ACID RESISTANCE OF SEWER PIPE CONCRETE

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A dissertation submitted to the Faculty of Engineering and the Built Environment, University of Cape Town, South Africa, in fulfilment of the requirements for the degree of Master of Science in Civil Engineering

Wallingford, England, United Kingdom, 2007

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ABSTRACT

A hydrochloric acid solution laboratory test was developed to assess the resistance of concrete used in the manufacture of pipes to sulphuric acid environments encountered in sewers. A hydrochloric acid solution (pH of 1,00) simulates the attack on concrete sewer pipes at the average daily sewage level region and in severely corrosive sulphuric acid environments (pH of less than 1,00) commonly encountered in South African sewers. Calcium sulphate, which precipitates in a sulphuric acid solution and masks further attack, is eliminated simulating the constant dissolution of the precipitate at the average daily sewage level region and loosely attached precipitate in the severely corrosive sewer environments. A straightforward procedure is used to determine the acid resistance of dolomite aggregate concrete used in the manufacture of sewer pipes for exposure to sulphuric acid sewer environments. Acid resistance and neutralisation capacity of the concrete are measured as functions of mass loss and hydrogen ion consumption with time (over a period of approximately 96 hours or less). A procedure to determine the acid resistance of siliceous aggregate concrete requires a longer test period (approximately 200 hours or more).

A concrete containing calcium aluminate cement and a synthetic alag™ aggregate made from the calcium aluminate cement clinker gave the best resistance to the hydrochloric acid solution (pH of 1,00) and a severely corrosive biologically-induced sulphuric acid environment (pH of less than 1,00). A similar concrete containing dolomite aggregate gave poorer resistance to the respective solutions. A dolomite aggregate concrete containing calcium aluminate cement gave better resistance in the biologically-induced sulphuric acid environment than a similar concrete containing ordinary portland cement but both concretes were of similar resistance in the hydrochloric acid solution. A poor quality dolomite stone (low strength and high porosity), which fractures during pipe manufacture gave poorer resistance in the hydrochloric solution than a concrete containing a sound dolomite stone but better resistance in the biologically-induced sulphuric acid environment. Concrete containing siliceous aggregate gave the poorest resistance to both the acidic environments.

Assessing acid resistance using the hydrochloric acid solution test method illustrates the manner in which the physical and chemical properties influences the attack and dissolution of concrete in an acidic environment, which is crucial in the development of a sewer pipe concrete to resist and neutralise a biologically-induced sulphuric acid sewer environment.

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Professor Mark Alexander for his assistance and patience during the completion of this thesis. I am grateful for the support and financial assistance giving to me from the various concrete industries and organisations in South Africa namely, The Concrete Pipe Association of South Africa, Lafarge Aluminates, Fraser Fyfe, Rocla, Concrete Units, Council of Scientific and Industrial Research and The Cement and Concrete Institute of South Africa. A special thanks to the Virginia Municipality in particular Mr Kassie Botha for their assistance and allowing me to tests on-site at the Virginia Experimental Sewer Line. I thank the staff and students whom assisted with the research within the Department of Civil Engineering at the University of Cape Town namely the workshop and laboratory staff, Mr Ike von Geurrard, Mr Charles Nicholas, Mr Charles May, Mr Noor Hassen and Mr Dennis Botha.

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CHAPTER 1

INTRODUCTION

1.1 Background

Concrete, traditionally the material chosen for the manufacture of medium to large sewer pipes, performs poorly in sulphuric acid environments generated in sewers commonly located in areas of flat topography and warm climate. Sulphate-reducing bacteria thrive in anaerobic zones formed within the sewage, and generate sulphide some of which escapes into the sewer atmosphere as hydrogen sulphide. Aerobic bacteria present in moisture condensing on the sewer walls above the sewage utilise the hydrogen sulphide. Oxidation of the sulphide to sulphuric acid releases energy required for their growth. Sulphuric acid attacks the acid-soluble components in concrete such as calcium hydroxide and other cement hydration products. Concrete disintegrates exposing the steel reinforcing, which corrodes leading to the eventual collapse of the sewer.

Sulphuric acid environments are common in sewers located throughout South Africa. Certain areas are flat, which necessitates pumping of sewage over long distances. In addition, a warm climate enhances activity of the bacteria, and the long retention times deplete the oxygen in sewage retained in sumps and rising mains. Anaerobic conditions develop leading to the generation of large amounts of sulphide and sulphuric acid in the sewer. Average daily temperatures in some areas are sufficient to sustain the sulphide and sulphuric acid generation throughout the year. A continuous attack on the concrete ensues drastically reducing the service life of sewer pipes.

Sewers located in areas in which appropriate sewer design techniques cannot eradicate the factors responsible for the generation of sulphuric acid require special concrete mixtures to resist the acidic conditions. One solution is to design a mixture that neutralises the sulphuric acid generated, slowing growth of the acid-loving bacterial species responsible for the severe attack in sewers (Parker, 1945). An option is to replace any acid-insoluble siliceous aggregate with acid-soluble dolomite or limestone aggregates, which effectively increases the neutralisation capacity of concrete (Stutterheim and van Aardt, 1953).

Concrete containing dolomite aggregate nevertheless may deteriorate at a fast rate in severely corrosive environments (Kelly and Krüger, 1996). Concrete must resist and/or prevent such environments to compete with acid resistant synthetic pipe materials such as glass-fibre and high density polyethylene (Goyns, 1991). Acid resistance of the concrete may be improved with inclusions of mineral extenders or chemical additives in the mixture. Concrete containing materials such as calcium aluminate cement or anti-bacterial agents that impede the growth of the acid-loving bacteria is imperative in severely corrosive environments.

1.2 Objective and scope of research

A primary objective of the research described here was to develop a laboratory test to measure acid resistance of sewer pipe concrete, where acid resistance is the ability of the concrete to withstand and/or neutralise an acidic environment. A secondary objective was to gain an understanding of the impact of concrete composition on resistance and attack mechanisms in mineral acid solutions and sulphuric acid environments generated biologically. The scope of the investigation involved measuring acid resistance of concrete mixtures such as:-

- common sewer pipe mixtures containing dolomite aggregates
- dolomite aggregate mixtures with modified mineral additive binders
- sewer pipe mixtures containing siliceous aggregates
- siliceous aggregate mixtures with modified mineral additive binders

- special sewer pipe lining mixtures

The aims of the investigation were to determine:-

- differences in sulphuric and hydrochloric acid attack mechanisms
- appropriateness of a hydrochloric acid solution to measure acid resistance of concrete
- dependence of acid resistance on dolomite aggregate properties
- effect of siliceous aggregate physical properties on acid resistance
- differences in acid attack mechanisms on dolomite and siliceous aggregate concrete
- influence of binder modifications on acid resistance
- effect of concrete composition on growth of the acid-loving bacterial colony

1.3 Limitations of research

A laboratory test using a sulphuric acid solution to model the attack on concrete in sewers was difficult to formulate. Assessing acid resistance in a sulphuric acid solution was found to be labour intensive, time consuming and did not accurately measure the ability of the concrete to withstand and/or neutralise an acidic environment. Calcium sulphate, a sparingly soluble reaction product, precipitates onto the concrete forming a barrier, which stifles attack and prohibits direct measurement of acid resistance which is a function of the physical and chemical properties of the concrete.

Sewage continuously dissolves the calcium sulphate at the average daily water level region of a sewer pipe and constantly exposes the concrete to the sulphuric acid environment. Sulphuric acid solutions require continuous renewal to simulate the dissolution of calcium sulphate into the sewage and eradicate the effect of the corrosion layer on the attack mechanism. A straightforward test allowing rapid measurements of acid resistance requires an acid solution of similar properties to sulphuric acid but which forms soluble reaction products, for example, a hydrochloric acid solution. A hydrochloric acid solution eliminates the need to renew solutions and ensures that the attack remains entirely dependant on the composition of the concrete.

A direct comparison of the acid resistance of dolomite aggregate concrete to that of siliceous aggregate concrete was impractical using the laboratory acid test. Siliceous aggregate particles entrap corrosion debris creating a barrier, which significantly hinders attack on the cement binder portion of the concrete. A factor to compensate for the interference was difficult to derive. Variation in the sizes and shapes of siliceous aggregate particles determine the amount of debris entrapped, which influences the rate of attack.

A mineral acid solution test cannot representatively determine the acid resistance of concrete in sulphuric acid environments encountered in sewers. Sulphuric acid attack in sewers is complex and depends on numerous factors. A representative test necessitates the biological generation of a sulphuric acid solution to assess the impact of concrete composition on the activity of the acid-loving bacteria.

1.4 Outline of thesis document

A literature survey (Chapter 2) follows this introductory chapter discussing:-

- sewer corrosion
- methods to alleviate the sewer corrosion problem
- growth and metabolism of the bacteria responsible for the sewer corrosion problem
- attack mechanisms on concrete in mineral acid solutions
- improving resistance of concrete to chemical environments
- work conducted in an experimental sewer line

- validation of research

Observations on the experimental section of the sewer line at Virginia in the Free State Province of South Africa were fundamental in establishing the test conditions for a laboratory method and conducting on-site investigations.

