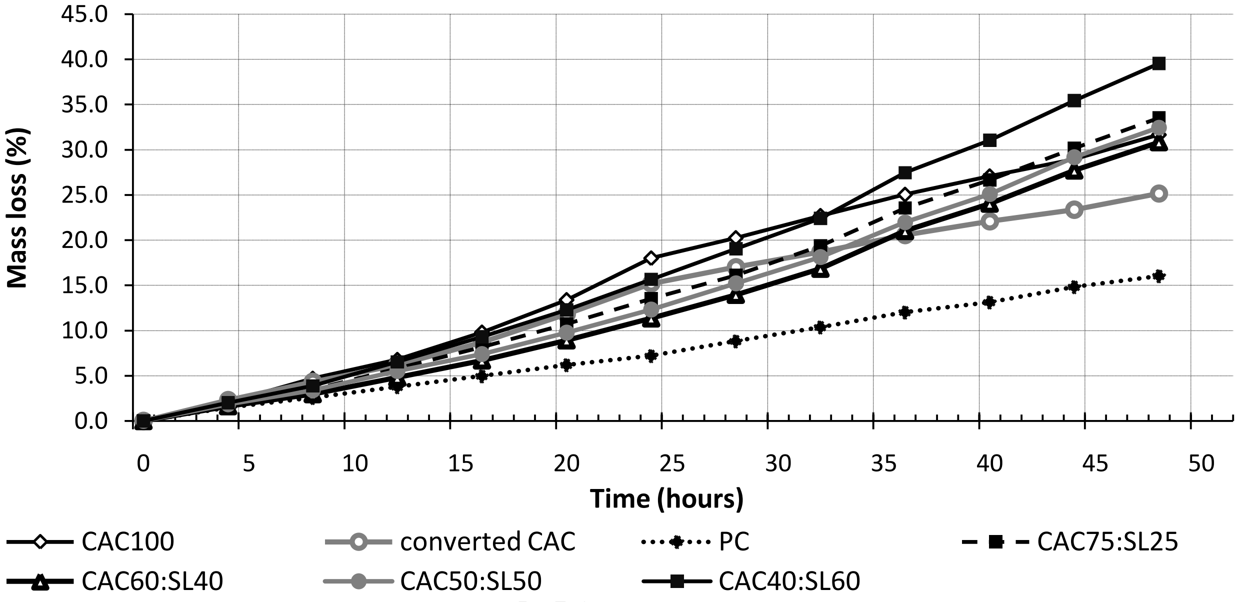

Figure 4.18 Mass loss with time of CAC – ggbs blended systems of Olifantsfontein dolomite aggregate in hydrochloric acid solution at pH adjusted to 1.0 every four hour.

Visual inspection in Figure 4.19 shows the corrosion in acid solution of different blends of ggbs replacement in a CAC concrete.

Discussion

A 40 % CAC: 60 % slag mix attained the highest mass loss in a hydrochloric acid solution after 48 hours compared with the other blended concretes as shown in Figure 4.18. This is because of inferred microstructural property of this blend that might not had fully developed or be retarded by slag. This behaviour is confirmed by low compressive and tensile strengths as seen in Section 4.2 and 4.3 respectively. The reaction with the acid seemed to attack the cement paste more than a dolomite aggregate thus leaving the aggregate protruding which later fell out (hence high mass loss or high rate of acid attack).

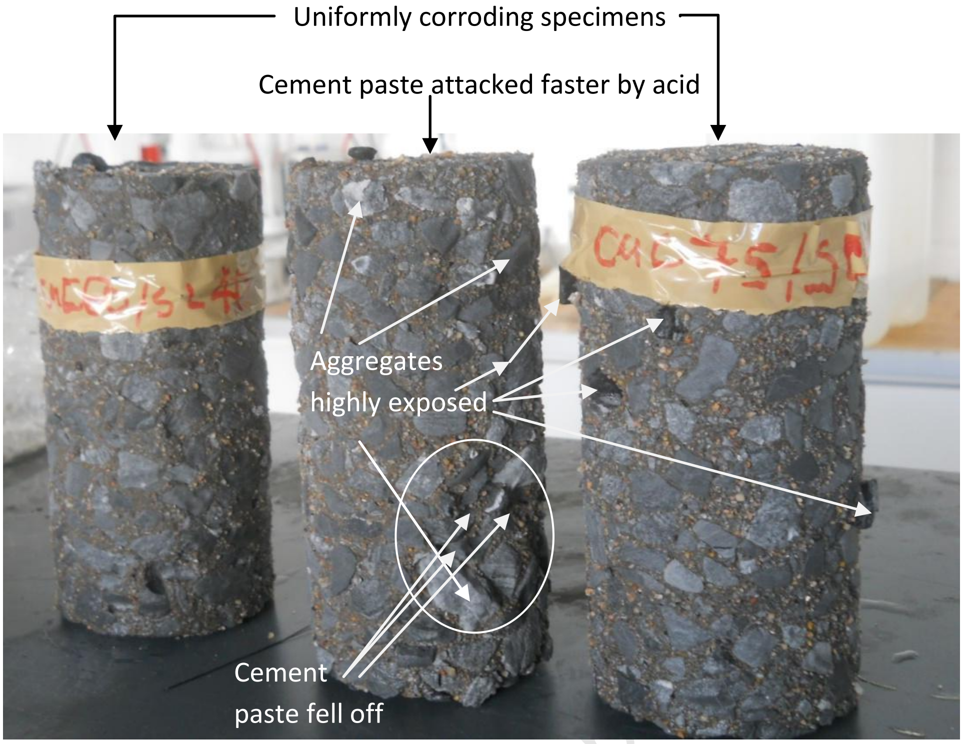

Figure 4.19 Attack of CAC60:SL40 (left), CAC40:SL60 (middle), CAC75:SL25 (right) after 48 hours in hydrochloric acid solution with pH maintained at 1.0 after every four hours.

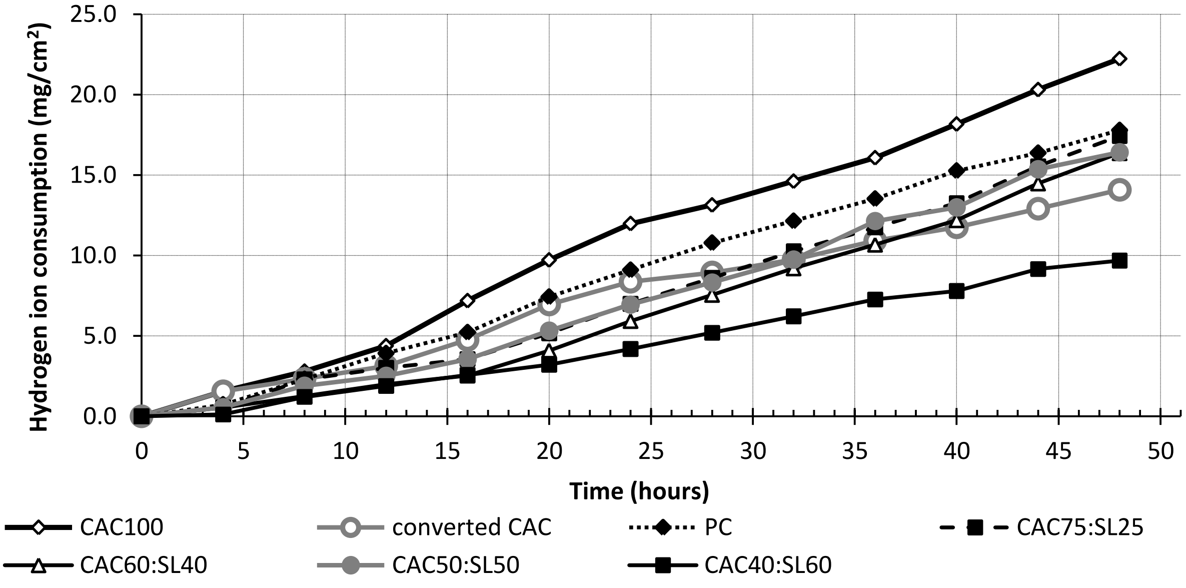

Figure 4.20 Hydrogen ion consumption with time of CAC – ggbs blended systems of Olifantsfontein dolomite aggregate in hydrochloric acid solution at pH adjusted to 1.0 every four hours.

The mass loss of blended mixes is approximately similar to that of plain CAC. This mass loss is mainly a function of fall out of acid insoluble particles of the cement paste, whereas the mass loss of CAC is mainly due to acid dissolution of the cement paste as illustrated by high hydrogen ion consumption in Figure 4.20. The other mixes such as 25 % ggbs, 40 % ggbs and 50 % ggbs were found to significantly outperform plain CAC in terms of hydrogen ion consumption, because of less neutralisation capacity due to reduced alumina gel by addition of silica bearing additives as illustrated in Table 2.6. On the other hand, the lowest hydrogen ion consumption of 40 % CAC mix is due to its higher acid insolubility of 21.45 % as determined by standard test (SANS, 6242) than those of other mixes as a result to high ggbs content. The higher ggbs content of 60 % probably affected hydraulicity of the cement and the hydration products formed. The ggbs used in this project has content of silica SiO_2 *circa* 37.1 %, and this increases the phase dicalcium aluminate silicate (C_2AS) during hydration which has very slow hydraulic activity and hence slow strength development (Robson, 1962).

4.8.5. General discussion

Acid resistance of Portland cement concrete is considerably higher than that of CAC concretes in a dynamic hydrochloric acid test at pH = 1.0. This result is clearly visible in Figure 4.14 and 4.16 respectively. This trend is similar to the results found by Fourie (2007). The performance of CAC concrete can be ascribed to three possible explanations: 1) high permeability as illustrated by OPI values in Section 4.5.2 and 4.5.3 respectively, 2) high alkalinity or neutralisation capacity due to the presence of alumina hydrate that readily dissolves in an acid below pH = 4 (Robson, 1962), 3). The attack of alumina hydrate as descibed in 2 above leads to a high mass loss of the paste and it is obvious that the mass loss of CAC concrete is mainly a function of acid dissolution followed by fall out of the insoluble particles in an acid solution test.

The ratio of mass loss to hydrogen ion consumption of blended CAC with cement extenders mixes was above unity, roughly between 1 - 2, with plain CAC in the lower range, CAC/FA mixes at 1.7 and CAC/ggbs mixes at 2. These values are considered high and this is an indication of high rate of acid attack for CAC concrete in highly aggressive acid solutions. This ratio becomes high when the content of cement extenders is increased due to reduction of alumina gel, thus the attack then becomes a function of fall out of acid insoluble particles than just dissolution

4.9. Neutralisation capacity

The ability to neutralise the acid is one crucial factor to evaluate acid resistance of the sewer pipe concrete. By definition, neutralisation capacity is regarded as the amount of acid in mM which is needed to attack an amount of the material in (g) (Dhir, 1999). The use of dolomite aggregate in CAC concrete mixes as a liner to a host pipe had been used successfully to provide sacrificial protection via provision of neutralisation capacity (Goyns, 2001). A good acid resistant sewer pipe concrete is one that corrodes uniformly with the cement paste, without the cement paste corroding prior to the aggregate to expose it to lower structural integrity of the pipe (Fourie, 2007). Hence the need to use a competent dolomite such as one from Olifantsfontein Quarry with acid insolubility of 4.18 % as determined by standard test (SANS, 6242). The selection of a dolomite in sewer pipe concrete must be accompanied by optimisation of the performance of blended CAC with fly ash and/or ggbs not only in terms of acid resistance but also cost, energy servings and protection of the environment through reductions in emmisions of greenhouse gases. Although, the availability of the competent dolomite for acid attack may be scarce in some regions, and transport cost could be incurred to deliver to the desired sites, selection of cementitious blends must also match the performance of dolomite aggregagates available in a given geographical area.

The higher the neutralisation capacity, the more acid is needed to corrode a concrete material and for the same material it takes longer to corrode and hence the service life of the sewer pipe concrete can be enhanced. Clearly concrete made from pure hydraulic binders have high neutralisation capacity than blended concretes with the supplementary cemetitious materials (fly ash, ggbs, silica fume etc.). However, PC is vulnerable to corrosion of sewer pipes due to high content of portlandite that is formed from its hydration reactions. Although, CAC concrete is found to underperform in terms of acid resistance in the hydrochloric acid solution test at pH of 1.0. A good performance in a 'live sewer' is more related to factors such as bacteriostatic effect of aluminium hydroxide, i.e. stifling of the bacterial growth (Alexander, 2011).

4.10. Chapter summary and conclusion

Partial replacement in Portland cement concrete by pozzolans such as fly ash and silica fume generally improves properties of hardened cement paste. Silica fume concrete produces higher compressive strength than fly ash concrete as a result of curing sensitivity and slow strength development of fly ash. Sewer pipe concretes are air cured and it shows that the application of 30 % fly ash mix is limited due to rapid striking times required thus the pipes may crack easily at early age during handling.

The permeability of silica fume concretes (PC/SF and PC/FA/SF) i.e. Portland cement concretes blended with silica fume is highly improved with OPI and sorptivity values of 10.93 and 3.2 mm/$\sqrt{\mathrm{hr}}$ for PC/SF concrete respectively, and 10.96 and 3.7 mm/$\sqrt{\mathrm{hr}}$ for PC/FA/SF concrete respectively. These improved transport properties are due to: 1) inferred refined microstructure as a result of pozzolanic reaction of silica fume and free lime in both the bulk paste, and in interfacial transition zone (ITZ) during hydration to produce more calcium silicate hydrate, 2) filling effect of fine grains in the capillary pores and ITZ to eliminate the wall effect hence produce a unified structure of the aggregate and cement paste. However, there is no information confirming the absence of ITZ in a ternary mix of PC/FA/SF in the literature.

The use of fly ash and ggbs in the blends of CAC concretes had adverse effects on strength of the blended concrete, due to their high silica content that increases the content of C_2AS that has low hydraulicity leading to inevitable low strength development of CAC concrete. Although these cement extenders lowers strength development of calcium aluminate cement concrete, after 28 days of air curing, 15 % fly ash and 25 % slag concrete mixes produced about the same strength of plain CAC at 14 hours with less strength reduction and without any conversion.

Generally, CAC concrete have high permeability specific to its hydration products and partly because of its relative coarseness as it is not finely grounded like rapid hardening Portland cement. Thus a hydrated paste may provide continuous interconnected pores. Fly ash and ggbs replacement in CAC do not improve durability indexes values of combined concrete probably due to poor microstructural development as illustrated by compressive and tensile strength results.

The CAC concretes had low OPI values of < 10 and high sorptivity values of > 11 mm/$\sqrt{\mathrm{hr}}$ and > 9.5 mm/$\sqrt{\mathrm{hr}}$ for CAC/FA and CAC/SL specimens respectively. However, the porosity of CAC concretes is generally less than that of Portland cement concretes because during hydration CAC uses higher proportion of mixing water for its high early strength than PC, this reduces the free water, which forms the voids. Thus, it is clear that the high acid resistance of CAC concrete in aggressive environments i.e. in a 'live sewer' as discussed in Chapter 5, is not mainly a function of its permeability or porosity but that of its hydration products that are toxic to *Thiobacillus* species.

The cumulative mass loss and hydrogen ion consumption in hydrochloric acid solution at pH = 1.0 were recorded for all concrete types, with high mass loss indicating higher rate of acid attack and high hydrogen ion consumption indicating less resistance to acid attack.

The following conclusions were reached regarding physico-chemical properties of the concretes and their respective performance in a dynamic hydrochloric acid resistance test:

- 10 % silica fume concrete and ternary mix concrete comprising (72 % Portland cement, 20 % fly ash) have higher acid resistance than a binary mix comprising 70 % PC and 30 % fly ash because of reduced permeability and sorptivity. This high performance can also be attributed to reduction in calcium hydroxide content of the cement paste, which decreases linearly with the amount of silica fume added as a result of pozzolanic reaction.