Work for the thesis was primarily of an experimental nature requiring special techniques for the preparation, characterisation and acid resistance measurements of concrete specimens in the laboratory. Chapter 3 documents the experimental methodology followed to derive a laboratory method to measure acid resistance of sewer pipe concrete and discusses attack mechanisms:-

- formulation of a specimen preparation method
- preliminary sulphuric and hydrochloric acid solution tests
- formulation of a hydrochloric acid solution method
- attack mechanisms in sulphuric and hydrochloric acid solutions
- solubility of concrete compounds in the acid solutions
- influence of corrosion product solubility on mechanisms of attack

Chapter 4 discusses the resistance of concrete to a hydrochloric acid solution and sulphuric acid environment generated biologically namely:-

- concrete containing dolomite aggregates
- concrete containing siliceous aggregates
- concrete modified with mineral additives and special cements

Chapter 5 discusses the aggressiveness of the sulphuric acid environment generated biologically in the manhole at the onset to the experimental section of the sewer line at Virginia and the resistance of concrete to the environment:-

- hydrogen sulphide content in manhole
- pH on concrete sewer walls in manhole
- experimental methodology
- acid resistance of dolomite aggregate concrete, siliceous aggregate concrete and concrete modified with mineral additives and special cements

Chapter 6 concludes the findings of the research:-

- importance of an acid solution method to measure acid resistance of sewer pipe concrete
- correlation between laboratory and field investigation
- future research to develop a holistic solution to sewer corrosion
- limitations of the research into sewer corrosion

1.5 Definitions

Sewer corrosion refers to the biologically-induced sulphuric acid attack on concrete in sewers above the sewage level.

Biologically-induced sulphuric acid environment refers to a sulphuric acid environment generated by an aerobic sulphur-oxidising bacterial colony encountered on moist sewer walls above the average daily sewage level.

Cover concrete refers to the surface layer of a concrete structure (inside surface layer of a sewer pipe) that protects the steel reinforcement from corrosion.

Acid environment refers to a corrosive environment resulting from the dissociation of an acid that gives rise to an excess amount of hydrogen ions in solution.

Mineral acid environment refers to an acid environment resulting from the dissociation of inorganic compounds such as sulphuric acid, hydrogen sulphide or hydrochloric acid.

A strong acid is an acid such as hydrochloric or sulphuric acid that completely dissociates in solution.

A weak acid is an acid such as hydrogen sulphide that partially dissociates in solution.

Acid resistance refers to the ability of concrete to resist/neutralise an acidic environment.

Acid solubility/insolubility refers to the dissolution of concrete in an acidic environment.

Neutralisation capacity is the potential of a concrete to neutralise the hydrogen ions in an acidic environment.

Sacrificial layer refers to the additional layer of concrete over and above the cover layer inside a sewer pipe to extend the service life in a biologically-induced sulphuric acid environment.

Life expectancy refers to service life of a concrete structure in a sewer prone to biological generation of sulphuric acid.

Durability index tests measures resistance of concrete to transport of fluids and ions responsible for mechanisms of deterioration.

Performance of concrete refers to the extent that concrete resists deterioration from environmental attack.

Durability is defined as the ability of a material to withstand conditions of service for which it was designed over a prolonged period without significant deterioration.

1.6 Cement chemistry notations

The general convention for chemistry notation is used in this thesis where appropriate. However, in sections dealing more particularly with cement chemistry, the relevant convention is used, namely:-

C = CaO
S = SiO_2
A = Al_2O_3
F = Fe_2O_3

Thus, for example, CH = $Ca(OH)_2$

1.7 References

Goyns A (1991), *Sewer-line corrosion control and material choice*, Seminar on Wastewater, Sewage Effluent Design and Management, Concrete Pipe Division, Concrete Society of Southern Africa, October 1991

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Parker CD (1945), *The corrosion of concrete: 2. The function of thiobacillus concretivorus in the corrosion of concrete exposed to atmosphere containing hydrogen sulphide*, Australian Journal of Experimental Biological and Medical Science, vol. 23, pp. 91-98, 1945.

Stutterheim N and van Aardt JHP (1953), *Corrosion of Concrete Sewers and Some Possible Remedies*, Annual Convention of South African Chemical Institute, South African Industrial Chemist, no. 7, Nov. 1953

CHAPTER 2

LITERATURE SURVEY ON ASPECTS OF SEWER CORROSION

2.1 Introduction

A literature survey was necessary to obtain relevant information for the development of a test to determine acid resistance of sewer pipe concrete. Aims of the survey were to:-

- formulate an understanding of the corrosion problem in sewers
- study the growth and metabolism of micro-organisms
- review methods to alleviate the problem
- identify existing laboratory tests for measurement of acid resistance
- review existing reports on sewer investigations

The scope of this chapter is to:-

- summarise information of relevance to this research
- critically evaluate the existing literature
- compare and interpret findings in relation to this research
- identify different design philosophies
- illustrate the relevance of sewer investigations for this research

Aspects relating to sewer corrosion discussed include:-

- the generation and existence of sulphide in sewage
- release of hydrogen sulphide into the sewer atmosphere
- generation of sulphuric acid on concrete sewer walls above the sewage
- sulphuric acid attack mechanisms on concrete
- measures to combat sewer corrosion, namely sewer design, sewage treatments, coating and lining concrete pipes and improving acid resistance of concrete
- an investigation conducted by the South African Council for Scientific and Industrial Research (CSIR) at the Virginia sewer and the relevance of the work to this research

A general discussion evaluating the literature survey follows, which documents findings in relation to this research identifying the areas requiring investigation.

2.2 Sewer corrosion

Sewer corrosion in this context relates to the sulphuric acid attack on concrete surfaces above the sewage level. Conditions leading to the biological generation of sulphuric acid arise from an interrelationship and interdependence of microorganisms in the sewage (Bibb and Hartmann, 1984). A multitude of microorganisms enters the sewage through the discharge of wastewater into the sewer. Aerobic species that favour the initial conditions proliferate. Oxygen levels in the sewage decrease allowing the growth of anaerobic species responsible for the generation of sulphide. Sulphide that escapes into the sewer atmosphere supports the growth of a bacterial colony that generates sulphuric acid on the moist concrete walls above the sewage. Sulphuric acid attacks acid-soluble components in the concrete significantly reducing the service life of the sewer pipes.

2.3 Sulphides in sewage

2.3.1 Sulphide generation in sewage

Anaerobic microorganisms generate most of the sulphide in sewers. Anaerobic regions suitable for the growth of the microorganisms form in (Figure 2.1):-

- slimes layer accumulating on underwater surfaces of sewer pipes
- silt deposited at the invert of sewer pipes
- septic sewage containing no dissolved oxygen

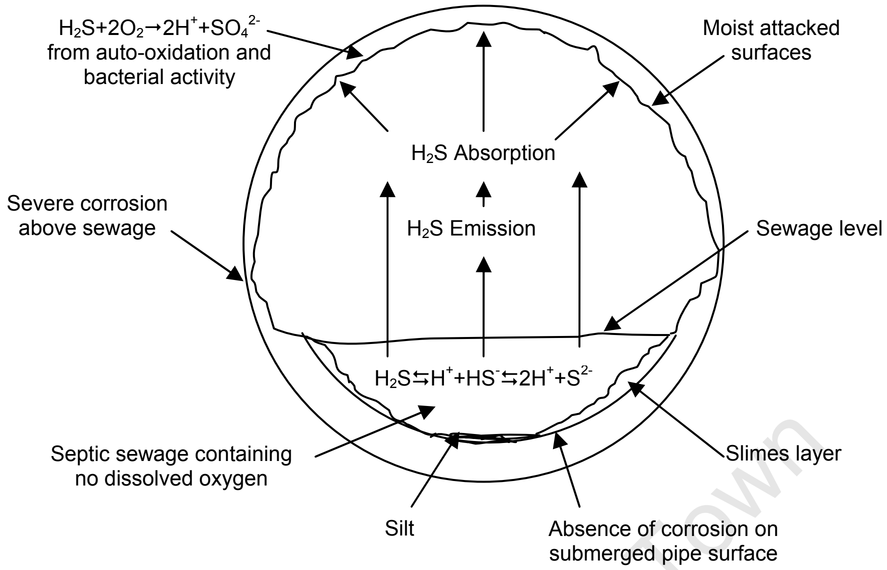

Figure 2.1 Sewer corrosion: emission and absorption of sulphide from septic sewage in a concrete pipe

Amount of sulphide generated depends on the nature of the slimes layer and the characteristics of the sewage such as age, type of flow, oxygen content, nutritional composition, viscosity and temperature (Thistlethwayte, 1972).

Slimes layers are the main source of sulphides (Pomeroy and Bowlus, 1946). Generation of sulphide rarely occurs in the body of the sewage. Sewage that flows albeit septic absorbs enough oxygen at the surface to inhibit growth of sulphide-generating anaerobic microorganisms. Sulphide generation only occurs in stagnant, septic sewage with no dissolved oxygen such as sewage contained in sumps and rising mains (Thistlethwayte, 1972). Concentration of sulphide decreases substantially once the sewage starts to flow due to the absorption of oxygen at the surface of the sewage.

A slimes layer starts to develop due to the entrapment of waste particles onto the rough concrete surface, forming a resilient primary layer. A build-up of particles continues until the layer reaches a critical thickness, which depends on the slope and geometry of the pipe, and the condition of the sewage. Slope of the pipe determines the velocity of the sewage. Sewage flows fast in pipes at a steep slope and sloughs off the particles accumulating onto the primary layer. Geometry of the pipe determines the wall shear, which increases with hydraulic radius allowing thinner layers to develop under deep flowing sewage that occurs at the invert of sewer pipes namely in large diameter pipes (Thistlethwayte 1972). Slimes layers are thicker under stale sewage due to the higher viscosity and particle content arising from the increasing bacterial activity with time.