- Converted CAC concrete has substantial better acid resistance than unconverted CAC for the same concrete mix because of stable hydration products. A converted CAC concrete has higher porosity than unconverted one, this directly indicates that the acid resistance of CAC concrete is not a function of its permeability or porosity alone but that of its hydration products.
- Portland cement concrete performs better than CAC concretes in aggressive hydrochloric acid environments at pH = 1.0 for both mass loss and hydrogen ion consumption respectively. The lower performance of CAC concrete can be ascribed in combination of the following three possible explanations: 1) high alkalinity or neutralisation capacity due to the presence of alumina gel hydrates that readily dissolve in an acid below pH = 4, 2) high permeability as illustrated by OPI values, 3) the attack of alumina hydrate as described in 1) above. This leads to a high mass loss of the paste and it is obvious that the mass loss of CAC concrete is more a function of acid dissolution followed by fall out of the insoluble particles in an acid solution test

- In terms of hydrogen ion consumption as a measure of acid resistance, a 40 % CAC: 60 % ggbs concrete mix performs well in hydrochloric acid solution at pH maintained at 1.0 for the duration of the test. However, the rate of acid attack of this mix is higher than that of other CAC concrete blends due to fall of acid insoluble particles as conformed by acid insolubility test or low hydraulicity. Hence, during the acid attack the cement paste is attacked more to leave the aggregate particles exposed. It is apparent that a good acid resistant sewer pipe concrete is one that both cement paste and dolomite aggregate corrodes uniformly without protruding aggregate during attack. Hence a selection of a dolomite aggregate in a given geographical area must match acid resistance of the hardened cement paste.
- In conclusion, it is clear that concrete made from pure hydraulic binders have higher neutralisation capacitity than blended concretes with supplementary cemetitious materials. A high percent replacement of these binders reduce the neatralisation capacity of the concrete, thus fall out of acid insolubles particles may not be desirable to improve the service life of sewer pipes.

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Chapter 5: Case study - Biogenic sulphuric acid resistance of concrete pipe samples in a 'live sewer'

5.1. Introduction

Unlike the laboratory hydrochloric mineral acid resistance test that determines, the acid resistance via transfer of hydrogen ions from the acid solution to concrete and neutralisation capacity of the dolomitic-based concrete, biogenically generated sulphuric acid in sewer pipes is a function of many factors some of which are: hydraulic design, biochemical oxygen demand of sewage, temperature and the content of hydrogen sulphide in a given sewer. The combination of these factors has resulted in failure of sewers worldwide. The results pertaining to hydrochloric mineral acid resistance test cannot fully characterise the behaviour of concrete when exposed to *Thiobacillus* bacteria species that convert H_2S to sulphuric acid in a 'live sewer'. Hence it was decided to investigate acid resistance of sewer pipe concrete in terms of both laboratory acid solution test and biogenic sulphuric acid resistance method in a 'live sewer'.

It is not easy to develop a test method that simulates the exact corrosion of the sewers because the corrosion process is not just a physical or chemical effect but involves living *Thiobacillus* species. Calcium aluminate cement (CAC) concrete, sulphur concrete and use of biocides in concrete can provide toxicity to the bacterial colonies and hence reduce the bio-sulphuric acid effect on the concrete in a 'live sewer'. This study will evaluate the acid resistance of a sewer pipe concrete under both simulated conditions in the laboratory and 'live sewer' conditions to implement the life factor method via inclusion of a material factor (M_F) for different pipe materials.

5.2. Objectives of Virginia Experimental Sewer

The Virginia Experimental Sewer is an on-going site experiment and the ultimate goal of this 'live sewer' biogenic corrosion research is to obtain realistic corrosion rates for different types of concretes and calibrate them for use in a Life Factor Method (LFM) or other appropriate corrosion prediction models so that:

- Designers can quantify the corrosion and make the correct material choice for a given sewer
- Concrete pipe retains a leading position in the outfall sewer market
- Cementitious remedial measures can be used as liners on concrete pipes
- Use of supplementary cementitious materials (fly ash, ggbs and silica fume) can be used to minimize the carbon footprint of cement production

- Blended calcium aluminate cement concrete with either fly ash or ggbs can provide bacteriostatic effects to *Thiobacillus* species similar to plain CAC concrete.

Finally, of all the concretes used in the experiments those that have biogenic acid resistance over their service lives will be selected for use in design while the economic cost of producing them is minimized.

5.3. Background and history of Virginia Experimental Sewer Project

The Virginia Experimental Sewer is a site used in South Africa by the Concrete Manufacturers Association & the University of Cape Town to assess the biogenic corrosion of concrete pipes. This assessment will be used to predict corrosion rate of concretes of different materials when exposed to *Thiobacillus* species i.e. the main agents for generation of sulphuric acid. What makes this site ideal for testing are the conditions of aggressiveness that favour generation of hydrogen sulphide. The location of the experimental sewer is at the end of a rising main as shown in Figure 5.1, whereby there is a high turbulence in the flow of the sewer. The high summer temperatures up to 36°C (Fourie 2007) and moist conditions within the sewer line favour the colonization of the *Thiobacillus* species (Goyns 2003). The experimental line was constructed with a bypass to make it easy to divert the sewage for inspection of the samples in the sewer.

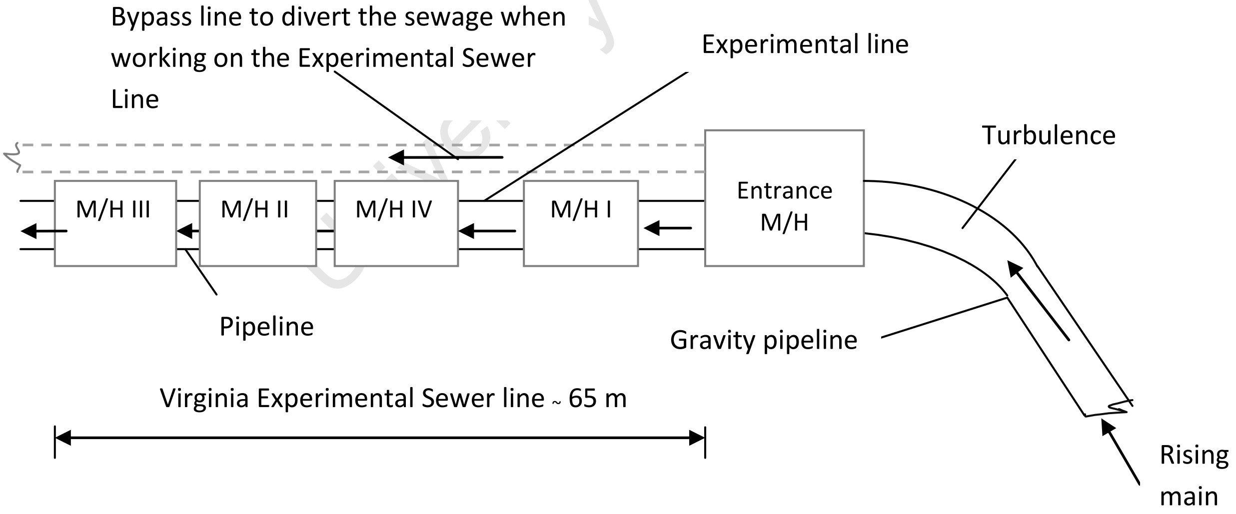

Figure 5.1 Typical layout in plan of existing Virginia Experimental Sewer and its suitability to promote biogenic corrosion (Not to scale)

Biogenic corrosion of concrete sewers is a problem that has a long history. In the 1960s the Council for Scientific and Industrial Research (CSIR) proposed Portland Cement (PC) and dolomitic aggregate with sacrificial layer for use in sewer pipes (Goyns, 2010). However, the report by (Goyns, 2003) revealed that in highly aggressive sewers OPC/DOL (Dolomite aggregate) concrete was limited to a certain extent and the life of a sewer line was compromised considerably. There have been four phases in Virginia Experimental Sewer project to date with phases 3 and 4 coexisting. However, phase 3 has been running over 5 years since 2004 and significant results are available whereas phase 4 started in 2009 and is ongoing .

Phase 1

The first phase was carried out by CSIR under a 5 year plan from 1988 - 1993, and the materials tested in the sewer comprised unprotected concretes and various protections such as plastic lining and coatings applied on OPC/SIL (siliceous aggregate) and fibre cement (FC) as listed below:

Unprotected cementitious pipes:

- Ordinary Portland Cement / Silica Aggregate (OPC/SIL)
- Ordinary Portland Cement / Dolomite (OPC/DOL)

Calcium Aluminate Cement / Silica Aggregate (CAC/SIL)

- Fibre Cement (FC)

Protected cementitious pipes:

- OPC/SIL lined with high density polyethylene (HDPE)
- FC coated with epoxy tar
- FC coated with polyurethane
- FC coated with epoxy

The predicted corrosion rates per year as modelled by the Life Factor method of the unprotected concretes are shown in Table 5.1. The actual corrosion was measured from pipe samples in the sewer whereas the design predictions were based on the assumed alkalinity at design stage of the project. Actual predictions on the other hand were back calculated from actual alkalinity measured on installed samples in the sewer. This phase also comprised static pure acid in the laboratory, however at the end of Phase 1 i.e. after 5 years the laboratory tests results did not match with those of concretes in the sewer (Goyns, 2003).

On completion of Phase 1, typical findings were:

- Corrosion took place at the pipe crown, and it was discovered that at daily average sewage flow of the pipe there is combined effect of both corrosion and abrasion erosion.
- Although the FC pipes had corrosion rate three times less than that of PC/SIL concrete, it became swollen as the products of corrosion were held together by the asbestos fibres and making it unserviceable for longer periods.
- The CAC concrete outperformed the OPC concrete

- The reinforcement of OPC/SIL samples corroded, hence the necessity to implement reinforcement cover, i.e. sacrificial concrete layer to counteract corrosion of the reinforcement.

Table 5.1 Comparison of predicted and actual corrosion of unprotected concretes in the period 1988-1993 i.e. 5 years (Goyns, 2010)

Material	**Wall thickness (mm)**	**Alkalinity (A)**		**Predicted Corrosion Rate**		**Actual Corrosion**	
		Design	Actual	Design	Actual		
				mm/yr	mm/yr	mm	mm/yr
OPC/SIL	64	0.16	0.20	7.9	6.3	30+	6+
CAC/SIL	64	0.25	0.45	5.1	2.8	5-10	1-2
OPC/DOL	77	0.95	0.70	1.3	1.8	10-15	2-3
FC	31	0.85	0.65	1.5	1.9	10-12	2+

Phase 2

While the experimental sewer continued to run, the second phase commenced in 1995 and ended in 2000. Phase 2 was undertaken by the University of Cape Town, in which a master's student Fourie attempted to simulate the onsite conditions in the laboratory through invention of a dynamic hydrochloric acid test. In this study, identical concretes were tested in the laboratory and some specimens were put in the Sewer and after 17 months the corrosion of CAC/DOL was found to be negligible compared to that of PC/SIL concrete as shown in Table 5.2.

The last column in Table 5.2 is an estimation of the material factor (M_F). This is a factor that differentiates each concrete mix in terms of acid resistance in a 'live sewer' if factors such as alkalinity and potential fall out of the aggregates are taken into account. M_F is a dimensionless coefficient that relates corrosion of each concrete to the most susceptible concrete in biogenic acid attack (PC/SIL) concrete. The concept of material factor is implemented into the Life Factor Method as shown in Equation 5.1.

$$C_{avg} = M_F \frac{11.5k}{A} \Phi_{sw} \quad \text{……} \quad (5.1)$$

Where:

C_{avg} - Average corrosion rate (mm/year)

k - Coefficient of efficiency of acid reaction with concrete considering a fraction of acid remaining on the sewer wall (0.3 to 1.0 for complete reaction).

A - Alkalinity of the concrete

11.5 - Converts Φ_{sw} in $g/m^2/h$ into C_{avg} units of mm/year

M_F – Material Factor (Table 5.2)

Using the concept of Material Factor as discussed in Section 2.5.3, the alternative corrosion rates of other materials to that of OPC/SIL and CAC/DOL is shown in Table 5.3.

Table 5.2 Comparison of measured and estimated corrosion rates (Goyns, 2003).

MATERIALS	**5 yr estimate (1988 - 1993)**		**12 yr estimate (1988 -2000)**		**14 yr measured (1988 - 2002)**		**Material Factor**
	mm	mm/yr	mm	mm/yr	mm	mm/yr	
PC/SIL	>30	>6,0	>64	>6,0	> 105	> 7.5	1.00
PC/DOL	10 – 15	2 – 3	20 – 30	1,7 – 2,5	55	3.9	0.40
CAC/SIL	5 – 10	1 – 2	10 – 15	0,8 – 1,2	35	2.5	0.29
FC	10 - 12	2 +	20 - 25	1,7 – 2,1	-	-	0.32
CAC/DOL *	3,0	0,6	7,2	0,6	8,4	0,6	0.12
CAC/ALAG *	Less than CAC/DOL-no mass loss after 17 months in sewer & pH >6,4						

NB: * Values estimated on basis of other materials and performance of UCT samples in sewer.

Table 5.3 Recommended relative corrosion rates based (Table 5.1) (Goyns, 2010)

Material Cement/Aggregate	**Relative Corrosion (mm)**	**Corrosion relative to CAC/DOL**	**Corrosion relative to OPC/SIL**
OPC/SIL	40	10.0	1.00
OPC/DOL	13	3.3	0.33
FC	8	2.0	0.20
CAC/SIL	6	1.5	0.15
CAC/DOL	4	1.0	0.10
CAC/ALAG	1	0.3	0.03

At the end of the Phase 2 i.e. in 2002, the PC/SIL concrete pipe sections in the sewer were completely corroded at average daily sewage flow and the reinforcement on the OPC/DOL pipes was exposed and corroding. After 12 years in service the corrosion was extreme such that the top part above the water line of OPC/SIL pipe section was missing, Figure 3.4 b and 5.2 are examples of those pipes.It was then decided to do rehabilitation of the experimental section i.e. Phase 3.

Phase 3 – (Currently running)

The third phase of the project was the rehabilitation of the experimental section whereby severely deteriorated pipes (Figure 5.2) were replaced in 2003 and manholes I, II, and III were constructed where these pipes were removed with 17 pipe samples installed in each manhole. A plan layout of existing experimental section and manholes was shown in Figure 5.1. and details of sample location in the sewer are shown in Appendixes (Figure A.8 – A.10). The Experimental section comprising

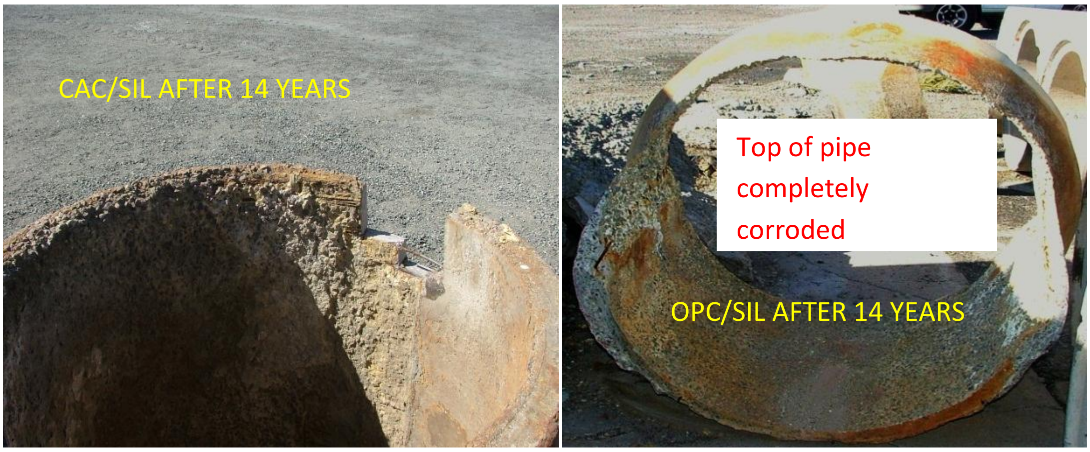

Figure 5.2 Severely deteriorated pipes after 14 years (1988 – 2002) in service (Goyns, 2010)

manholes I, II, and III started running in October 2004. At rehabilitation stage, . the HDPE linings and coatings were eliminated as part of the experiment because of the involvement of Concrete Manufacturer's Associations (CMA), Cement companies, and Concrete pipe manufacturers who only wanted to evaluate different combinations of cements, cement extenders, aggregates and biocides etc. Short pipe sections of approximately 300 mm length of different materials were cut from whole pipes and connected as one pipe to allow sewage to flow normally with each pipe exposed to biogenic corrosion (Figure 5.4). This allowed each concrete to be evaluated independently.

Phase 4 – (Currently running)

The success of Virginia Experimental Sewer in South Africa to investigate biogenic acid resistance of sewer pipe concrete brought attention to various material suppliers such as Kerneos, Calucem, Xypex and Conshield to have their materials tested in this Experimental Sewer. Therefore, an additional manhole number IV was built in 2009 to install materials from the respective sponsors. This new manhole is located between Manhole I and II as shown in Figure 5.1 and layout of specimen's detail installed in this manhole is shown in the Appendixes in Figure A.11. The specimens in this manhole are monitored in the same way as those in Manholes I, II and III.

The main objectives for the construction of this new manhole involved the following strategies:

- Comparing additional materials to those used in manhole I and II and III with implementation of lessons from previous phases of the project.
- In order to define a material factor for each concrete confidently, more samples had to be installed in the sewer to investigate effects of sewer environment, presence of toxic elements and mix proportion on the metabolic rate of the *Thiobacillus* bacteria. This involves monitoring of duplicate cores to pipe mixes placed in baskets in the headspace of the sewer

pipe at the exposure of hydrogen sulphide gas, so mass loss of this cores can be compared o those of the pipe sections before calibrating material factor model.

However, the samples installed in this manhole will not be discussed and analysed in this document in terms of their performance in a ‘live sewer’ for the following two reasons: 1) they are proprietary to the companies mentioned above and their mix details are unknown, 2) they were only installed in 2009 and so far have been gaining rather than loosing mass.

The University of Cape Town (UCT) is also involved in the research towards the development of acid resistant concretes and calibration of a life factor method via inclusion of material factor. The author prepared various small cylindrical samples and installed them in the sewer. The preparation of these samples is discussed in following sections.

5.4. Experimental methodology

5.4.1. Full- scale sewer pipe sample preparation and installation (Manhole I, II and III)

The aim of the sample preparation and selection of raw materials for pipe manufacture was to monitor the performance of different materials already installed in the sewer. This will enable the modification of the life factor method (LFM) and incorporate the material factor (MF) for predicting corrosion and making the pipe material choice for a particular sewer where the conditions have been established (Goyns, 2010). Identical and duplicate pipe sections were installed in Manholes I, II and III, so that any difference in performance of the specimens can be assessed over the 65 m length of the experimental sewer line. The materials and mix compositions are shown in Table 5.4, however, pipe number 15 and 16 are proprietary mixes to Kerneos. The key variables of the concretes in the exposure to biogenic sulphuric acid listed below:

- Two cements- rapid hardening Portland Cement CEM 42.5 R and low alumina Calcium aluminate cement (CAC) with chemical compositions similar to the one shown in Table 3.3
- Different types of cement contents i.e. 16 %, 18 % & 23 % in a whole pipe exposed to biogenic acid attack.
- Two aggregates (Siliceous & Dolomite aggregate)
- The effect of cement extenders such as fly ash, slag and silica fume with CEM I 42.5 R cement i.e. rapid hardening cement
- Effect of siliceous and dolomite aggregate with CAC cement
- Reinforced versus non-reinforced concrete pipes

- Different types of linings with and without combined aggregates (dolomite and siliceous) such as: 1) OPC and CAC mortar linings, 2) CAC concrete as linings on PC/SIL host pipes respectively.

The dolomite crusher sand was blended with siliceous sand for some of the mixes (Table 5.4) to increase the workability as the crushed particles from parent rock have angular shapes and rough surface texture. The pipe materials were prepared in the same way as normal pipes by the roller suspension method and cut into sections as shown in Figure 5.3 and 5.4, whereby all the various small sections were made up of different pipe materials. However, the cutting of the pipe sections was complicated by the following factors

- The wall thickness of approximately 80-95 mm
- High compressive strengths of about 100 MPa
- Lastly, some of the pipes were reinforced with spiral grid and after cutting the reinforcement bar was exposed and thus needed further trimming as during the service the steel can corrode and cause spalling.

The cutting was outsourced to a company that built a frame that held the pipes in place while being cut by a specialised concrete cutting machine (Goyns, 2008).

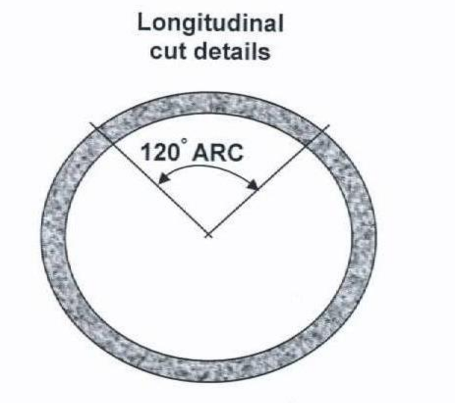

Figure 5.3 Cross sectional cut detail of the pipe lid section

The longitudinal 300 mm pipe cuts were made through the pipe wall at approximately 60 ° on either side of the centre-line as shown in Figure 5.3 and Figure 5.4; this angle seemed to enable the remaining pipe to be structurally efficient to resist breakage during installation and weighing of the lids. The joints between the pipe lids of different concretes were externally sealed with putty so that the lids could later be taken off when taking mass measurements, and to keep the atmosphere within the sealed pipe airtight to enable: 1) accumulation of hydrogen sulphide, 2) moist environment for survival of *Thiobacillus* species. An 8 mm diameter hole was bored through one pipe lid sample in each manhole to enable future measurement of the hydrogen sulphide gas inside the pipe without disturbing the flow of the sewage.

Table 5.4 Mix proportions of the pipe samples installed in Manhole I, II and III (CMA samples)

Pipe sample	Cement		Extender		Stone		Sand		Notes
Number	**Type**	**%**	**Type**	**%**	**Type**	**%**	**Type**	**%**	
	CEM I DOL aggregate concretes for whole pipe								
1 2	CEM I 42.5R	16	-	-	Dolomite aggregate (DOL)	48	Dolomite crusher sand/ Siliceous sand (DOL/SIL)	36	One section non-reinforced
3		18	-	-		47		35	
4		23	-	-		44		33	
5		12	Slag	6		47		35	
6		13.5	Fly Ash	4.5		47		35	
		16.5	Silica Fume	1.5		47		35	
*7,8, 13**	**CAC Concretes as linings on PC/SIL Host pipes**								
9	Calcium Aluminate Cement (CAC)	23	-	-	SIL	44	SIL	33	One section non-reinforced
10		16	-	-	Dolomite aggregate (DOL)	48	Dolomite crusher sand/ Siliceous (DOL/SIL)	36	
11		18	-	-		47		35	
12		23	-	-		44		33	
14		11	Fly ash/SF	6		47		36	
15#	CFL	20	-	-	ALAG™	50	ALAG™	30	
16#	SECAR	20	-	-	R50(6-9)	30	R50(3-6)	20	
	Mortar Linings to PC/SIL Host Pipes								
19*	CEM 1 42.5R	50	-	-	-	-	SIL	50	
20*		50	-	-	-	-	DOL/SIL	50	50/50 blend
21*	CAC	50	-	-	-	-	SIL	50	
22*		50	-	-	-	-	DOL/SIL	50	50/50 blend

NB*: The missing pipe sample numbers are those that were not cut into lids, due to the complexities outlined in the previous paragraph. These pipes are beneath the cross wall that connects to the diaphragm wall and separate concretes of different mixes as shown in Figure 5.4. These pipes are installed in the sewer and the order is as the pipe samples are installed in the sewer as shown in Appendix D.2. The samples 19 to 22 are also not cut into lids and are not accessible for mass weighing. One part of these pipe sections is reinforced and the other non-reinforced, hence samples will be assessed in the future.

NB#: Proprietary mixes to Kerneos.

The metal handles made when the pipes were installed in 2004 are currently non-existent due to corrosion. After installing the pipe sections, each pipe section was labelled to quantify the number and mix detail of the pipe such that it was correctly orientated when looking at the pipe from the spigot end as illustrated in Figure 5.4. Full details of the installation procedure can be found from (Goyns 2004).

5.4.2. Full- scale sewer pipe sample preparation and installation (Manhole IV)

In view of the problems encountered with the manholes I, II and III manhole number IV was modified with no reinforcement on the pipe samples, reduced wall thickness of 63 mm and reduced length in a longitudinal direction from 300 to 200 mm. This reduced the overall mass of pipe sample from 66 kg as in manhole I, II and III to 33 kg in manhole IV to make it easy for lifting when doing mass measurement.

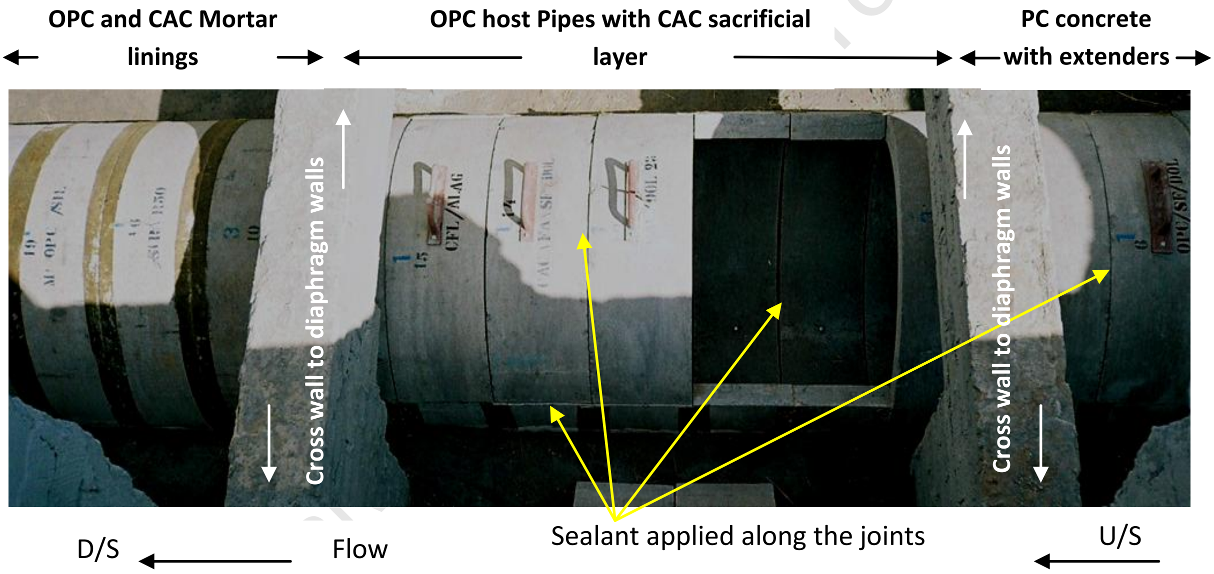

Figure 5.4 Typical orientation of the pipe sections, labeling and sequences as installed in the sewer (Adopted from Goyns, Personal communication 2010).

5.4.3. Preparation and installation of small cylindrical samples from University of Cape Town

Small cylindrical samples (80 mm diameter × 45 mm) were installed in the sewer. They were cut from cast cylinders (80 mm diameter × 150 mm) that were prepared by hand compaction in the laboratory at UCT. Three groups of concrete mixes were used and these are: calcium aluminate cement, blended with 1) fly ash and 2) ggbs, and 3) Portland cement (CEM I 42.5 R) concrete blended with both binary and ternary blends of fly ash and silica fume. These concretes are duplicate mixes of those used for laboratory hydrochloric acid resistance test at UCT as shown in Table 5.5

Table 5.5 Concrete mix composition of 80 mm diameter × 45 mm concrete cylindrical samples installed in the Virginia Experimental Sewer .

Portland Cement Mixes				**Calcium Aluminate Cement mixes**							
Control	**Binary**		**Ternary**	**Control**	**CAC blended cements**						
PC	PC:FA	PC:SF	PC:FA:SF	CAC	CAC :FA	CAC :FA	CAC :FA	CAC :SL	CAC :SL	CAC :SL	CAC:SL
100	70/30	90:10.	72:20:8	100	85:15	75:25	60:40	75:25	60:40	40:60	50:50

After casting and heavy compaction, the specimens were water cured in hot water at 38 °C for 14 hours similar to 4 hours of steam curing in pipe manufacturing. The specimens were then stored in air conditioned room after 14 hours at a temperature maintained at 22 °C and a relative humidity of 50 % for 28 days . The end faces of the specimens were then ground smooth as shown in Figure 5.5 such that the signs of corrosion can be visible after some time in the sewer. A specific size of 80 mm by 45 mm was chosen so that the surface area of the specimens matches those of the cored pipes (70 mm diameter by 60 mm) already installed in Manhole IV in the sewer to test the performance of some typical pipes. It is the mass loss per surface area that is critical when the specimens are attacked by the *Thiobacillus* species on the surface of the concrete than the mass loss per unit volume.

Figure 5.5 The appearance of the specimens before installation in the sewer

The samples were placed in acid resistant PVC baskets that were hung on PVC tubes supported by the free edges of the walls of the concrete pipe as shown Figure 5.6. The samples were labelled using flat corrosion resistant plastic that is fastened to the sample by a PVC strop to quantify the sample number and mix design. Three samples were installed per mix; in total there were 36 specimens. These specimens were installed in the sewer in April 2011. On closing the open sewer pipe, the hydrogen sulphide can accumulate in the atmosphere of the pipe and hence allow the colonisation of the bacteria causing biogenic corrosion. There have been two set of mass measurement data one after installation one in July 2011 and the other in October 2011. The initial masses are tabulated in Appendix D.3. These samples have only gained weight so far and this is probably due to moisture absorption. The density, porosity, permeability, strengths, acid insolubility of these samples can be found in Chapter 4. When these samples have sufficiently corroded, their acid resistance in a 'live sewer' will be compared directly to those of duplicate samples tested in a laboratory in Chapter 4.

Figure 5.6 The experimental setup showing installation of cylindrical samples in Virginia experimental sewer.

5.5. Assessing aggressiveness of the sewer

5.5.1. Hydrogen sulphide monitoring

Monitoring of hydrogen sulphide (H_2S) in the sewer was used as the measure of aggressiveness of the sewer. A hydrogen sulphide concentration of more than 10 ppm is sufficient to sustain the growth of a *Thiobacillus* colony capable of causing severe corrosion to concrete sewer walls (Thistlethwayte, 1972 as cited by Fourie, 2007). Thus, the concentration of 10 ppm is high enough to start corrosion on the concrete.