A slimes layer developing under sewage recently discharged into a sewer consists of an aerobic zone and an anaerobic zone (American Concrete Pipe Association, 1984). Oxygen diffuses into the slimes layer forming an aerobic zone in contact with the fresh sewage. An anaerobic zone in contact with the sewer wall remains. Size of the anaerobic zone depends on the oxygen content of the sewage, which itself depends on the sewage age.

Aerobic microorganisms in the sewage consume oxygen. Oxygen molecules accept electrons (Equation 2.2) released during the oxidative breakdown of carbohydrates such as glucose ($C_6H_{12}O_6$) in water (Equation 2.1), which allows the supply of energy necessary to assimilate carbon required for reproduction of the organisms. Oxygen levels in the sewage decrease with time limiting the diffusion of oxygen into the slimes layer and increasing the size of the anaerobic zone. Slimes layers under stale sewage are entirely anaerobic due to the lack of dissolved oxygen in the sewage.

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \qquad (2.1)$$
$$6O_2 + 24e^- + 24H^+ \rightarrow 12H_2O \qquad (2.2)$$

Anaerobic zones favour the growth of strictly anaerobic bacteria namely members of the family desulphovibrio, which generate large amounts of sulphide (Stanier et al, 1971). A desulphovibrio bacterium is extremely motile consisting of a single cell 0,5 to 1,0 µm wide and 2,0 to 5,0 µm long (Figure 2.2). Organisms possess a specialised cell metabolism in which respiration to generate energy for reproduction occurs in the absence of oxygen. Sulphate (SO_4^{2-}) diffusing into the slimes layer from the sewage acts as the electron acceptor during anaerobic respiration instead of oxygen as in aerobic respiration (Equation 2.3). Sulphate reduces to sulphide (S^{2-}) generating the energy required for the oxidative decomposition of organic compounds to assimilate the carbon necessary for the reproduction of the bacterial cells. Species such as the desulphovibrio desulphuricans reproduce rapidly and are capable of generating sulphide concentrations of up to 10g/ℓ in the sewage.

$$3SO_4^{2-} + 24e^- + 24H^+ \rightarrow 3S^{2-} + 12H_2O \qquad (2.3)$$

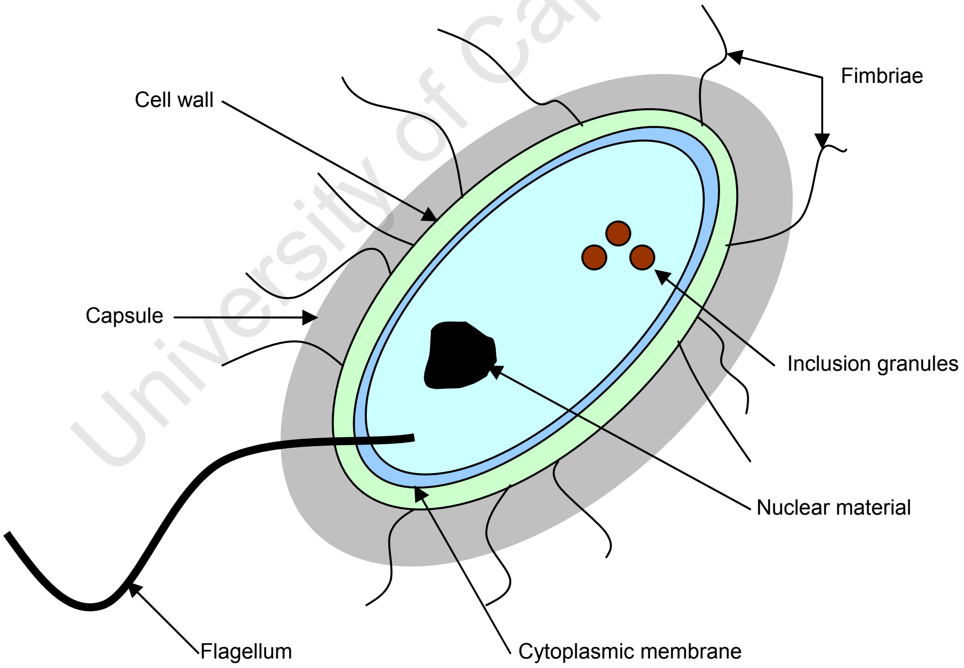

Figure 2.2 A typical bacterial cell

The amount of sulphide generated depends on activity of the sulphate-reducing anaerobic bacteria. Activity, that is growth and metabolism of the bacteria, depends on oxygen concentration and temperature. Oxygen stifles growth of strict anaerobes restricting the generation of sulphide in fresh sewage. An increase in sewage temperature increases activity of the organisms increasing sulphide generation. Activity of bacteria is greatest between 25°C and 30ºC, rapidly decreasing below 18ºC and above 37ºC (Parker, 1945a).

Sufficient nutrients are available in the sewage to support growth and metabolism of the sulphate-reducing organisms in the slimes layers (Thistlethwayte, 1972). Synthesis of cell materials requires elements such as carbon, oxygen, hydrogen, nitrogen, phosphorus and sulphur. Organic compounds in sewage provide a source of carbon, water a source of oxygen and hydrogen and inorganic compounds containing sulphates, nitrates and phosphates a source of sulphur, nitrogen and phosphorus respectively. Additional elements such as potassium, sodium, calcium, magnesium, chlorine and iron derive from the decomposition and utilisation of organic and/or inorganic compounds. Trace elements required such as manganese, cobalt, copper, molybdenum and zinc are present as impurities in the inorganic compounds.

Activity of sulphate-reducing organisms also depends on the transfer of nutrients from the sewage into the slimes layer. Sewage flow determines the rate of nutrient transfer (Thistlethwayte, 1972). Fast flowing sewage gives rise to turbulent flow conditions at the interfacial region ensuring a constant nutrient supply to the layer. Slow flowing sewage forms a laminar layer at the interface. Slow diffusion from the main body of sewage causes a depletion of nutrients in the laminar layer over time limiting nutrient transfer, decreasing the activity of the organisms.

An added effect of temperature on the generation of sulphide is that at higher temperatures, sewage is less viscous resulting in an increase in turbulence, which prohibits/disrupts the laminar layer increasing nutrient transfer and microbial activity (Thistlethwayte, 1972).

2.3.2 Sulphide existence in sewage

Sulphide diffusing towards a body of fresh sewage reacts with any oxygen present to reform sulphate (Equation 2.4). Sulphide entering the fresh sewage completely oxidises, provided there is sufficient oxygen.

$$S^{2-} + 2O_2 \rightarrow SO_4^{2-} \qquad (2.4)$$

Sulphide freely diffuses into a body of stale sewage. Concentration of the sulphide depends entirely on the level of dissolved oxygen in the stale sewage. Sulphide accumulates in sewage containing negligible amounts of dissolved oxygen. Oxygen level in the sewage depends on:-

- oxygen consumption/demand
- absorption of oxygen from the sewer atmosphere
- age, flow, viscosity and temperature of the sewage

A biological and a chemical oxygen demand exist in the body of sewage. Aerobic microorganisms consume substantial amounts of oxygen allowing anaerobic areas to develop within the sewage. Anaerobic microorganisms proliferate, generating sulphide that readily reacts with the dissolved oxygen remaining or entering the sewage.

Absorption of oxygen at the sewage surface must satisfy demands of aerobic bacteria and sulphide generated to prevent septic conditions leading to the build-up of sulphide. Oxygen absorption depends on the flow characteristics of the sewage. Shallow fast-flowing sewage generates sufficient turbulence to mix the oxygen absorbed at the surface maintaining a continuous high oxygen concentration gradient between the sewage surface and sewer atmosphere. Absorption is continuous ensuring a constant and uniform concentration of oxygen throughout the body of the sewage. Slow-flowing deep sewage generates negligible turbulence prohibiting the mixing of the oxygen absorbed at the surface. Absorption is slow due to the low oxygen concentration gradient at the surface. Solubility of the oxygen decreases with increasing temperature.

Sulphide exists in stale sewage as sulphide ions (S^{2-}), hydrogen sulphide ions (HS^-) and hydrogen sulphide molecules (H_2S) (Figure 2.3). Some of the sulphide precipitates out as iron sulphide (FeS) and zinc sulphide (ZnS).