A multi-gas meter (IBRID MX6 supplied by Industrial Scientific) was used for measuring H_2S in the pipe atmosphere. The meter uses suction to sample the gas and the readings were logged during the test. The hydrogen sulphide concentration was measured on the following two counts: The first was hot days of 1 - 2 March 2011 at ambient temperature range of 30 - 36 °C, with measurements taken at the entrance manhole shown in Figure 5.1 directly above sewage. The measured gas concentrations are presented in Figure 5.7 and Figure 5.8. The second measurement was taken on the 24 to 27 October 2011, this time a 3 m sampling tube connected to a meter was placed inside the pipe through a drilled 8 mm hole on one of the lid sections of the pipes in each manhole per day. The gas concentration was measured in manhole I, IV, II and III on the 24, 25, 26 and 27 October respectively, this data is presented in Figure 5.9. The temperature inside the sewer pipe was in the range 15- 22 °C whereas the optimum temperature range for *Thiobacillus thioxidans* the main species generating sulphuric acid attack in sewers is between 28 - 30 °C (Eglinton, 1998).

The moving average gas concentration calculated on five points data is also plotted in Figure 5.10 to compare reduction or any change in hydrogen sulphide concentration in all existing 4 manholes of Virginia Experimental Sewer.

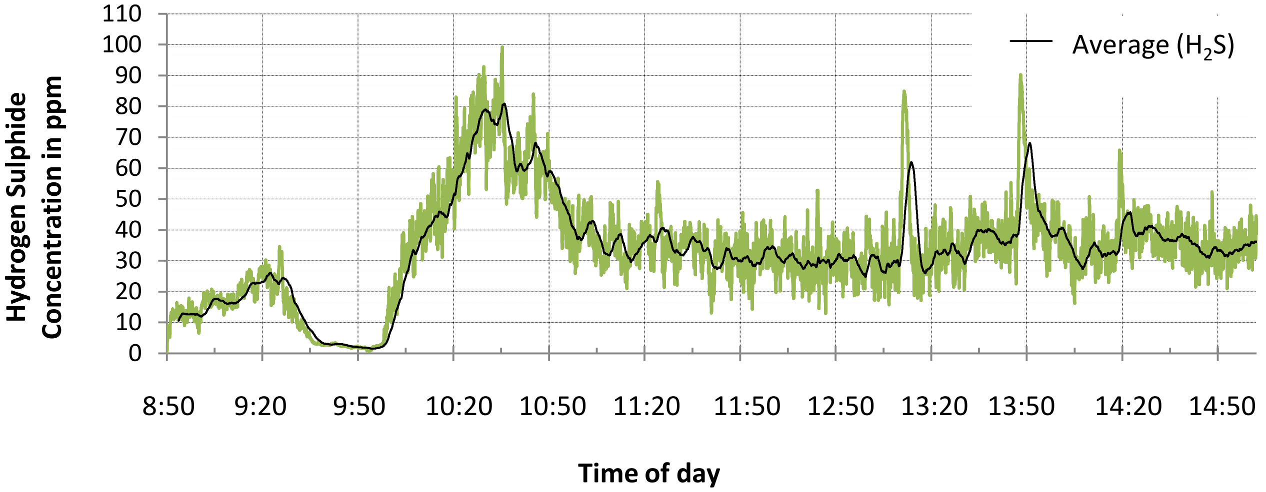

Figure 5.7 Typical hydrogen sulphide gas concentration in the entrance manhole of the Virginia Experimental sewer measured on the 1st March 2011.

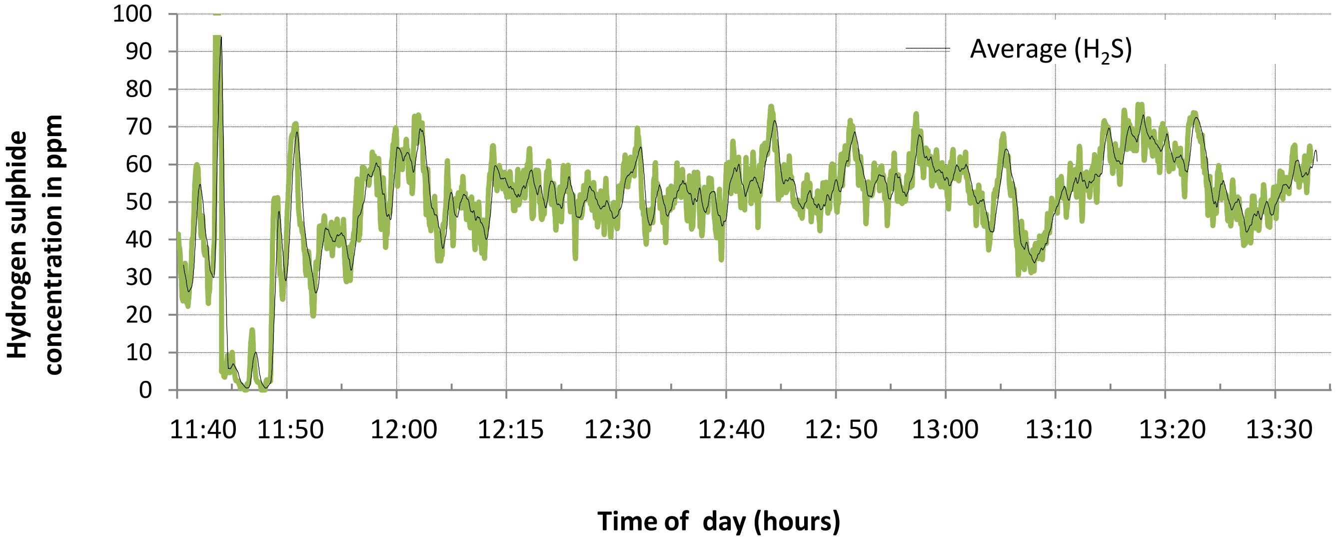

Figure 5.8 Typical hydrogen sulphide gas concentration measured in the Entrance Manhole of the Virginia Experimental sewer measured on 02nd March 2011.

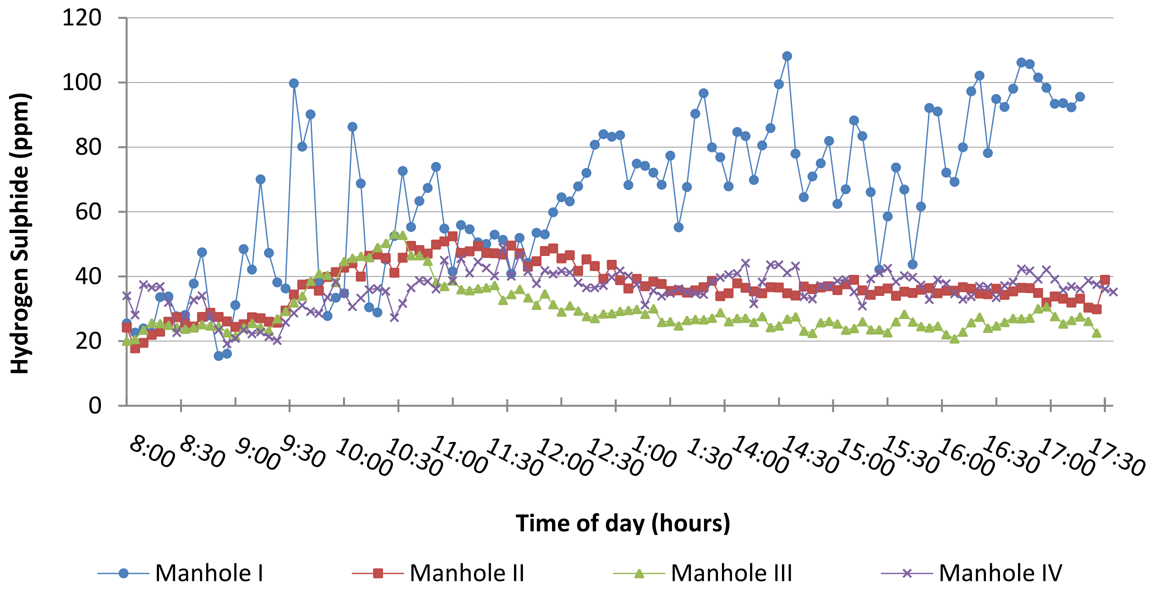

Figure 5.9 Typical profile of hydrogen sulphide gas inside the pipe of Virginia Experimental Sewer, with measurements taken in Manhole I to IV on the 24 to 27 October 2011.

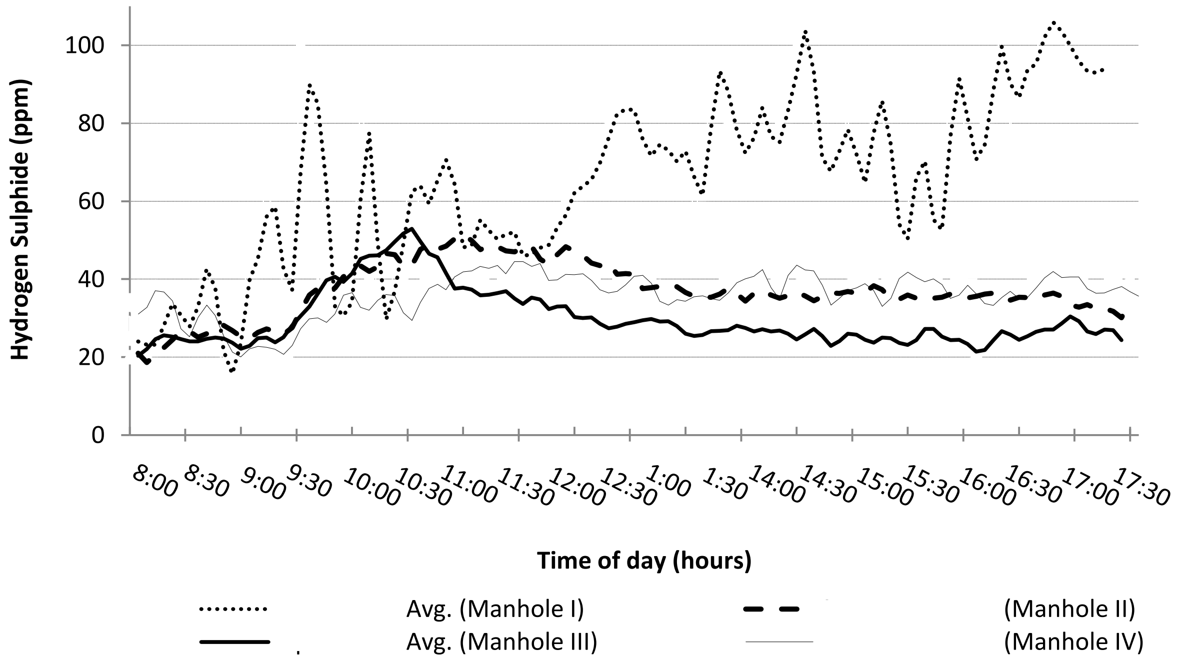

Figure 5.10 Moving average of hydrogen sulphide in Virginia Experimental Sewer to show reduction in gas concentration down the manholes from Manhole I to IV, II and III

5.5.2. Results and discussion

Virginia Sewer project is ongoing research and H_2S will be monitored over time i.e. seasonally over the year at critical times of the day to determine the possible highest concentration in the sewer, and the possible average concentration that can sustain biogenic corrosion. However, this is part of future work and goes beyond the scope of this dissertation.

The gas concentration measured in the Entrance Manhole of about 100 ppm is higher than that in the pipes measured in the experimental manholes because of high turbulence generated due to change of direction of the sewer line from the rising main at the given location as shown in Figure 5.1. The high concentration is noticed mainly after a pump surge that elevated the concentration from about zero at 09:50 AM to about 100 ppm in Figure 5.7 and thereafter dropped. When there was no surge, the concentration remained at about 50 ppm as shown in Figure 5.8.

The hydrogen sulphide concentration in Manhole I is similar to that in the Entrance Manhole with maximum value of 108.2 ppm, whereas that in the downstream manholes is lower. This is due to: 1) dissipation of the gas in large Entrance Manhole 2) the ventilation chambers located on it and 3) reduction in turbulence at downstream manholes in the pipeline from the Entrance manhole (Figure 5.1). The location of Manhole IV is just downstream of Manhole I before Manhole II, and the average values in Figure 5.10 conform to this.

The high sulphide generation in the sewer directly relates to less absorption of oxygen in the sewage because of high biochemical oxygen demand (Goyns, 2008). This agrees with measured hydrogen sulphide and oxygen levels in the sewer whereby oxygen levels decreases directly with increasing sulphide concentrations or vice versa (Figure 5.11). Thus, it shows that reduced oxygen level in the sewer enables growth of anaerobic aerobes to decompose sulphates in the sewer for sulphides

In all the given graphs from Figure 5.7 to 5.10, the gas concentration is above the critical base line of 10 ppm and this shows that the experimental site is aggressive enough to produce hydrogen sulphide concentrations that can cause the corrosion of the sewer pipe concrete.

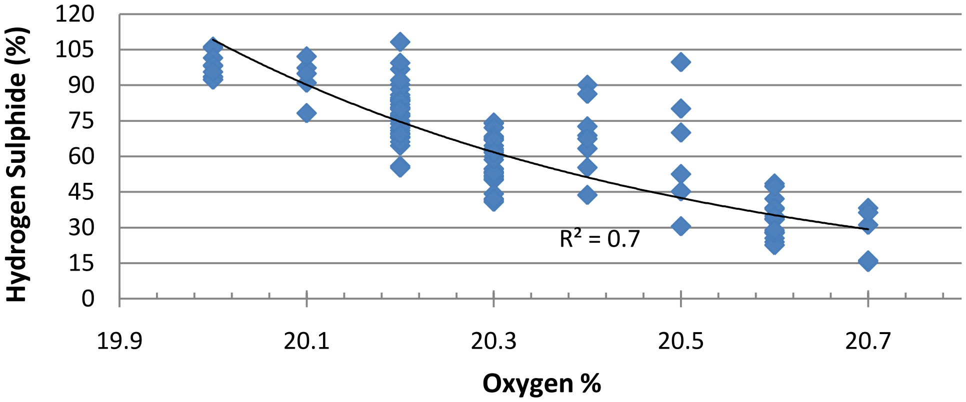

Figure 5.11 Typical relationship of hydrogen sulphide concentration and oxygen level in the sewer pipe measured in Manhole I.

5.6. Assessing the resistance of concrete specimens to a 'live sewer' acid attack

The lids of the pipe sections permit the corrosion assessment at the crown of the pipe, whereas the laboratory test simulates that at average daily sewage flow due to added abrasion effect of flowing water and /or suspended abrasive particles carried by the water. Although there is less corrosion noticed at the crown of the pipe the corrosion at daily sewage flow is clearly visible as in Figure 5.12. The slight corrosion at the crown of the sewer is the result of biogenic corrosion, because the only factor responsible for the attack is sulphuric acid and the bacteria causing it. The deterioration at average daily sewage flow is combined effect of the biogenic corrosion and abrasion effect by suspended particles and due to high turbulence as the Experimental Sewer connects to the end of rising main (Figure 5.1). This abrasion effect was more visible on OPC concrete than CAC concretes because of their differences in abrasion resistance with the later being more abrasion resistant (Scrivener 1999).

The details of the sample designation in the sewer is shown in Table 5.6 with the specimens cast using mixes in Table 5.4. In all three manholes, the pipe sections are duplicates of each other. However, it must be noted that the ordering of the samples is not identical, but sample number and mix composition is exact. The pipe sections in these manholes were installed in 2004 and since biogenic acid attack is a long term process, the samples were inspected over a six month interval for a period of four years without any measurable results. However, from 2008 until 2011 yearly, the samples were weighed to check if there were any trends, with 2008 taken as the base period (Goyns, 2010).

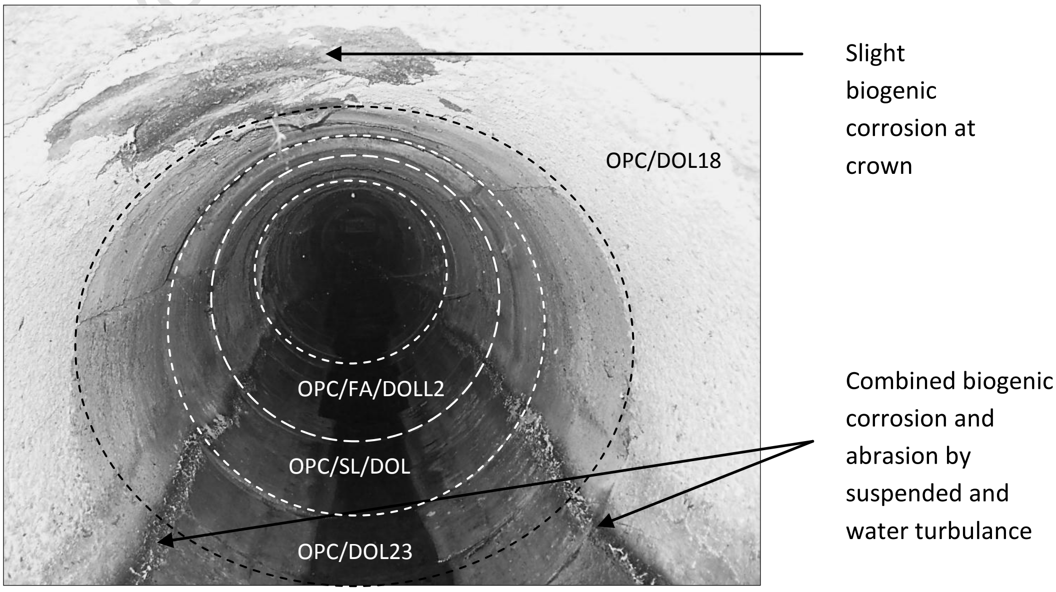

Figure 5.12 Slight corrosion at the crown of pipe sections and corrosion at daily sewage flow level in Manhole 1 (OPC samples), in service since October 2004.

Table 5.6 Pipe samples labelled according to their mix composition (Table 5.4) and the order as installed in the sewer from upstream to downstream of the Experimental Sewer.

U/S → D/S

U/S

MANHOLE I		**MANHOLE II**		**MANHOLE III**	
Pipe number	Mix Composition	Pipe number	Mix Composition	Pipe number	Mix Composition
2[#]	OPC/DOL 18	1[*]	OPC/DOL 16	1[*]	OPC/DOL 16
3	OPC/DOL 23	3	OPC/DOL 23	2[#]	OPC/DOL 18
4	OPC/SL/DOL	4	OPC/SL/DOL	4	OPC/SL/DOL
5	OPC/FA/DOL	5	OPC/FA/DOL	5	OPC/FA/DOL
6	OPC/SF/DOL	6	OPC/SF/DOL	6	OPC/SF/DOL
9	CAC/SIL 23	9	CAC/SIL 23	9	CAC/SIL 23
11	CAC/DOL 18	10	CAC/DOL 16	10	CAC/DOL 16
12	CAC/DOL 23	12	CAC/DOL 23	11	CAC/DOL 18
14	CAC/FA/SF/DOL	14	CAC/FA/SF/DOL	14	CAC/FA/SF/DOL
15	CFL/ALAG	15	CFL/ALAG	15	CFL/ALAG

D/S

NB [*], [#]: The sample number represents the samples as appear in the manholes, each sample number has exact mix composition in all manholes. However the order is different for some pipes because of the pipes that were not cut and into the lids because they were placed under acrosswalls that connect to the diaphragm walls.

5.7. Results and discussion - The pipe lid sections (manhole I, II and III)

The acid resistance of the pipe lid sections was measured from the percentage of mass loss, and the results are presented in Figure 5.13 to 5.15 for Manhole I to Manhole III respectively, for all the samples installed in these manholes. Ordinary Portland cement (OPC) concretes had lost mass due to corrosion (Figure 5.12) and the high mass loss is a result of this effect. The high vulnerability of OPC concrete to acid attack is due to inferred presence of portlandite.

The CAC concretes are found to perform better than respective OPC concretes because of high neutralisation capacity and its effect on bacterial colonies. The better performance of CAC is due to combined effects of neutralisation capacity and the alumina gel from stable hydration products that stifle bacterial activity (Zivicaa, 2002). Other than stable acid resistant hydration products, the absence of calcium hydroxide in a hydrated CAC also makes it more competent in aggressive acid environment (Scrivener, 1999).

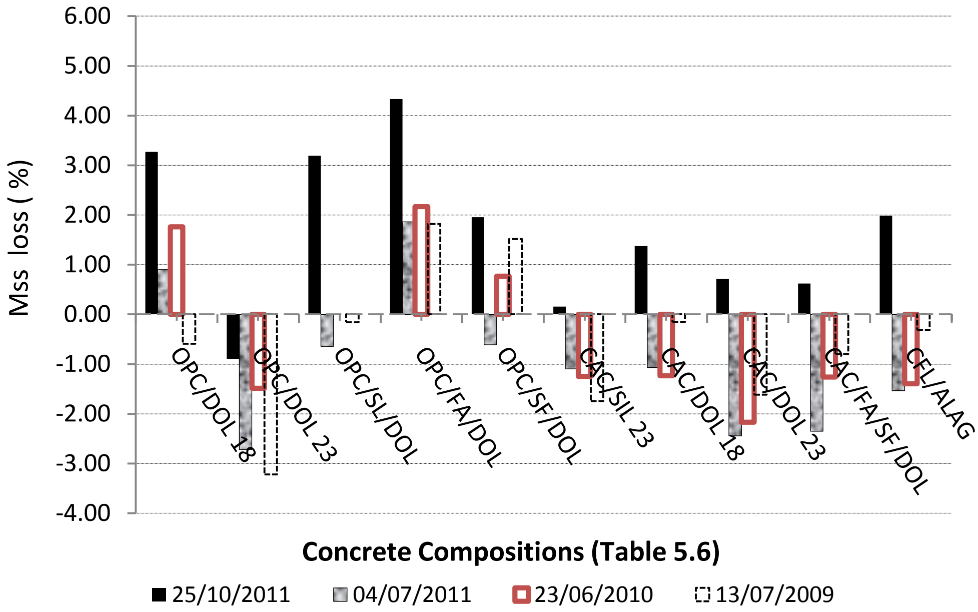

Figure 5.13 Mass loss (%) of various concrete pipe sections (lids) in Manhole I of aggressive 'live sewer'. NB: Negative mass indicates mass gain.

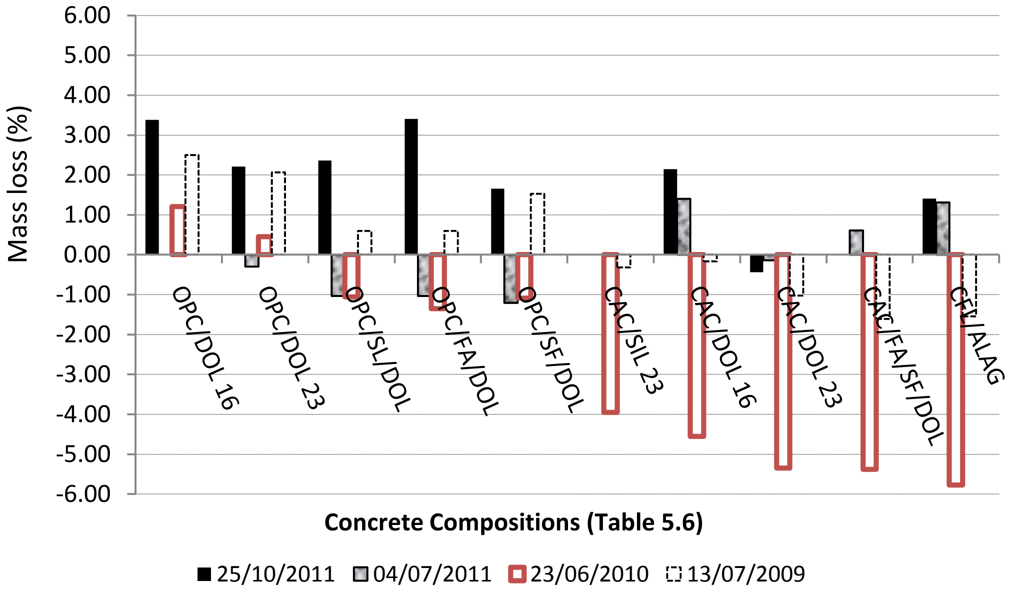

Figure 5.14 Mass loss (%) of various concrete pipe sections (lids) in Manhole II of aggressive 'live sewer'. NB: Negative mass indicates mass gain.

There had been an increase in mass of CAC concretes in aggressive sewer acid environment. The pipe samples in manhole I to III were installed in October 2004 and mass measurement was first taken in June 2008. Thus it is possible that mass gain is not purely determined by moisture absorption from sewer atmosphere. The mass gain of CAC concrete when exposed to acidic environment is partly due to precipitation of complex calcium aluminates such as calcium

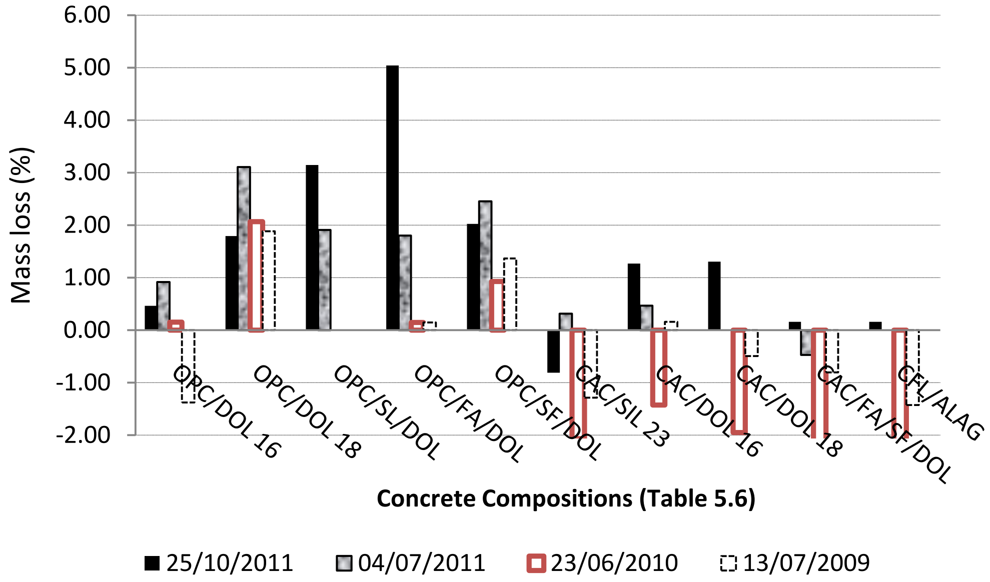

Figure 5.15 Mass loss (%) of various concrete pipe sections (lids) in Manhole III of aggressive 'live sewer'. NB: Negative mass indicates mass gain.

monocarboaluminate and calcium monosulfoaluminate in acidic pH environments less than 3.5 (Allahverdi 2000). Nevertheless, the last set of data taken (25 Oct 2011) indicated that CAC concretes have lost mass but there is less visible corrosion as illustrated by visual inspection in Section 5.7.1.

The results of the performance of each pipe section made of the same materials in all manholes are shown in Figure 5.16, although the mixes are duplicated in the manholes with at least one sample not cut due to reasons explained in Section 5.4. (Table5.4). The results are different in all manholes for the same mixes; this is probably because of other variables incorporated in site research, with the following factors partly influencing the results:

- The hydrogen sulphide gas concentration is not uniform inside the entire Experimental Section as shown in Figure 5.9
- Unlike in a laboratory, i.e. where the curing of specimens is conditioned, the conditions in a 'live sewer' are not controlled e.g. temperature changes are high, the specimens can be exposed to about 1 °C in winter and to 25 °C in summer.
- Biogenic corrosion is localised in some pipe sections because it forms on a slime layer.
- Therefore, for the above reasons, it was decided not to average the results in Figure 5.16 until a clear trend is noticed for all the specimens.

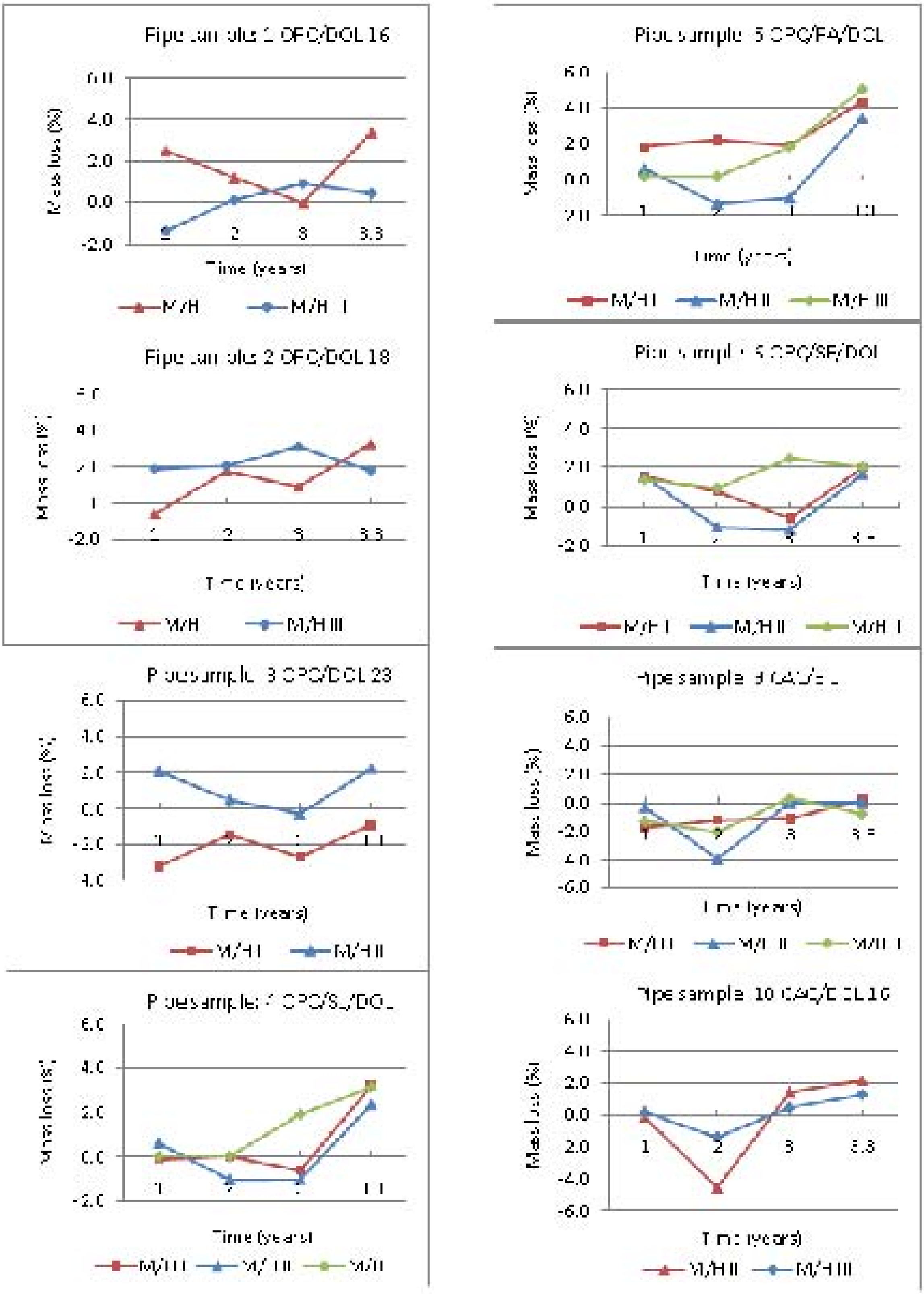

Figure 5.16 Mass loss of sewer pipe concrete (lids) due to exposure of biogenic acid attack in a life sewer (continued..)