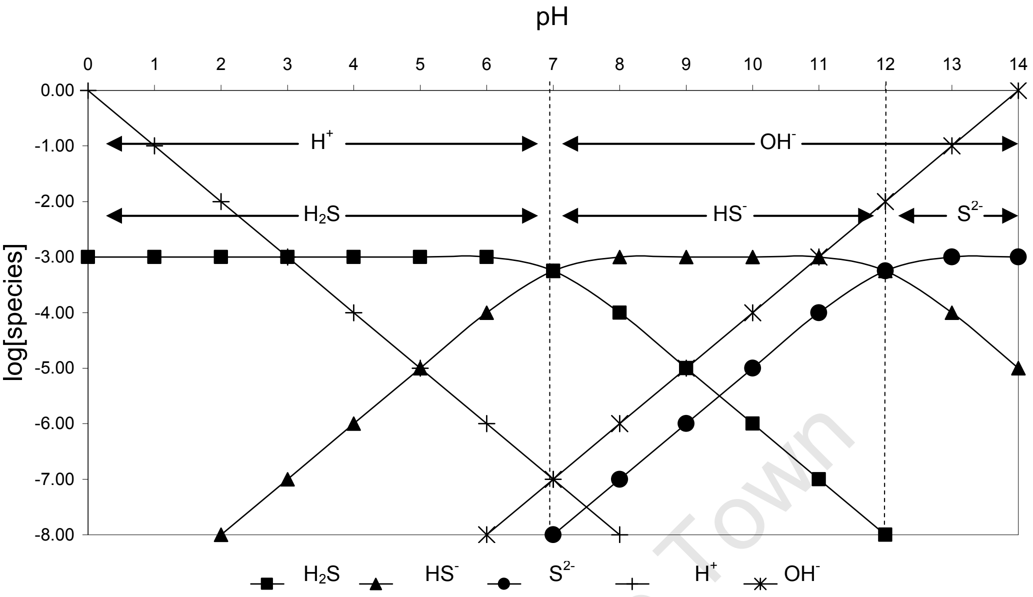

Figure 2.3 Sulphide species existence in aqueous solutions at varying pH

Sulphide species exist in equilibrium. Sulphide ions react in an aqueous solution to form the stable hydrogen sulphide ions and molecules, which are weak acids (Equation 2.5). A weak acid partially dissociates liberating a small amount of hydrogen ions, the degree of ionisation depending entirely on the stability of the corresponding anion as hydrogen ions attain stability by associating to water molecules (Equation 2.6). Stability of the hydrogen sulphide ion is significantly higher than that of the hydrogen sulphide molecule. After dissociation of the first hydrogen ion, the second becomes significantly more difficult to dissociate (Ebbing, 1984). Stability of the hydrogen sulphide ion is the driving force for the reaction of the sulphide ion.

$H_2S \leftrightarrows H^+ + HS^- \leftrightarrows 2H^+ + S^{2-}$ (2.5)

$H^+ + H_2O \leftrightarrows H_3O^+$ (2.6)

A change in the hydrogen ion concentration or pH (Equation 2.7) of the sewage significantly affects the equilibrium of the sulphide species. A decrease in hydrogen ion concentration (increase in pH) shifts the equilibrium to the right forming more sulphide ions, effectively decreasing the molecular hydrogen sulphide concentration (Ebbing, 1984). An increase in the hydrogen ion concentration (decrease in pH) shifts the equilibrium towards the left forming more molecular hydrogen sulphide, decreasing the sulphide ion concentration.

$pH = -\log[H^+]$ where [ ] denotes concentration in moles per litre (mol/l) (2.7)

Hydrogen sulphide molecules are predominant in an aqueous solution at pH less than 2,00 (Figure 2.3). Concentrations of the hydrogen sulphide ions and sulphide ions are negligible. A sharp increase in the concentration of the hydrogen sulphide ions occurs above pH 2,00. Concentrations of the hydrogen sulphide molecules remain similar and that of the sulphide ions negligible. A decrease in the concentration of the hydrogen sulphide molecules occurs at pH 6,00 (pKa_1 - Equation 2.8). At pH 7,00, concentration of hydrogen sulphide molecules is similar to that of hydrogen sulphide ions. At pH greater than 7,00, concentration of hydrogen sulphide molecules decreases sharply, that of sulphide ions increases sharply, and that of hydrogen sulphide ions remains constant.

An excess of hydrogen sulphide ions persists until a pH of 12,00 (pKa_2 – Equation 2.8) at which point the concentration of sulphide ions is similar and that of the hydrogen sulphide molecules negligible. Approximately 80 % of the sulphide exists as hydrogen sulphide at a pH of 6,0 compared to 30 % at a pH of 7,0 and 5 % at a pH of 8,0 (Stutterheim and van Aardt, 1953).

Dissociation constants: $Ka_1 = [HS^-][H^+]/[H_2S]$ and $Ka_2 = [S^{2-}][H^+]^2/[HS^-]$ (2.8)

Alkaline conditions favouring the existence of sulphide ions are rare in sewage, especially in older sewage where the bacterial activity is prominent and numerous species that excrete acidic substances exist (Thistlethwayte, 1972).

2.3.3 Sulphide emission from sewage

Molecular hydrogen sulphide is a gas and readily escapes from the sewage into the sewer atmosphere. A decrease in the concentration of molecular hydrogen sulphide shifts the equilibrium in the sewage towards the right consuming sulphide ions and emitting more hydrogen sulphide, the rate of emission depending on the sulphide ion concentration of the sewage. Concentrations of the molecular hydrogen sulphide in the sewer atmosphere negligibly influence the emission rate. Sufficient aeration and large volumes usually prevent the saturation of the sewer atmosphere.

Surface-active agents and stagnant films on the sewage may entrap the molecular hydrogen sulphide. A disruption of the surface such as that produced by turbulence, readily releases hydrogen sulphide gas into the sewer atmosphere. Changes in temperature negligibly affect the emission of hydrogen sulphide. An increase in the emission rate with temperature results from the increase in the microbial activity, decrease in oxygen solubility and increase in nutrient supply to the sulphate-reducing organisms in the slimes layers. Sewage retained in rising mains or storage tanks contain high levels of sulphide. Absorption of oxygen is negligible allowing an accumulation of sulphide. Severe corrosion problems occur downstream due to the emission of the hydrogen sulphide from the sewage flowing down gravity mains.

2.3.4 Absorption of hydrogen sulphide above the sewage level

Absorption of hydrogen sulphide escaping into the sewer atmosphere readily occurs into moisture condensing on surfaces above the sewage level (Figure 2.1). Constant evaporation of the sewage in warm climates normally associated with sewer corrosion ensures that surfaces remain moist. Absorption depends solely on the hydrogen sulphide concentration in the sewer atmosphere. A high concentration leads to a high rate of absorption. Turbulence in the sewer atmosphere ensures hydrogen sulphide remains in contact with the moisture layer. Oxidation of the hydrogen sulphide in the moisture layer prevents saturation and maintains a high concentration gradient with the sewer atmosphere, thus favouring absorption.

2.4 Sulphuric acid generation

Oxidation of hydrogen sulphide to sulphuric acid occurs naturally and biologically. Auto-oxidation is a spontaneous reaction of hydrogen sulphide with oxygen in an aqueous environment to form sulphuric acid (Equation 2.9). Biological oxidation occurs due to aerobic microorganisms, namely thiobacillus bacteria, that thrive in the moisture layer and that oxidise sulphide (Equation 2.10) to generate energy to assimilate carbon for synthesis of cell materials (Equation 2.11). Species of thiobacillus are physiologically highly specialised organisms. Carbon is obtained from the reduction of carbon dioxide (Stanier et al, 1971), which requires a significantly larger amount of energy than that to reduce organic substrates. Oxidation level of carbon in carbon dioxide is substantially higher than that of carbon in organic compounds such as glucose, which is similar to that of carbon in the cell materials.

$H_2S + 2O_2 \rightarrow 2H^+ + SO_4^{2-}$ (2.9)
$2H_2S + O_2 \rightarrow 2S + 2H_2O + 3O_2 \rightarrow 4H^+ + 2SO_4^{2-}$ (2.10)
$CO_2 + 4H^+ \rightarrow CH_2O$ (cell carbohydrate) $+ H_2O$ (2.11)

The aerobic respiratory process utilises large amounts of sulphide to yield the energy for cell synthesis, which results in the excretion of a substantially higher amount of sulphuric acid than that produced via the auto-oxidation reaction in aqueous solutions.

Conditions that favour the growth of the acid-loving thiobacillus species develop with time (Figure 2.4). Condensation of sewage continually moistens concrete surfaces and assists in seeding microorganisms onto the sewer walls. Some microorganisms migrate directly from the sewage and slimes layers. A mixed flora of microorganisms develops in the moisture layer on the concrete walls above the sewage level ((SA)CSIR, 1958). An alkaline environment (pH 10,5 to 12,5) resulting from the dissolution of calcium hydroxide in the cement paste (Lea, 1970) initially stifles the growth of the thiobacillus species seeded onto the concrete surfaces (Parker, 1945a).

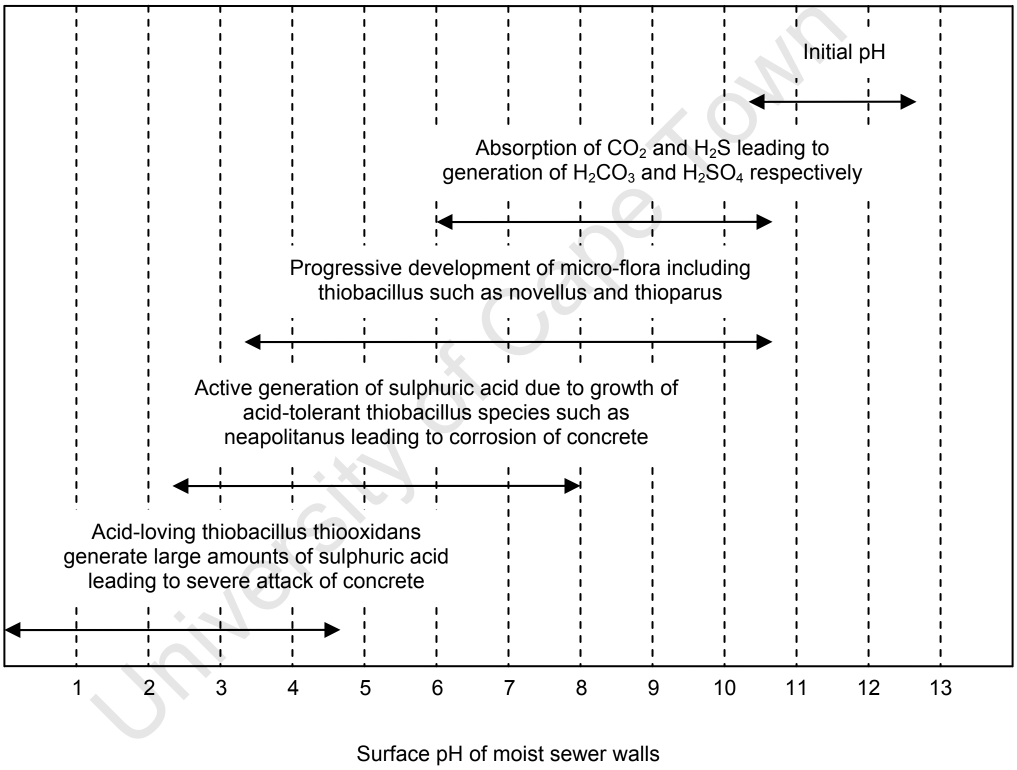

Figure 2.4 Conditions in the moisture layer resulting from the progressive deterioration of concrete surfaces above the sewage level (Thistlethwayte, 1972)

Acid conditions that favour the growth of the thiobacillus species gradually develop in the moisture layer due to the absorption of carbon dioxide and hydrogen sulphide. Absorption of carbon dioxide forms carbonic acid (H_2CO_3) that dissociates into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions (Equation 2.12), which causes a decrease in the pH (Ebbing, 1984). A carbon dioxide concentration of approximately 0,03 % in the sewer atmosphere results in a pH of approximately 5,72 (Lea, 1970). Carbon dioxide concentrations are often significantly higher (± 1,0 %) due to bacterial activity in the sewage (Parker, 1945a), which results in a pH of approximately 4,95 (Lea, 1970). A continuous supply of hydrogen sulphide without the acidic influence of the carbon dioxide confers a pH of between 6,5 and 7,0 (Abbott, 1951).

$CO_2 + H_2O \leftrightarrows H_2CO_3 \leftrightarrows HCO_3^- + H^+ \leftrightarrows CO_3^{2-} + 2H^+$ (2.12)

Acidic conditions gradually corrode the concrete surfaces. Hydrogen ions react with acid-soluble compounds such as calcium hydroxide (Equation 2.13) precipitating a film of debris, which creates niches for the growth of the thiobacillus bacteria (Parker, 1965). Slightly acidic conditions create an ideal environment for the progressive development of a thiobacillus bacterial colony (Parker, 1945b).

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O \qquad (2.13)$$

Species of the thiobacillus family are rod-shaped unicellular organisms approximately 0,5 µm in diameter and between 1 to 3 µm in length (Figure 2.5). A cell is similar to that previously described for the anaerobic bacteria (Figure 2.2) and consists of a wall with an inner cytoplasm membrane that surrounds the cytoplasm in which energy yielding and generating metabolic processes occur. Cytoplasm contains a single genetic nucleus and solid granular particles. A slimy capsule surrounds the cell wall from which short hair-like fibriae protrude. Motility is from a single polar flagellum that extends from the cytoplasm. All species of thiobacillus oxidise elemental sulphur and many oxidise sulphide and thiosulphate ions. All use only inorganic compounds as energy and carbon sources. Growth is rapid in environments containing such minerals. Cell generation times are between 4 to 5 hours.

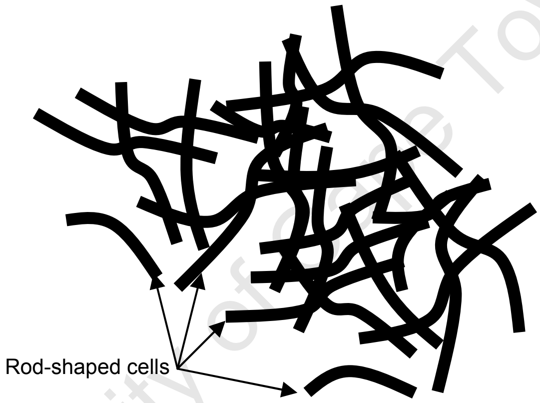

Figure 2.5 A thiobacillus bacterial colony

Acidic environments are suitable for the growth of most thiobacillus, all of which excrete sulphuric acid. Some such as the species novellus and thioparus grow in neutral or slightly alkaline environments. Alkaline conditions initially favour growth of the lesser acid-tolerant thiobacillus novellus. Sulphuric acid excreted maintains the pH of between 5,0 and 8,0 in the moisture layer initiating growth of the thiobacillus thioparus species capable of tolerating a pH of 3,5. Sulphuric acid generated is sufficient to cause a drop in pH to below 3,0 inhibiting the growth of the novellus and thioparus species. Acid-soluble components dissolving from the concrete neutralise the acid environment allowing the species to remain active.

Acidic conditions stimulate growths of acid-tolerant species such as thiobacillus neopolitanes capable of generating sulphuric acid at faster rates. Acidity of the environment increases to a pH of below 4,0 stimulating the growth of acid-loving species such as the thiobacillus thiooxidans, which possess the ability to tolerate extremely acidic conditions (Parker, 1965). Strains of thiooxidans grow in environments with a pH of 1,0 and below (Stanier et al, 1971).

Severe corrosion in sewers only occurs after the establishment of the thiobacillus thiooxidans species (Parker, 1947). Strains of the thiobacillus thiooxidans ensure a constant supply of sulphuric acid that severely attacks the concrete. Acid-soluble components in the concrete cannot effectively neutralise the sulphuric acid generated to stifle the activity of the acid-tolerant thiobacillus thiooxidans. Counts in sewers indicate that a mass loss of between 1 % and 10 % per annum correlates with a thiobacillus thiooxidans concentration of between 10^6 and 10^8 cells/cm^2 on the concrete surfaces (Parker, 1947).

Strengths of sulphuric acid environments fluctuate throughout the year. Strengths increase in warmer months. An increase in temperature increases the bacterial activity resulting in the generation of more hydrogen sulphide and sulphuric acid. A concentration of as low as 1 ppm of hydrogen sulphide in the sewer atmosphere gives rise to corrosion and above a concentration above 10 ppm, results in severe corrosion (Thistlethwayte, 1972). An extremely corrosive sulphuric acid environment ($pH < 1,0$) develops in areas such as the Virginia sewer where warm climatic conditions persist throughout the year and hydrogen sulphide levels in excess of 100 ppm are common (Kelly and Krüger, 1996).

2.5 Acid attack on concrete

Attack on concrete in acid solutions, that is a solution containing an excess of hydrogen ions, is straightforward. Compounds in the cement binders and acid-soluble aggregates (dolomite or limestone) are thermodynamically unstable in a solution containing an excess of hydrogen ions. Cement binders and/or aggregates degrade leading to the disintegration of the concrete. Severity of the attack depends on acid type, acid concentration and composition of the concrete. Attack on concrete in sewers depends on the amount of sulphuric acid generated, which depends on the activity of the thiobacillus bacterial colony on the surfaces above the sewage level, which in turn depends on the composition of the concrete, sulphide generation rate in the sewage and emission rate from the sewage and temperature.

2.5.1 Acid attack mechanisms

Cement hydration products such as free lime (CH) and those formed from the hydration of the calcium silicates (C_3S and C_2S), calcium aluminate (C_3A) and calcium alumino-ferrite (C_4AF) in the cement clinker react with the excess hydrogen ions in acidic mediums to form salts (Rombèn, 1979). Reactions are similar to that of an acid (HA) with a base (BOH) in an aqueous solution, which forms a salt (BA) and liberates water (Equation 2.14).

$$HA + BOH \rightarrow B^+ + A^- + H_2O \qquad (2.14)$$

Stabilities of the cement hydration products in acidic mediums differ. Calcium hydroxide ($Ca(OH)_2$) or free lime is the most reactive and completely dissociates into the acid solution (Equation 2.15). Calcium silicates are less reactive followed by calcium aluminates and then the calcium alumino-ferrites (Rombèn, 1979). Calcium oxide (CaO) bound into the complex cement hydrate structures dissociate at the slowest rate.