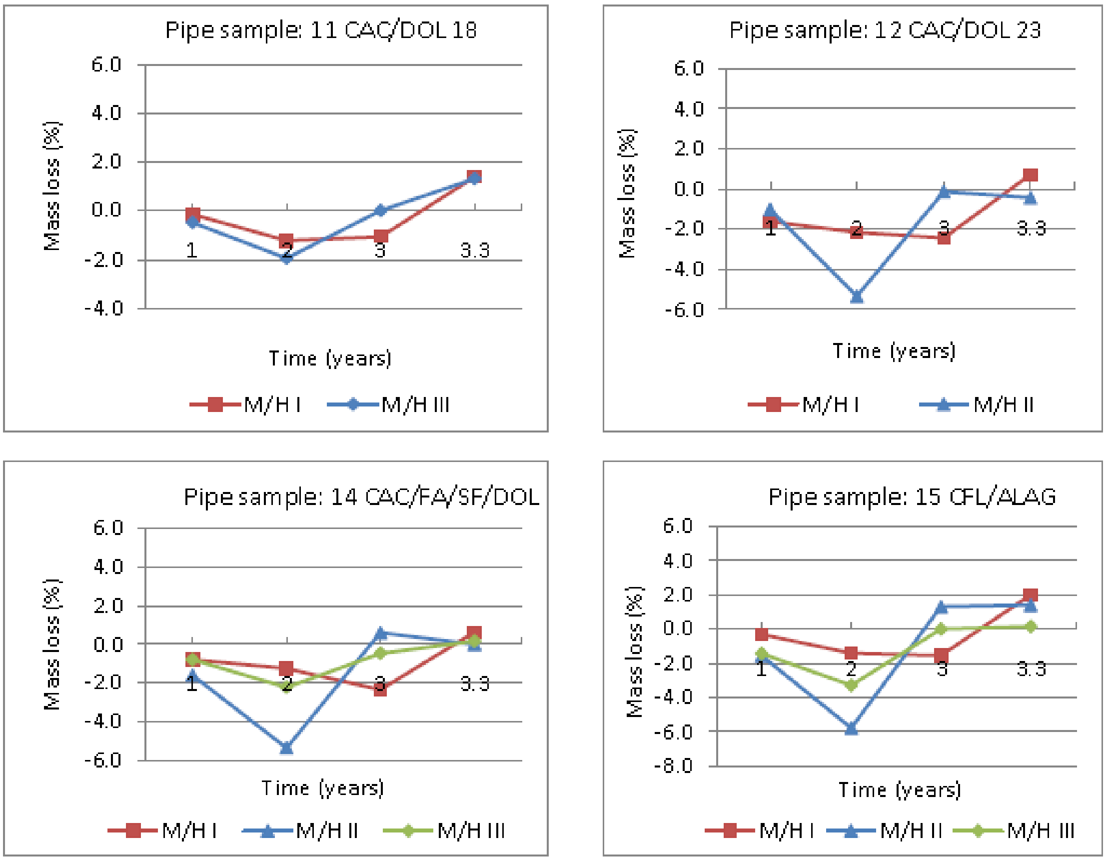

Figure 5.16 Mass loss of sewer pipe concrete (lids) due to exposure of biogenic acid attack in a live sewer.

In general, specimens in manhole I have higher mass loss than the other manholes downstream. This is because of the aggressivity of the sewer due to released hydrogen sulphide at Entrance manhole, whereby there is a high turbulence in the flow of the sewer water. The results of H_2S in Figures 5.9 and 5.10 show that H_2S in manhole II and III is lower than in manhole III. Clearly the effect of turbulence and aggressivity reduces down the Experimental Section of the sewer as shown in Figure 5.17. However, there might be a possibility that there is leaking of H_2S down the Experimental Section due to poorly sealed samples.

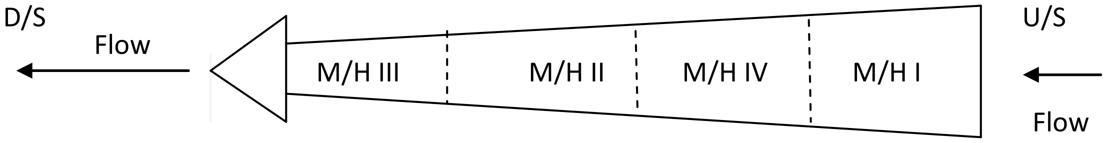

Figure 5.17 Decreasing aggressivity of the manholes down the Experimental Sewer Line to cause biogenic corrosion

5.7.1. Visual inspection of sewer pipe exposed to biogenic corrosion

Visual inspection was carried out on all the samples to indicate extent and mechanism of corrosion of these concretes as shown in Table 5.7.

Table 5.7 Physical inspection of a full – scale Experimental Sewer

MANHOLE I		**Slight Corrosion**	**Moderate Corrosion**	**Uniform Corrosion**	**Differential Corrosion**
Sample No	**Mix Composition**				
2	OPC/DOL 18		✓	✓	
3	OPC/DOL 23		✓	✓	
4	OPC/SL/DOL		✓	✓	
5	OPC/FA/DOL		✓		✓
6	OPC/SF/DOL		✓	✓	
9	CAC/SIL 23	✓			✓
11	CAC/DOL 18	✓			✓
12	CAC/DOL 23	✓			✓
14	CAC/FA/SF/DOL	✓			✓
15	CFL/ALAG	✓		✓	
MANHOLE II					
1	OPC/DOL 16		✓		✓
3	OPC/DOL 23		✓		✓
4	OPC/SL/DOL		✓	✓	
5	OPC/FA/DOL		✓		✓
6	OPC/SF/DOL		✓		☑
9	CAC/SIL 23	✓			
10	CAC/DOL 16	✓			✓
12	CAC/DOL 23	✓			
14	CAC/FA/SF/DOL	✓			✓
15	CFL/ALAG	✓		✓	
MANHOLE III					
1	OPC/DOL 16		✓		✓
2	OPC/DOL 18		✓		✓
4	OPC/SL/DOL		✓	✓	
5	OPC/FA/DOL		✓		✓
6	OPC/SF/DOL	✓		✓	
9	CAC/SIL 23	✓			✓
10	CAC/DOL 16	✓			✓
11	CAC/DOL 18	✓			✓
14	CAC/FA/SF/DOL	✓			✓
15	CFL/ALAG		✓	✓	

☑ NB: See Figure 5.22

Key:

Slight corrosion Signs of corrosion are not clearly visible but are present (Figure 5.18)

Moderate corrosion The corrosion is clearly visible, with all signs manifested (Figure 5.19)

Uniform corrosion Hardened cement paste (HCP) corrodes uniformly with the aggregate (Figure 5.20)

Differential corrosion Hardened cement paste (HCP) corroding at faster rate than the aggregate (Figure 5.21)

Similar to quantitative mass loss results, the qualitative assessment shows that CAC concretes are classified under slight corrosion whereas OPC concretes are classified under moderate corrosion. These corrosion mechanisms are explained in the key to Table 5.7. However it was noticed that OPC/SF/DOL concrete falls under both uniform corrosion in manhole I and II and also under differential corrosion in manhole III probably for the same reasons outlined in previous Section. Thus this data needs continuous monitoring probably up to 5 years until a proper trend is noticed for conclusive decisions.

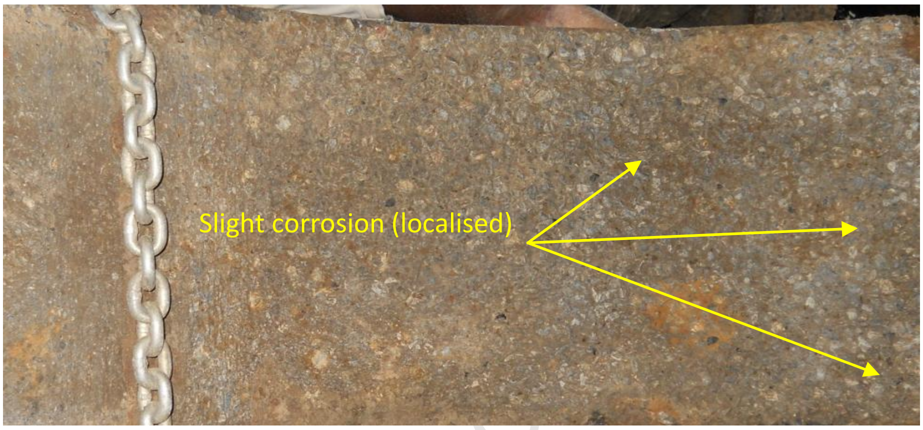

Figure 5.18 Slight corrosion of a CAC/SIL concrete in Manhole I with aggregates surfaces exposed. Pipe sample was installed in October 2004.

Figure 5.19 Moderate corrosion of OPC/FA/DOL concrete in Manhole III with aggregate particles clearly visible. Pipe sample was installed in October 2004.

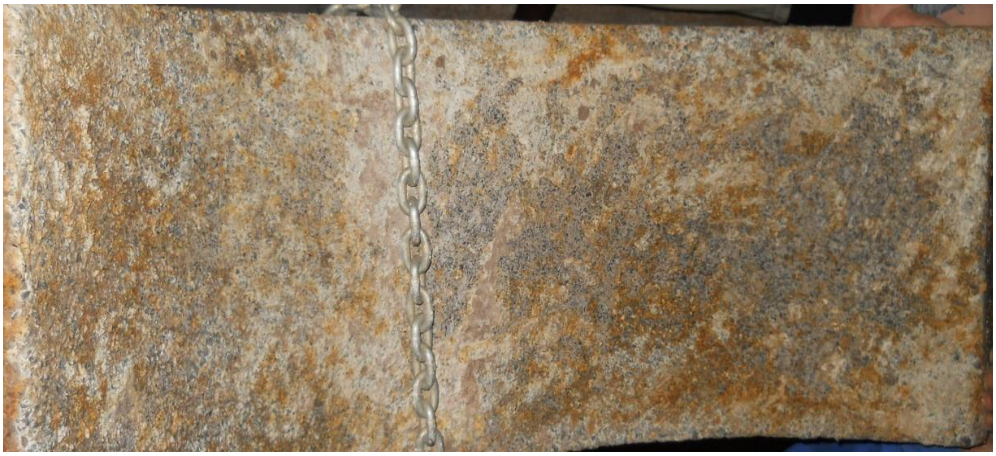

Figure 5.20 Uniform corrosion CFL/ALAG in Manhole III with no protruding aggregates but with significant mass loss. Pipe sample was installed in October 2004

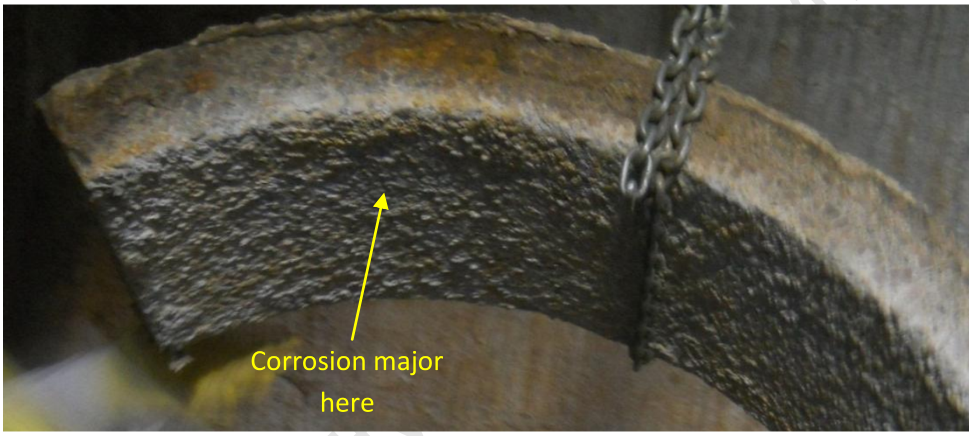

Figure 5.21 Differential corrosion of OPC/DOL 23 concrete in Manhole I due to varying acid solubility of aggregate and cement paste leading to protruding of dolomite aggregate. Pipe sample was installed in October 2004

The OPC concrete using dolomitic aggregate performs better than that using siliceous aggregate (Fourie 2007, Goyns. 2010). However, in OPC/FA/DOL concrete, the cement paste was attacked more leaving the aggregate exposed (Figure 5.19) and this is because of difference in acid solubility of the dolomite and hardened cement paste. The OPC concrete still had high neutralisation capacity to counteract the acid attack, but it lacks the ability to stifle the bacterial growth as CAC concrete does (Goyns, 2010).

Differential corrosion is also noticed between two pipe sections as shown in Figure 5.22; where there is entrapment of H_2S, due to unequal thickness of the specimens. The corrosion at this location is high, probably because of conditions such as moisture and optimum temperature suitable for habitability of *Thiobacillus* species converting H_2S to sulphuric acid. The gaps between the pipe samples installed in the manholes were considered small and did not make any allowance for the placing of internal sealants, however since the corrosion has manifested in such spaces, it is a requirement to use the joint sealant so corrosion can happen only inside the pipe.

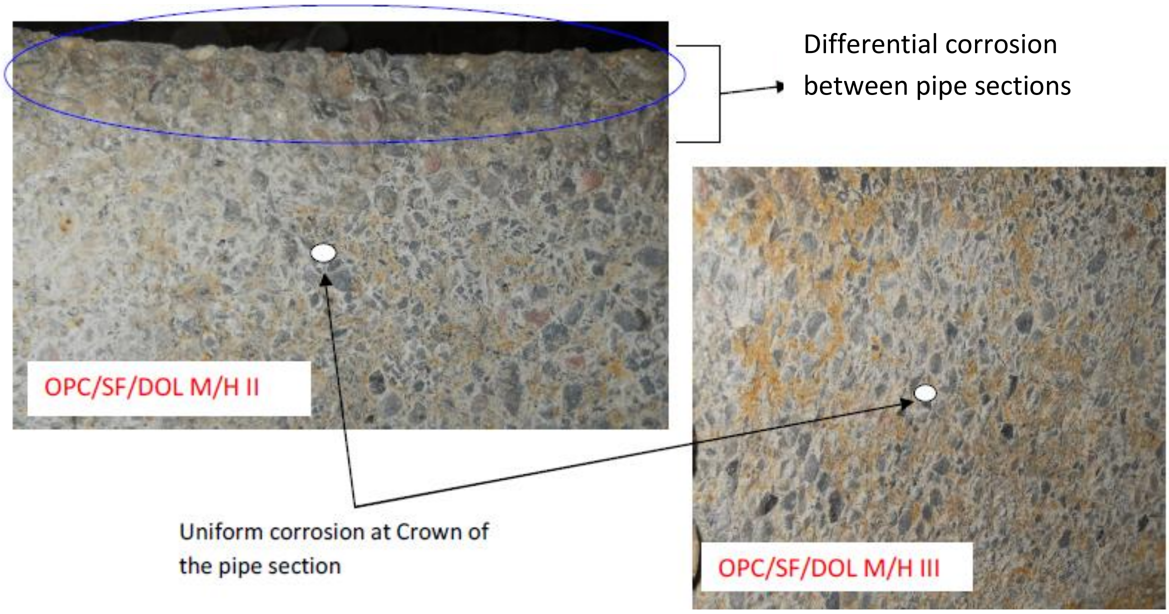

Figure 5.22 Differential corrosion visible between lid pipe sections due to entrapment of hydrogen sulphide, and conditions habitable for *Thiobacillus* species.

5.7.2. Effect of cement content (16 %, 18 % and 23 %)

The effect of cement content on acid resistance of concrete has been mentioned in Section 2.4.2. Low cement content increases acid resistance of concrete. This effect is clearly visible in Manhole III, as shown in Figure 5.15 whereby mass loss of 16 % cement content OPC/dolomite aggregate concrete is less than 18 % cement content concrete. Concrete with high cement content ultimately results in a more porous corroded layer promoting acid diffusion than concrete with less cement content (Beddoe, 2005). The overall acid uptake becomes high, hence promoting high rate of acid attack. However, in manhole I and II, the converse is true. Therefore, the results found in three manholes regarding this variable are not conclusive at this stage of the research; maybe more exposure time in biogenic acid attack is needed to clarify the trends.

The effect of cement content is not visible for CAC concrete at present because of slight corrosion as illustrated by visual inspection in Table 5.7. However, the same effect is expected as in OPC concrete in sewer pipe environment with pH = 1.0 or less. Although the hydration products of CAC are stable in acid attack, this is limited to a certain extent at pH =3.5. The use of low cement content does not only improve acid resistance, it also reduces the cost. However, the cement content of CAC does not have to be less than 400 kg/m^3 because of thixotropic properties of wet CAC concrete and for good placement purposes (Scrivener 2001). In the end CAC is a hydraulic binder as well and will not resist attack forever.

5.7.3. Effect of supplementary cementitious materials

The mass loss of OPC/SL/DOL concrete specimens due to biogenic acid attack is moderately less at about 3 % from data taken in October 2011, compared with the highest value of 4 % for OPC/FA/DOL concrete. The OPC/SL/DOL concrete has significant acid resistance with the aggregate and cement paste corroding at the same rate as illustrated by physical inspection in Table 5.7. The addition of slag to OPC concrete is generally found to increase acid resistance of concrete with pH range 4.0 – 5.5 in mineral acid test (Swamy 1986). This resistance to acid attack might be due to reduced diffusivity of mobile hydrogen ions as determined by high oxygen pemeability index of 10.35 and low sorptivity value of $3.89\ \mathrm{mm}/\sqrt{\mathrm{hr}}$ (Fourie 2007). Uniform corrosion of sewer pipe concrete is one desired property for longer service life of sewer pipe and this is achieved if neutralisation capacity of dolomite concrete matches that of the cement paste.

The OPC/FA/DOL concrete performs relatively poorly compared to OPC/SF and OPC/SL blends, having highest mass loss compared to other mixes in the sewer from data in October 2011. Qualitative data outlined in Table 5.7 also shows the poorer behaviour of OPC/FA concrete is an acid attack as the corrosion mechanism is differential i.e. hardened cement paste corrodes at a faster rate than the aggregate. This is probably because of reduced neutralisation capacity due to addition of acid insoluble fly ash as described in Section 4.9. This concrete has little or no effect on the stifling of *Thiobacillus* bacteria.

OPC/SF/DOL concrete performs moderately well in biogenic acid attack with low mass loss of about 2 % as at weighing done in October 2011. Qualitative data in Table 5.7 also shows that the mechanism of corrosion is uniform which is preferred in sewer pipe applications as compared to differential corrosion of aggregates and cement paste. OPC/SF/DOL concrete performs better than either fly ash or slag blends for the same dolomite aggregate. This is probably due to refined microstructure with absence of ITZ as a result of pozzolanic reaction of silica fume and more calcium silicate hydrate that results in reduction of portlandite (Chandra, 2002). Interestingly, OPC/SF/DOL concrete is more acid resistant in a dynamic hydrochloric acid test than in the biogenic acid attack and this is probably because of high impermeability and fine filler effect when exposed to an acid solution at pH = 1.0. A visible corrosion in a 'live sewer ' was shown in Figure 5.22, Biogenic sulphuric acid attack is mainly a surface reaction because mobilisation of H^+ ions is probably inhibited due to high impermeability of OPC/SF/ DOL concrete.

The CAC concrete mixes are generally performing well so far with mass loss of less than 2 % for CAC/DOL concretes and zero mass loss for a ternary mix (CAC/FA/SF) and CAC/SIL concrete. Although the latter concretes do not show any quantitative proof on mass loss due to gaining weight, the signs of corrosion are visible and are classified as 'slight corrosion' by visual inspection in Table 5.7. The use of fly ash and silica fume in CAC mixes is described earlier in Section 4.7.3 to increase Si/Al ratio that lead to an increase in the content of hydration product (C_2ASH_8) stratlingite which concurrently reduces aluminium hydroxide (Hidalgo *et al.,* 2009). However, the performance of these concretes in biogenic acid attack will be fully analysed when enough data on acid resistance if available.

5.7.4. General discussion

There is a high variability in mass loss for all the concretes across all three manholes, probably due to variables such as moisture, temperature, BOD etc. (Section 2.4.3.3). The varying concentration of hydrogen sulphide in the manholes is one obvious factor that may lead to this variability (Figure 5.10). It is clear that mass loss alone is not sufficient for predicting acid resistance of the sewer pipes in a 'live sewer', because the CAC concrete samples have started corroding but their mass loss was close to zero because these concretes first gained mass when exposed to biogenic acid attack. Various techniques such as physical assessment i.e. visual inspection are crucial in comparing to quantitative data.

In terms of updating the Life Factor Method (LFM), the worst-case scenario probably needs to be considered i.e. the specimens that have corroded more. Average of corrosion values may not be the best selection because the conditions (temperature, wetting and drying) in the sewer are natural and not controlled and this leads to high variability.

Although hydrogen sulphide used for prediction of corrosion rate by the LFM is based on the effluent concentration of the sewage, the attack is mainly caused by the gas concentration in the atmosphere of the pipe. In addition, the variability of mass loss for the same specimens in different manholes as shown in Figure 5.13 to 5.15 dictates that various strategies may be helpful to fully predict and assess corrosion rate using both quantitative method (LFM), qualitative method (physical inspection) and technology (CCTV camera or laser profiling) (Figure 5.23). Physical inspection method may assess corrosion where other methods fail, for instance if pH of the sewage drops to a certain level corrosion of the sewer invert can happen and CCTV may not capture this location because it is below the water line. Physical inspection can also assess the corrosion in between the lids where CCTV cannot reach, and the LFM does not take into account long retention time of the gas at such location.

All these methods can be compared to LFM method and the results must complement each other, if not certain adjustments e.g. safety factors may be applied before any pipe material can ultimately be used in design or recommended as acid resistant concrete.

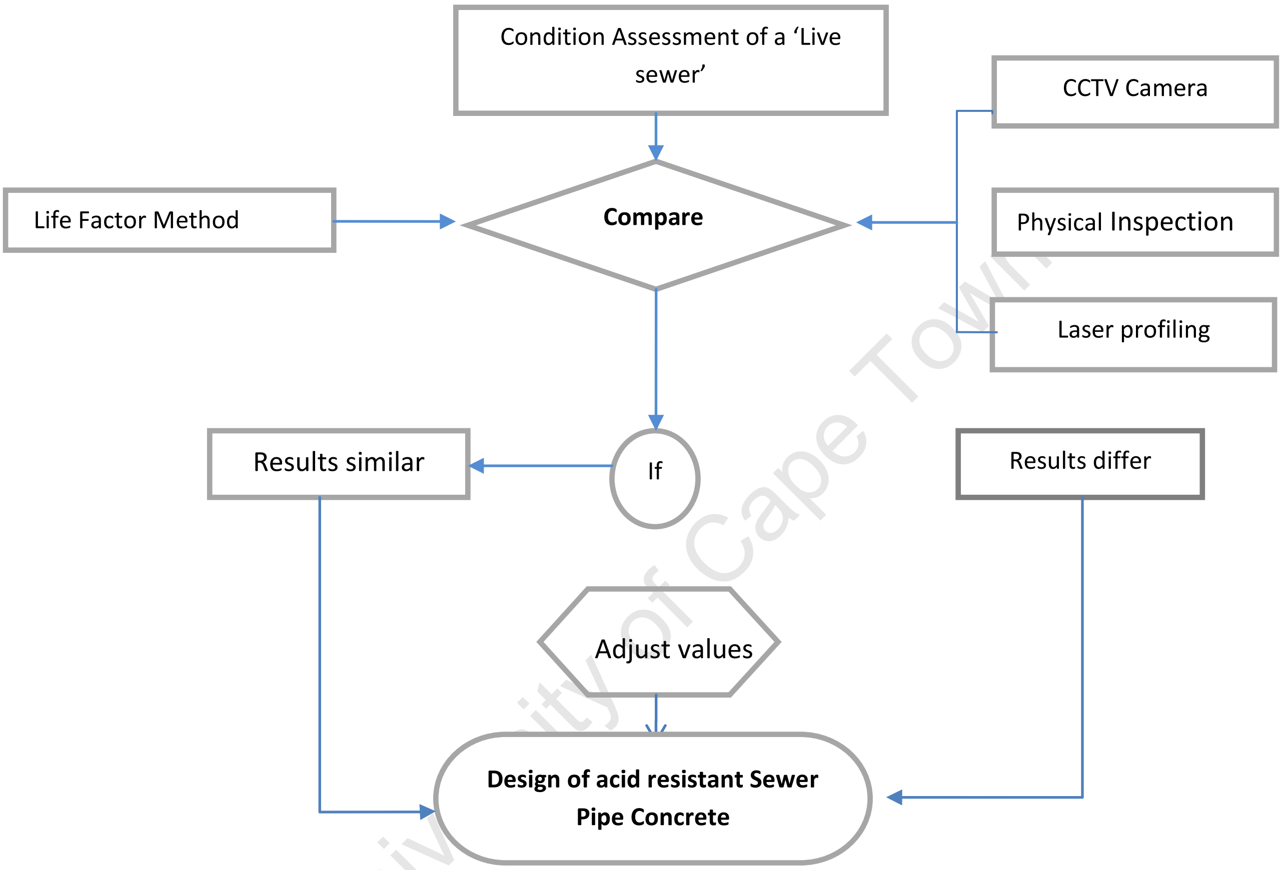

Figure 5.23 Complementing the Life Factor Method with other assessment technologies including physical inspection of the sewers such as mass weighing (Adapted from Goyns, 2010)

5.8. Assessing the resistance of small cylindrical specimens in a 'live sewer' acid attack

The mass loss of the (80 mm diameter by 45 mm) cylindrical samples from UCT is presented in Appendix D.3. However these samples have only been installed in the sewer in April 2011 and thus far have only been gaining mass probably because of moisture absorption. However, the initial results indicate that PC/FA, ternary mix and CAC/SL concretes have highest mass gain (data measured in October 2011) Figure 5.24. The mass gain corresponds roughly to the trend in water absorption values, in Table 4.14, 4.16 and 4.18 for PC concretes, CAC/fly ash and CAC/ggbs concretes respectively. Biogenic corrosion is a long term process, and there is not much information available to analyse their acid resistance and/or rate of acid attack in a 'live sewer' as of yet.

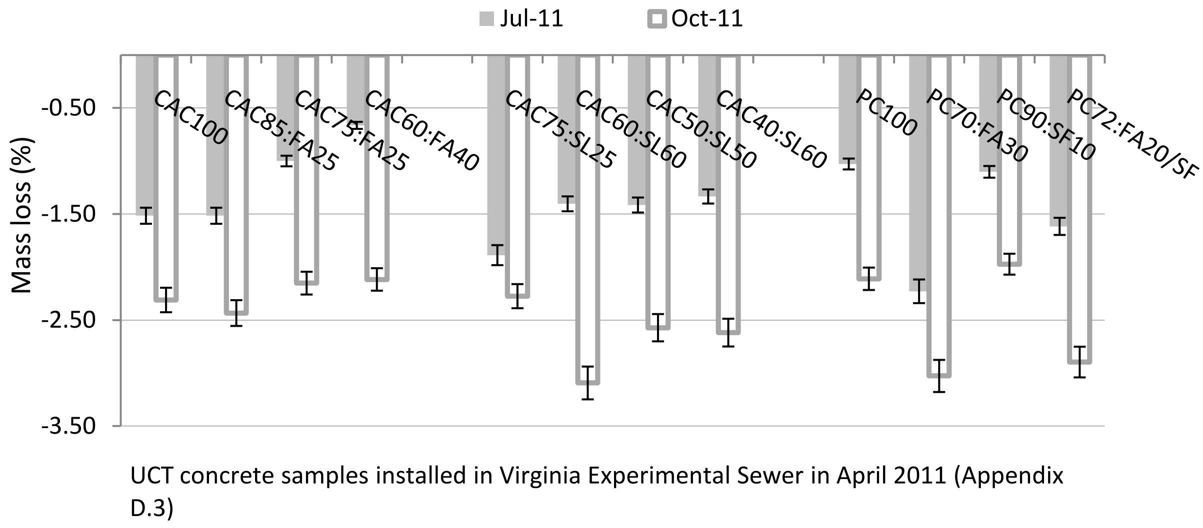

Figure 5.24 Mass gain of small cylindrical samples (80 mm diameter × 45 mm) installed in Virginia Experimental

5.9. Findings at Virginia Experimental Sewer and general conclusions

- High corrosion occurs at daily average sewage flow (Fourie, 2007), whereby suspended abrasive particle in the sewer abrade and deteriorate concrete and expose new surfaces for further attack. A dynamic hydrochloric acid test developed at University of Cape Town to simulate this effect but does not simulate the biogenic corrosion at the crown of the pipe.

- Generally, there is an increase in mass of CAC concretes in aggressive acid environment due to formation of complex aluminates, the CAC concretes are also found to perform better than respective OPC concretes because of high neutralisation capacity and its effect on bacterial colonies. However, the data in October 2011 indicated that CAC concretes have lost mass but there was less visible corrosion as compared to OPC concretes.

- The OPC/FA with dolomite aggregate does not improve the biogenic acid resistance of the sewer pipe concrete

- There is high variability in the mass loss of all concrete types across the three manholes.

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Chapter 6: Conclusions, limitations and future related work

6.1. Introduction

The primary objective of the research was to investigate acid resistance of various cementitious materials under both simulated conditions in the laboratory and 'live sewer' conditions in order to implement the Life Factor Method via inclusion of a material factor (M_F) for different pipe materials. However, duplicate samples of those tested in a laboratory and installed in a 'live sewer' have not corroded and form part of the ongoing work at Virginia Experimental Sewer. The various binders used comprised 1) blends of calcium aluminate cement with fly ash and ggbs, 2) binary mixes and ternary mix comprising Portland cement, fly ash and silica fume. The physico-chemical properties (strength, porosity, permeability and acid insolubility) of the concretes made with these blends were also investigated to determine if the concrete can be applied for use in sewer pipes. The secondary objective of the research was to monitor the hydrogen sulphide in the sewer where the specimens are installed. The study was also to investigate the biogenic acid resistance of the concrete pipe sections at the crown, represented by the lids for specific pipe materials.

6.2. Mechanical properties of Portland cement concrete blended with cement extenders

The compressive and tensile splitting tests performed on all the samples were used to assess the quality of the concrete, its compaction efficiency and potential to cracking /fracture at early age of a pipe immediately after steam curing in a plant. The latter was assessed by both tests in laboratory after 14 hours in hot water bath (38 °C), the former was assessed by compressive strength at 28 days. A plain PC concrete had higher early strength than blended cements due to rapid strength development and high heat of hydration from hydraulic activity of the cement. Although the reaction involving silica fume is rapid and no long curing period is necessary before desired strength is achieved, strength development of silica fume is noticeable after 3 days. After 28 days of air curing, a 10 % silica fume concrete mix had 10 % higher compressive strength than PC concrete, and a ternary mix had 17 % less compressive strength, the reduced strength is attributed to the curing sensitivity of fly ash. Superior compressive strength of silica fume concrete was attributed to high pozzolanic reactivity of silica fume and properties of the hardened cement paste formed thereof.