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O \qquad (2.15)$$

A gel layer consisting mainly of acid-insoluble silica (SiO_2) and water remains on the surface of the cement after the dissociation of the calcium silicates. Amounts of alumina (Al_2O_3) and ferrite (Fe_2O_3) remaining in the layer after dissolution of the calcium aluminates and calcium alumino-ferrites depend on the hydrogen ion concentration of the solution. At a hydrogen ion concentration of below 0,1 mol/ℓ (pH of above 1,0) iron hydroxide ($Fe(OH)_3$) precipitates (Equation 2.16) and at a concentration of below 0,001 mol/ℓ (pH of above 3,0) aluminium hydroxide ($Al(OH)_3$) precipitates (Equation 2.17).

$$Fe_2O_3 + 3H_2O \rightarrow 2Fe(OH)_3 \qquad (2.16)$$
$$Al_2O_3 + 3H_2O \rightarrow 2Al(OH)_3 \qquad (2.17)$$

Solubility of salts or reaction products (BA) formed also influences the composition of the layer. Solubility of the salt depends on acid type. A soluble salt such as calcium chloride (CaCl) forms in a hydrochloric acid solution (Equation 2.18). A sparingly soluble salt such as calcium sulphate ($CaSO_4$) forms in a sulphuric acid solution (Equation 2.19). Calcium sulphate precipitates as gypsum ($CaSO_4.2H_2O$), which binds together the insoluble residue in the gel layer creating a barrier on the surface of the concrete.

$$Ca(OH)_2 + 2HCl \rightarrow Ca^{2+} + 2Cl^- + 2H_2O \qquad (2.18)$$
$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O \qquad (2.19)$$

Corrosion products that precipitate onto the concrete surface hinder the diffusion of ions involved in the acid-base reactions thus slowing the attack rate. A porous silica gel layer that forms in a hydrochloric acid solution offers little protection against further attack (Pavlik, 1994). A dense gypsum layer that forms in a sulphuric acid solution offers excellent resistance to further attack (Pavlik, 1994). As the thickness of the gypsum layer increases so the rate of attack decreases. At a certain thickness, the sulphuric acid attack depends on the rate of diffusion of the ions involved in the reaction through the layer, that is the rate of attack depends on the diffusion coefficients of the ions and the thickness of the layer (Rombèn, 1979).

2.5.2 Aggressiveness of acidic solutions

Aggressiveness of an acid solution towards concrete directly relates to the hydrogen ion concentration of the solution. The amount of hydrogen ions liberated in an aqueous solution depends on acid type and concentration. At similar concentrations, a solution of a strong acid contains significantly more hydrogen ions than a solution of a weak acid. Strong acids such as hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) completely dissociate (Equation 2.20 and 2.21) liberating all hydrogen ions into solution. Weak acids such as hydrogen sulphide (Equation 2.5) partially dissociate liberating few hydrogen ions into solution (Section 2.3.2).

$$HCl \rightarrow H^+ + Cl^- \qquad (2.20)$$
$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \qquad (2.21)$$

An increase in acid concentration increases the amount of hydrogen ions available to react with the acid-soluble compounds in concrete. An increase in the concentration of a strong acid results in a corresponding increase in hydrogen ion concentration of the solution. Aggressiveness of the solution towards the concrete increases, because:-

- soluble compounds dissociate at a faster rate
- compounds stable at the lower hydrogen ion concentrations dissociate at the higher concentrations
- a larger percentage of soluble compounds dissolve due to the larger amount of hydrogen ions available

An increase in the concentration of a weak acid does not increase the free hydrogen ion concentration of the solution. Hydrogen ions remain bound to the weak acid molecule and do not dissociate. However, the amount of hydrogen ions available in the solution to react with the acid-soluble compounds in the concrete does increase by increasing the concentration of a weak acid, which increases the weak acid solutions potential to dissolve more of the acid- soluble compounds in the concrete with time.

2.5.3 Acid attack in sewers

Over the first year, a powdery layer develops on the concrete surface after which a brown crust forms (Thistlethwayte, 1972). An acidic paste consisting of calcium sulphate, iron sulphate, aluminium sulphate and silicon dioxide forms directly behind the crust as the attack front progresses into the concrete.

Sulphate attack, that is the reaction of calcium sulphate with calcium aluminate in the concrete substrate to form calcium sulpho-aluminates or ettringite, is rarely associated with sulphuric acid attack in sewers (Meyer and Ledbetter, 1970). Acidic conditions in the corrosion layer prevent the formation of ettringite, which only forms at a pH greater than 8,0 (Lea, 1970). A solid whitish corrosion layer that isolates the concrete from the sulphuric acidic environment sometimes forms in sewers. Alkaline conditions allow the bulky ettringite compounds to form, which may lead to cracking in the concrete substrate.

Attack at the average daily sewage level region is severe in comparison to that at the crown of concrete pipes (Figure 2.1). A number of factors contribute to the higher attack rate namely:-

- constant wetting and drying creating stress cracks in the corrosion layer
- continuous dissolution of the calcium sulphate layer into the sewage
- acidified condensate flows down sewer walls towards the sewage
- a higher generation of sulphuric acid directly above the sewage

Sulphuric acid generation is higher due to a higher bacterial activity resulting from:-

- the thicker slimes layer below the sewage level ensuring a high level of sulphide
- continuous seeding of thiobacillus bacteria from the sewage
- a constant supply of nutrients from the sewage

2.6 Measures to combat acid attack in sewers

Sewer design techniques are fundamental in minimising or even eliminating the adverse conditions responsible for the generation of sulphuric acid. Where sewer design is unable to eliminate the adverse conditions, additional measures to protect the concrete structures are required. Sewage treatments, which either prevent or eradicate the adverse conditions, are available. Concrete sewer pipes containing an acid-resistant coating or lining such as epoxy-tar or high-density polyethylene (HDPE) that isolate the structure from the corrosive conditions are common. An alternative to concrete is to manufacture sewer pipes with acid-resistant polymeric materials such as HDPE.

Sacrificial linings containing acid-soluble calcareous aggregates such as limestone or dolomite are a cost effective solution to extend service life of concrete pipes. Acid-soluble aggregates neutralise acidic environments slowing the attack rate. Calcium aluminate cement (CAC) linings improve resistance of concrete pipes to acidic environments. These aspects are discussed below.

2.6.1 Sewer design

Sewer design aims to minimise areas on which slimes develops, that is the area which determines sulphide generation capacity of a sewer. A self-cleansing velocity greater than about 0,8 m/s reduces slimes build-up on inverts of sewer pipes and ensures sufficient oxygen absorption into the sewage to oxidise sulphides (Davy, 1950). Sewers require regular cleansing to remove slimes, particularly on the insides of rising mains (Nischer, 1995). Stagnant conditions in rising mains favour slimes build-up and inhibits oxygen absorption allowing sulphide to accumulate. A common practice is to use rising mains of a small diameter and length to reduce the retention time of the sewage in the line.

A slow sewage flow followed by a fast flow is detrimental (Kienow et al, 1978). Sulphide that accumulates in slow flowing sewage readily escapes from the faster flowing sewage due to the increase in turbulence. A step or vertical drop in sewers to allow for oxygen uptake releases substantial amounts of hydrogen sulphide from stale or septic sewage. A total dissolved sulphide content of less than 1 ppm in sewage prevents corrosion (Thistlethwayte, 1972).

Ventilation to prevent the moist conditions essential for growth of the microorganisms on concrete surfaces above the sewage is seldom successful. Condensation, groundwater infiltration and capillary movement effects of sewage through concrete require extensive ventilation to maintain dry surfaces.

A life factor method (Goyns, 1991) established from empirical formulae (Parkhurst and Pomeroy, 1976) to calculate corrosiveness of sewer environments exists (Equations 2.22 to 2.28). A formula that estimates the amount of sulphide generated in sewage/slimes layer allows for calculation of hydrogen sulphide flux from the sewage into the moisture layer on the sewer walls and consequently the amount of sulphuric acid generated. Calculations depend on parameters such as:-

- flow velocity, pH and age of sewage
- volume and level of sewage in sewer pipes
- slope and dimension of sewer pipes
- oxygen demand and absorption of sewage
- atmospheric temperature
- biological activity

Sulphide generation rates in sewers are calculated as follows:-

Sewers flowing partly full:-

$$S_{lim} = (M_{sf} / m_s) \times EBOD \times (sv)^{-3/8} \times (P/b) \qquad (2.22)$$

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)

$$EBOD = BOD_5 \times (1.07)^{T-20} \qquad (2.23)$$

BOD_5 = biological oxygen demand of sewage measured after 5 days
T = temperature (°C)

Sulphide determined at end of sewer reach:-

$$S_2 = S_{lim} - (S_{lim} - S_1) / (\log^{-1}(m_s \times (sv)^{3/8} \times \Delta t / (2{,}31 \times d))) \qquad (2.24)$$

S_2 = sulphide concentration at time t + Δt (mg/ℓ)
S_1 = sulphide concentration at time t (mg/ℓ)
Δt = flow time in given sewer reach with constant slope, diameter and flow
d = diameter of pipe (m)

Sewers flowing full accounts for sulphide generation within the body of sewage:-

$$S_2 = S_1 + (M \times \Delta t \times EBOD \times (4 / (d + 1.57)) \qquad (2.25)$$

M = sulphide flux coefficient for filled pipe (m/h)

M_{sf}, m_s and M are determined experimentally for a given sewage flowing in a sewer system or the following values are used:-

$M_{sf} = 0.32 \times 10^{-3}$ m/m

m_s = 0.96 to 0.64
M = 1.0×10^{-3} m/h

Sulphide released from the sewage is calculated as follows:-

$$ø_{sf} = 0,69 \times (sv)^{3/8} \times J \times DS \quad (2.26)$$

$ø_{sf}$ = hydrogen sulphide flux from sewage ($g/m^2/h$)
s = energy gradient of wastewater stream (m/m)
v = stream velocity (m/s)
J = fraction of dissolved sulphide present as hydrogen sulphide (function of sewage)
DS = average annual dissolved sulphide concentration in wastewater (mg/ℓ)