6.3. Properties of concrete made from calcium aluminate cement blended with cement extenders

The workability of CAC: fly ash system is better than that of plain CAC concrete and makes compaction easier, whereas CAC: ggbs systems are stiffer than the plain CAC concrete and would need some superplasticers for easing compaction. The use of fly ash and ggbs cause a significant reduction in hardening properties of CAC concrete due to formation of the hydration product (C_2ASH_8) stratlingite that has very low strength development. This is noticed by reduced compressive and tensile strengths for blended CAC concrete at early age, which are considered low for sewer pipe application. However, due to high cost of CAC, the blended mixes are only to be used as a liner in sewer pipes while the structural capacity is totally carried by a host pipe. Although CAC concrete is known to undergo conversion, the CAC concrete blended with silica bearing additives (fly ash and ggbs) is found not to undergo any conversion mechanisms thus making its applicability robust in aggressive environments. However if plain CAC used as a host pipe or structural applications, a control test specimen must be allowed to undergo conversion then the compressive strength of that control be used for design.

The use of fly ash and ggbs replacements in CAC concrete does not improve durability indeces values. Generally, the CAC concretes had low OPI values of < 10 and high sorptivity values of > 11 $\mathrm{mm}/\sqrt{\mathrm{hr}}$ for CAC/FA specimens and > 9.5 $\mathrm{mm}/\sqrt{\mathrm{hr}}$ for CAC/SL specimens. The high permeability of CAC concretes is thought to be the result of continuous pores since their porosities were roughly less than those of equivalent Portland cement concretes. The lower porosity of CAC concretes results from hydration reactions which use high proportion of mixing water for its high early strength development than PC concrete and thus reduces the free water, which forms the voids.

6.4. Acid attack of blended Portland cement concrete

Portland cement concrete performs better than CAC concretes in highly aggressive laboratory hydrochloric acid resistance tests at pH =1.0 on the basis of mass loss and hydrogen ion consumption. This is because below pH 4.0 the hydration products of CAC react with acid (Scrivener, 1999). However, in a 'live sewer' it is the opposite case. The behaviour is due to high content of Portlandite from the hydration of the Portland cement concrete that readily reacts with sulphuric acid and has no effect on stifling bacterial colonies. Thus, it shows that the bacterial activity in biogenic acid attack is a major factor in the deterioration of the sewer pipe concrete.

In a laboratory acid resistance test, a 30 % fly ash concrete has high mass loss due to fall out of acid insoluble particles as reflected by acid digestion test SANS (6242, 2008) with acid insolubility of 23.52 % as compared to 19.94 % of PC concrete for the same w/c ratio. This is a similar trend to that in a 'live sewer' whereby PC/FA/Dol is found to have the highest mass loss of about 5 % compared to other concretes, with corrosion of the hardened cement paste and a dolomite not being uniform, the cement paste having the highest rate of corrosion. Fly ash does not improve acid resistance of the sewer pipe concrete. A 10 % silica fume concrete mix is found to perform well in aggressive acid solution at pH =1.0 with similar low mass loss and hydrogen ion consumption to that of a ternary mix (PC/FA/SF). This can probably be explained in terms of refinement of the microstructure and fine filler effect of silica fume.

The rate of aggregate dissolution in relation to binder dissolution is a factor, leading to fall out of acid insoluble particles of the aggregates. The acid insolubility test (SANS, 6242) does not reflect these features. It is noticed that silica fume concrete mixes have less mass loss due to interaction of binder-aggregrate and inferred absence of interfacial transision zone. This feature of silica fume concrete mix is also found useful in a 'live sewer' whereby an PC/SF/DOL concrete has significantly less mass loss compared to other PC concretes (Section 5.6). The use of ggbs in blended PC/dolomite concrete is also found to perform well in aggressive 'live sewer' with less mass loss. The visual inspection of this concrete showed a uniform corrosion which is a desired failure mechanism compared to differential corrosion of aggregate and cement paste.

6.5. Acid attack of blended calcium aluminate cement concrete with cement extenders

A converted CAC concrete has substantially higher acid resistance than unconverted plain CAC and CAC blended with fly ash and ggbs because of increased alumina gel from the conversion reactions and stable hydration products. Thus, the high acid resistance of CAC concrete in aggressive environments is not a function of its porosity or permeability, but of its hydration products.

The blended CAC concretes had higher acid resistance than unconverted plain CAC concrete. The use of supplementary cementitious materials (SMCs) reduces the content of alumina gel i.e. neutralisation capacity of the CAC concrete. Thus, during the attack the mass loss is a function of fall out of acid insoluble particles which increases the rate of acid attack. A percent replacement of CAC by SMCs needs to be optimised in terms of early age strength and acid resistance and must not be greater than 25 % and 40 % for fly ash and slag respectively. A good acid resistant sewer pipe concrete is one in which both cement paste and dolomite aggregate corrodes uniformly without protruding of the aggregate during the attack. Hence, a selection of a dolomite aggregate in a given geographical area must match acid resistance of a hardened cement paste.

When determining hydrogen ion consumption or neutralisation capacity in a laboratory acid resistance test, the precipitate formation of Al_2OH_3 that results from concrete with high alumina content in a titration method lowers the accuracy of equivalent point of titration. This is typical for CAC concretes blended with fly as or ggbs, renewing the solution as early as about 12 hours or adding sodium fluoride to the solution to remove any precipitate formation as shown in Equation 6.1 and 6.2 can improve the accuracy of equivalent point during titration.

$$Al^{3+} + 3NaOH \rightarrow Al(OH)_3 + 3Na^{+} \quad (6.1)$$

$$3H^{+} + 3NaOH + 3NaF + Al^{3+} \rightarrow AlF_3 + 3Na^{+} + 3H_2O \quad (6.2)$$

6.6. Monitoring of hydrogen sulphide in a 'live sewer'

The hydrogen sulphide (H_2S) gas concentration was measured in four locations at Virginia Experimental Sewer, namely the Entrance Manhole (near the end of a rising main), Manhole I, II, III and IV. There is a hight H_2S concentration at the Entrance Manhole up to 100.0 ppm, and highest of 108.2 ppm in Manhole I. The other manholes II to IV have less maximum gas concentrations 50.8 ppm, 53.1 ppm, 48.9 ppm for Manhole II, III and IV respectively. The high concentrations in Manhole I similar to that of Entrance Manhole is due to high turbulence due to a curve at the end of rising main and the start of the Experimental Sewer. The lower concentration in downstream manholes maybe due to: 1) dissipation of the gas in large Entrance Manhole 2) the ventilation chambers located on it and 3) reduction in turbulence at downstream manholes.

6.7. Biogenic sulphuric acid attack of sewer pipe concrete

There is a high variability in the mass loss of all concrete pipe sections (lids) across the three manholes for the same concrete composition. This is probably because uncontrolled conditions such as gas concentrations that keep changing within the sewer, temperature, and the *Thiobacillus* bacteria that may not be found across all samples. In addition, the biogenic corrosion is localised in one pipe sample. Thus, mass loss alone is not enough to predict the rate of corrosion in sewer pipes due to its high variability in duplicate specimens used in different manholes.

The laboratory physico-chemical tests, permeability, acid insolubility and acid resistance were performed on all concretes i.e. PC with blended additives (fly ash, silica fume) and CAC blended with (fly ash and ggbs). The results showed that all PC concretes have high oxygen permeability index in the range 10.55 - 10.95, water sorptivity in the range 3.2 – 6.1 mm/$\sqrt{\mathrm{hr}}$ indicating less permeability of potential aggressive ions. CAC concrete has the higher permeability but performs well in biogenic acid environment. In general acid resistance of a sewer concrete pipe is a complex phenomenon that involves full attention to selection of the most appropriate materials and their mix proportioning. Thus based on the study done in the laboratory and the Virginia Experimental Sewer, an acid resistant concrete pipe can be produced by following a flowchart in Figure 6.1.

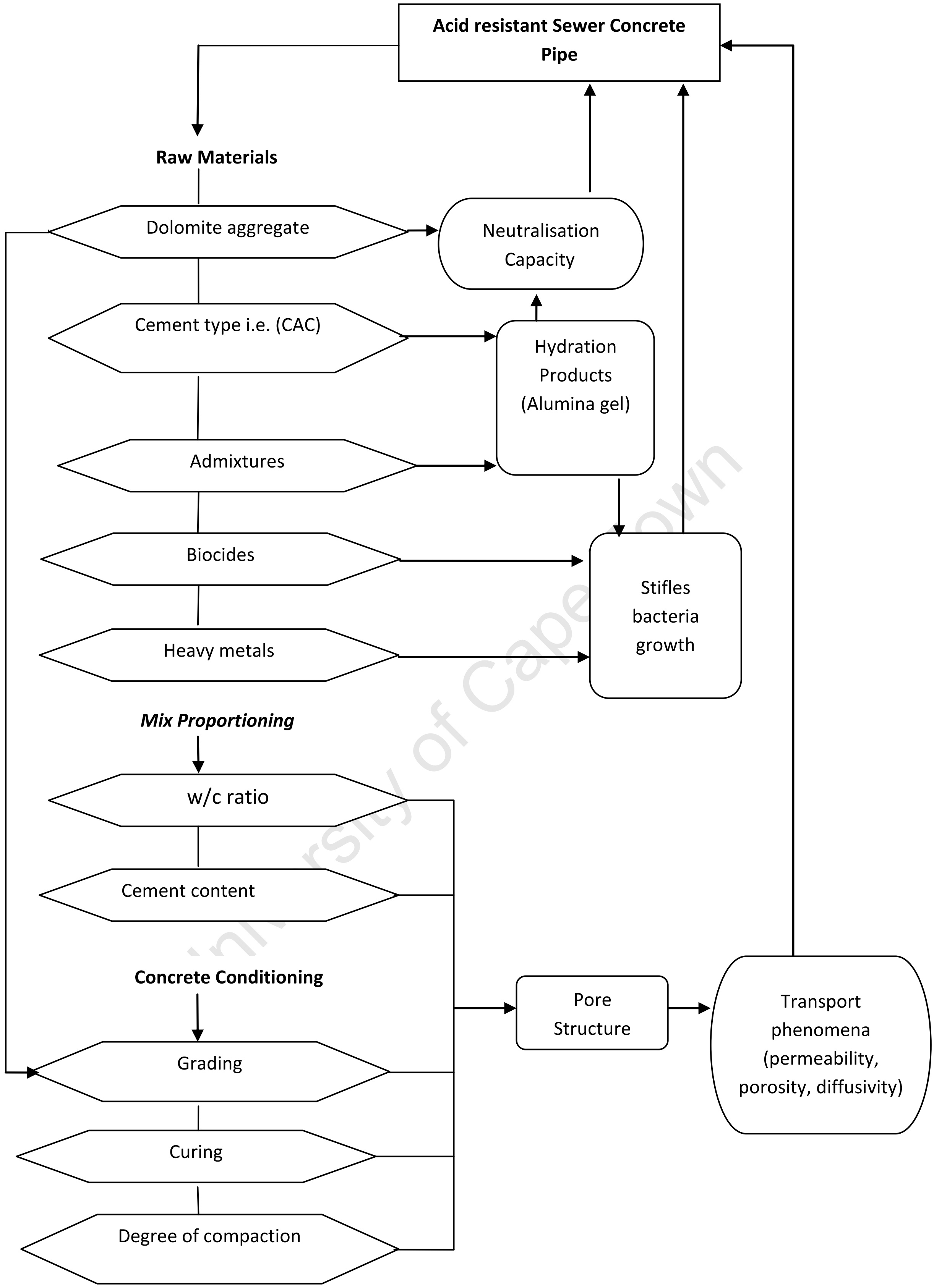

Figure 6.1 Flow diagram showing improvement of acid resistance of sewer pipe concrete based on the input parameters, physico –chemical properties of the concrete and external factors

This figure shows the most important factors that produce a competent sewer concrete pipe in aggressive acid attack.

6.8. Limitations of the research

Part of the research was to present a case study on the performance of various concrete types with various cement/aggregate types that had been installed in a ‘live sewer’ for seven years since 2004. In this study it was only the material performance that was discussed and analysed. The acid resistance of the concrete pipe sections (lids) in a ‘live sewer’ was analysed in terms of mass loss, and visual inspection. These two techniques alone cannot successfully determine acid resistance of the sewer pipe concrete. Mass loss only measures the rate of acid attack due to removal of the particles in an acid attack. Mass loss is a function of both the acid dissolution and fall out of acid insoluble particles in a concrete. There is a high variability in mass loss in different manholes for concretes made of the same materials.

Biogenic corrosion is a long-term process that takes years and assessing the acid resistance of the specimens that were cast in the laboratory in 2010/2011 was not possible in a project of relatively short duration i.e. 18 months. Such specimens are presented in Appendix D.5. The study could not develop a biological test method that compares with confidence the hydrogen ion consumption of the specimens in hydrochloric acid test to the performance of concrete specimens in aggressive sewer environment of the *Thiobacillus* species.

Hydrogen sulphide gas is converted to sulphuric acid in a sewer pipes to cause corrosion. In this study the gas concentrations was not monitored fully over A period of a year to get its profile in all seasons of the year, months, days and nights. This could help to get accurate concentrations for design. However, it must be noted that gas concentration is a function of the hydraulic design, temperature, BOD. The Virginia Experimental Sewer may be taken representing the more aggressive environment of most sewers in South Africa because of the major conditions responsible for a biogenic corrosion as discussed in Section 5.3.

6.9. Recommendations for future research

Mass measurement of the lids in the sewer has specific challenges i.e. some specimens especially CAC concretes expand making it difficult to fit back the last specimen after weighing, and this can cause material loss to a certain extent. The results of mass loss are not conclusive at this stage due to high variability. Advanced techniques such as laser profiling, and CCTV inspection may be implemented in the future to assess the corrosion and its depth without having to remove the samples for visual inspection. This would make the inspection easier and less risky to individuals doing the job.

The physical properties of corroded sewer pipe concrete are different from that of uncorroded pipes due to existence of products of corrosion and/or a change in mineralogy etc. It was in the interest of the author to do some petrographic tests and analyses on corroded concretes from the sewer in terms of various minerals present, and compare these to controls i.e. duplicate uncorroded specimens. This is highly recommended in the future work along with the biogenic acid attack research in a 'live sewer' at Virginia when biogenic acid attack is prominent.

The thickness of the lid sections has not changed much since the installation of the pipes as the corrosion has only recently manifested itself; it is changing as corrosion progresses and will have to be measured in the near future. Thickness measurement is important information to incorporate into material loss due to corrosion because this changes certain parameters in a Life Factor Method i.e. pipe diameter. Monitoring of hydrogen sulphide must be done over extended periods of at least a year across all seasons of the year.

There was a difference in the concentration of H_2S in all manholes along the Virginia Experimental Sewer due to: dissipation of the gas in large entrance manhole, the ventilation chambers located on it and reduction in turbulence at downstream manholes in the pipeline from the entrance manhole. However, in the near future quality control must be ensured so there are no leakages down the Experimental line to add to this loss.

Future studies must implement corrosion rate of the specimens so that material factor (M_F) of various concretes installed in the Virginia Experimental Sewer can be developed. The results from the acid resistance test must be compared critically to those of the specimens in the sewer to compare mass loss, bearing in mind that mass loss is also measure of abrasion loss and fall out of acid insoluble particles. The corrosion at the crown of the pipe in the sewer on the other hand can be compared to the results of hydrogen ion consumption from the acid resistance test because this represents the attack due to acid dissolution. The raw data i.e. mass measurement is recorded in Appendix D.1 to D.3 for all existing samples in the manholes of Virginia Experimental Sewer for future reference. The monitoring of small cylindrical samples cast at UCT is also an ongoing study that must be reported in future studies.