Sulphide flux to sewer walls assuming all sulphide emitted from sewage is oxidised to sulphuric acid is calculated as follows:-

$$ø_{sw} = 0,69 \times (sv)^{3/8} \times J \times DS \times (b/P) \quad (2.27)$$

$ø_{sw}$ = hydrogen sulphide flux to pipe wall ($g/m^2/h$)
b/P = wastewater stream width at surface/perimeter of pipe wall above water surface ratio

An annual corrosion rate calculated from the amount of sulphuric acid generated and the alkalinity (expressed as $CaO/CaCO_3$) of the concrete determines the cover to reinforcing or the thickness of a sacrificial layer required to obtain a pipe with the desired service life. Assuming that 34 g of hydrogen sulphide is required to dissolve 100 g of alkalinity the annual corrosion rate is calculated as follows

$$c_{avg} = 11,5 \times k \times ø_{sw} / A \quad (2.28)$$

c_{avg} = average corrosion rate (mm/year)
k = coefficient of efficiency for sulphuric acid reaction with concrete considering a fraction of acid remains on the sewer wall (0.3 to 1.0 for complete reaction)
A = alkalinity of the concrete (0.18 to 0.23 for granite aggregates, 0.9 for calcareous aggregates and 0.4 for mortar linings)
11.5 is the factor to convert $ø_{sw}$ units of $g/m^2/h$ into c_{avg} units of mm/year

As estimated from the above calculation, a dolomite aggregate sacrificial lining of 50 mm is required to protect a concrete pipe for a period of 50 years in which the hydrogen sulphide flux to the sewer walls is 0,08 $g/m^2/h$. Considering a complete reaction of the sulphuric acid generated with the dolomite concrete:-

$c_{avg} = 11,5 \times 1,0 \times 0,08/0,9 = 1,02$ mm/year (corrosion rate of approximately 1cm/year)

2.6.2 Sewage treatments

Substances such as air or chemical compounds added to sewage may prevent or eliminate the adverse conditions, which lead to generation of sulphide. Sewage treatments are costly. Successful treatments require the addition of large amounts of substances either continuously or at regular intervals using expensive dosage systems.

Alkaline or acidic substances respectively raise or lower the pH of the sewage (Pomeroy and Bowlus, 1946). Sewage maintained at a pH above 10,0 or below 5,0 inhibits growth of the sulphate-reducing bacteria minimising sulphide generation. Substantially changing the pH of sewage self-cleanses the sewer (Stutterheim and van Aardt, 1953). Organism death weakens forces of cohesion between the slimes particles allowing sloughing-off of the layer by the flowing sewage. Additions of alkaline substances before or after conditions leading to the development of sulphides are acceptable. Alkaline substances stabilise sulphide ions minimising emission of hydrogen sulphide into the sewer atmosphere. Additions of acids prior to sulphide generation are vital to eliminate emission of the hydrogen sulphide.

Sulphuric acid added to sewage effectively removes slimes (Stutterheim and van Aardt, 1953). Sulphate ions from the sulphuric acid added are not reduced to sulphide ions as the anaerobic sulphur reducing bacteria (desulphovibrio desulphuricans) responsible for sulphide generation thrive in the slimes layer. Caustic soda or lime added periodically to raise the pH of sewage to above 12,0 for approximately 30 minutes is a successful treatment (Pomeroy and Bowlus, 1946). Amounts of acid or alkali added depend on the temperature and biological activity in the sewage.

Oxidising agents such as air, oxygen, hydrogen peroxide and potassium permanganate added to sewage in rising mains effectively reduce sulphides (Krüger and Botha, 1987). Air injected into rising mains is also successful. Such treatments are extremely expensive due to the large doses and the dosing equipment required. Chlorine assists in eliminating sulphides by facilitating aeration in sewage. A disadvantage is the potential damage to the steel reinforcing in the concrete structures.

An even distribution of activated carbon successfully absorbs hydrogen sulphide in sewage (Tims, 1949). Adding salts of metals such as iron, copper and zinc form insoluble sulphides that precipitate out of the sewage (Krüger and Botha, 1987). Salts of copper are also toxic towards the bacteria in the sewage. Adding biocides inhibit growth of organisms responsible for the generation of sulphide. Continuous dosing of the substances to inhibit the sulphide is extremely expensive and negatively influences the bacterial processes in sewage treatment plants.

2.6.3 Acid resistant concrete pipes

Sewer pipes require a durable concrete that offers resistance to sulphuric acid environments. A suitable mixture gives a dense concrete impermeable to gases and liquids. Steam curing in comparison to wet curing further improves durability of concrete (Crennan et al, 1980). A more ordered crystalline calcium silicate gel structure (C-S-H) forms in the ordinary portland cement (OPC). Calcium hydroxide precipitating during the cement hydration reacts with the fine silica particles remaining in the hydrated cement paste to form additional C-S-H. Stable small cubic crystals of tri-calcium aluminate (C_3AH_6) also form and ferrite phases change to a solid solution of lime, alumina, silica and iron.

Additional techniques to improve the resistance of concrete pipes towards sulphuric acid environments include:-

- developing acid resistant mixtures
- improving acid solubility/alkalinity of mixtures
- designing mixtures that are toxic towards the thiobacillus bacterial colony
- methods of isolating the concrete substrate from the corrosive environments

Acid resistant and acid solubility techniques are different approaches that achieve similar results. Concrete designed to improve acid resistance withstands attack, remaining structurally intact. Acid soluble concrete dissolves thus neutralising sulphuric acid and renders the environment less corrosive. Adding chemical additives, mineral extenders and/or special cements to mixtures may improve acid resistance of concrete. Alkalinity of concrete improves with the inclusion of acid-soluble calcareous aggregate such as dolomite or limestone. Adding chemical compounds toxic towards the thiobacillus bacteria decreases activity and generation of sulphuric acid. Acid resistant polymer coatings or linings on the insides of sewer pipes isolate the concrete from the corrosive environment.

Asbestos-fibre cement pipes and calcareous aggregate concrete pipes give better performance than siliceous aggregate concrete pipes in acidic sewer environments (Kelly and Krüger, 1996). Acid preferentially dissolves the cement binder in concrete containing acid-insoluble siliceous aggregates. Siliceous aggregate particles exposed eventually fall-out causing a rapid degradation of the concrete. Attack spreads uniformly over the entire surfaces of asbestos-fibre cement and calcareous aggregate concrete pipes eliminating aggregate fall-out. The acid-soluble nature of the materials neutralises the acidic environment more effectively than the siliceous aggregate concrete. Asbestos-fibre pipes contain more cement than siliceous aggregate concrete pipes. Acid-soluble calcareous aggregates such as dolomite and limestone increase the alkalinity of sewer pipes.

One study showed that a calcareous aggregate concrete pipe proved more resistant to acid attack than an asbestos-cement pipe. Alkalinity of the calcareous aggregate pipe was approximately 1,5 times that of the asbestos-cement pipe conferring a better capacity to neutralise the sulphuric acid environment (Stutterheim and van Aardt, 1953). A further study showed that the service life of an asbestos-cement pipe was longer than that of a calcareous aggregate concrete pipe (Krüger, 1989). An asbestos-cement pipe is highly compacted using the roller suspension method. A resilient corrosion layer forms due to fibres bonding the debris together, which interferes with the acid attack mechanism. A poor quality calcareous aggregate such as one of low acid-solubility, does not efficiently neutralise an acidic environment. Concrete sewer pipes made from poor dolomite aggregates show similar rates of attack to those made from siliceous aggregates (van Aardt, 1953). Cement binders dissolve at faster rates leading to the fall-out of aggregate particles.

Adding chemical additives or mineral additives with the exception of silica fume to OPC mixtures gave no significant improvements in resistance of concrete towards acid solutions (Fattuhi and Hughes, 1986). Attack on concrete with a cement binder containing 70% slag and that with a cement binder containing 25% fly ash was similar to that on concrete containing a 100 % PC binder after exposure to a concentrated sulphuric acid solution for two years (Krüger, 1991). A mixture of portland cement and silica fume tested in a sulphuric acid solution at a pH of 2,00 gave good resistance to acid attack (Fattuhi and Hughes, 1986). CAC concrete gave good resistance to mineral acid solutions and to biologically-induced sulphuric acid environments (Ehrich et al, 1999).

Adding an emulsion of styrene butadiene to concrete mixtures improved resistance of the materials towards sulphuric acid solutions maintained at a pH of 2,00 (Fattuhi and Hughes, 1986) and at a pH of 1,00 (Pomeroy, 1990). A methyl methacrylate emulsion improved resistance of concrete towards a sulphuric acid solution maintained at a pH of 1,00 (Pomeroy, 1990). Amino-alcohol and glycol-ether derivatives added to styrene butadiene, ethylene-vinyl acetate and poly-acrylic ester emulsions gave no improvement in acid resistance. Silicon polymer dispersions gave a concrete with low water absorption, which showed no improvement in acid resistance (Ohama et al, 1989). An acrylic acid copolymer and silica fume gave good resistance to attack in a hydrochloric acid solution at a pH of 1,00 (Atzeni et al, 1989). Surfaces treated with silicon tetra-fluoride gas improve resistance of concrete to acid attack (Fulton, 1986).

Anti-bacterial additives such as mercuric chloride, phenyl mercuric nitrate, ammonium molybdate and copper oxide were successful in improving resistance of concrete towards sulphuric acid sewer environments (Crennan et al, 1980). Such additives contain heavy metals such as copper, mercury, molybdenum and tin which are toxic towards the thiobacillus bacteria and reduce the sulphuric acid generation and attack on concrete.

Coatings such as asphalt, polymer, tar and epoxy resist aggressive conditions in sewers. A disadvantage is that pinholes form during application of a coating. Oxygen, hydrogen sulphide and moisture penetrate to the concrete substrate leading to generation of sulphuric acid. Attack behind the layer causes blistering leading to the de-lamination of the coating. An expensive solution is to apply the coating in several layers, which reduces the number of pinholes. Coatings consisting of epoxy or polyester resin and sand subjected to a concentrated sulphuric acid solution (10%) for two years showed excellent resistance (Redner and Esfandi, 1991). An epoxy-tar-sand mixture gave good resistance. Silicone rubber, polyurethane and phenol coatings gave negligible improvement in resistance due to pinholes causing severe blistering.

A method significantly improving the service life of concrete is the lining of sewer pipes with polyvinyl chloride, high-density polyethylene or polypropylene integral liners. Such linings are only economically viable in large (> 1,5 m) diameter pipes. Anchor knobs cast into the concrete permanently fix the linings to the insides of the sewer pipes. Welding the linings at the pipe joints completely isolates the concrete from the corrosive environment. A lining to save costs need only cover regions above the sewage level on which generation of sulphuric acid occurs.

2.7 Sewer investigations

A study of findings of an investigation into aspects of sewer corrosion in a live sewer section (Kelly and Krüger, 1996) provided constructive information for the development of the laboratory test procedure used in this thesis. Severe corrosive conditions anticipated in a sewer located in Virginia, South Africa, led to the installation of an experimental section. Climate in the area is warm through most of the year with daily temperatures of 35 °C in summer months and occasionally up to 27 °C in the winter months. Flat topography requires storage of sewage in holding sumps prior to pumping along a rising main into a gravity sewer. Such conditions lead to sewage retained in the storage sumps and the rising main turning septic giving rise to the generation of sulphide, which on discharge into the gravity sewer section releases hydrogen sulphide.

Construction of the experimental section was approximately 600 m downstream from the rising main. Objectives of the investigation were to study conditions in the sewage and sewer atmosphere in relation to sulphuric acid generation and compare the attack on ten different materials (Krüger, 1989):-

- asbestos-cement similar to that in the main line
- siliceous aggregate PC concrete
- dolomite aggregate PC pipes concrete
- siliceous aggregate CAC concrete
- epoxy-tar coated asbestos-cement
- epoxy coated asbestos-cement
- polyurethane coated asbestos-cement
- polyethylene lined siliceous aggregate PC concrete
- polyethylene lined dolomite aggregate PC concrete
- high-density polyethylene

Substantial sulphide generation occurs in the sewer line all year round. Average sulphide content of the sewage in the experimental section throughout the year was 0,7 mg/l (Krüger, 1990). Sewage pH was approximately 7.00 allowing 55% of the sulphide to exist as molecular hydrogen sulphide. Amount of hydrogen sulphide in the sewer atmosphere over a day in the winter months with an average temperature of 17 °C ranged from 8 ppm to 40 ppm, while over a day in the summer months with an average daily temperature of 26 °C, it ranged from 6 ppm to 200 ppm.

An inspection after 8 months revealed that depth of attack was approximately 8 to 10 mm in places on the siliceous and dolomite aggregate PC concrete pipe sections (Krüger, 1990). CAC siliceous aggregate concrete pipe sections showed negligible signs of attack. Surfaces of the asbestos-cement pipe sections were in good condition. Coated asbestos-cement, lined concrete and high-density polyethylene pipe sections showed no sign of attack.

Stone particles were loose and standing proud of the attacked surface of the siliceous aggregate PC concrete pipe sections after 23 months (Krüger, 1991) (Figure 2.6). Attack was approximately 10 mm deep at places. Attack on the dolomite aggregate PC concrete pipe sections was lower. Attack exposed some stone particles indicating that the PC binder dissolves at a faster rate. However, stone particles remained firmly bound into the cement matrix. Attack exposed stone particles on the CAC siliceous aggregate concrete pipe sections. Amount of exposure was less than that in the dolomite and siliceous aggregate PC pipe sections. Attack was evident on asbestos-cement pipe sections, which were in a good condition compared to the concrete pipe sections. A few blisters were appearing on the coated asbestos-cement pipe sections. Attack was not evident on the polyethylene lined concrete and high-density polyethylene pipe sections.

Figure 2.6 Siliceous concrete pipe showing severe signs of corrosion typical of that in the Virginia experimental sewer section after 23 months of exposure

Attack exposed severely corroding steel reinforcing of siliceous aggregate PC concrete pipe sections after 35 months (Krüger, 1992) (Figure 2.7 and 2.8). Depth of attack was approximately 15 mm in places. Siliceous stone particles were falling-out. Attack depth on the dolomite aggregate PC pipe sections was approximately 7 mm in places. Attack on the CAC siliceous aggregate concrete pipe sections was less. Siliceous stone particles were standing proud of the attacked surfaces. A gypsum-fibre layer detected on the asbestos-cement pipe sections was approximately 15 mm thick. Blisters and cracks appeared on the coated asbestos-cement pipe sections. Coatings were delaminating at the edges of the pipe sections. Attack was not evident on the polyethylene lined concrete and high-density polyethylene pipe sections.

2.8 General discussion

Adequate information is available to formulate a comprehensive understanding of the aspects leading to sewer corrosion such as:-

- adverse conditions in sewage
- sulphide generation and accumulation in sewage
- hydrogen sulphide emission and absorption
- sulphuric acid generation

- activity of microorganisms in sewers

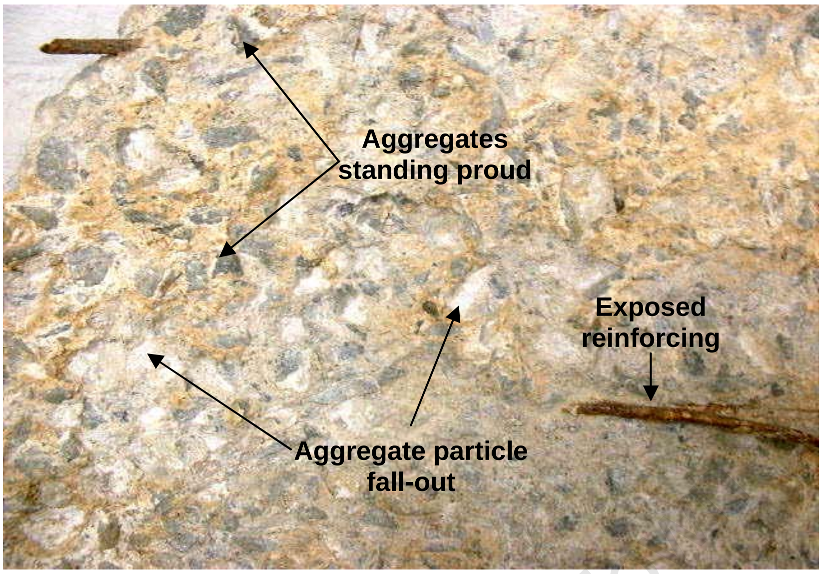

Figure 2.7 Section of siliceous aggregate concrete pipe showing aggregate particles standing proud, fall-out of aggregate particles and exposure of reinforcing

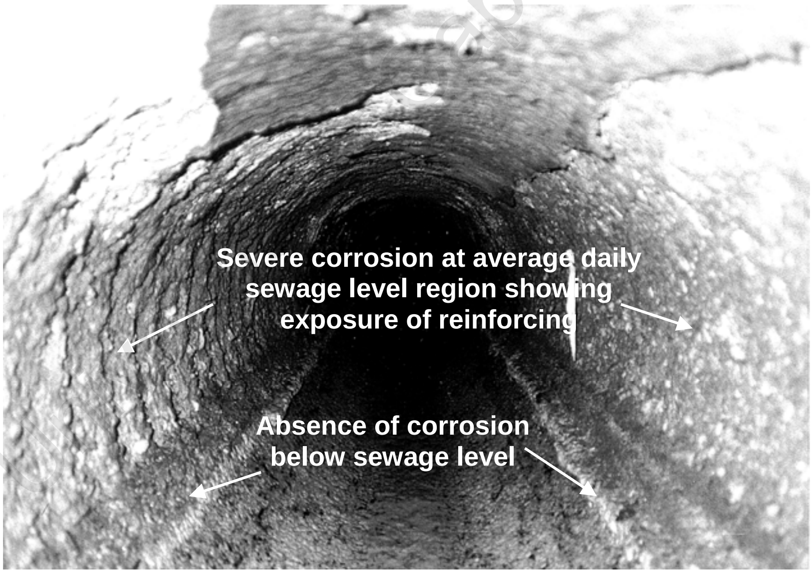

Figure 2.8 Siliceous concrete pipe showing severe corrosion and exposure of reinforcing typical of that in the Virginia experimental section after 35 months of exposure

An understanding of the above factors can permit designs and operations that minimise the conditions responsible for corrosion. Sewer design successfully inhibits corrosion on concrete pipes in many areas. Certain areas in which design alone cannot alleviate the adverse conditions require alternative methods to sustain the service life of concrete sewer pipes. An effective means to combat attack on concrete pipes in such areas requires a procedure to predict the corrosiveness of the sewer environment prior to the installation of the line and a test to monitor the performance of the concrete in an acidic environment of similar strength.

A limitation of the life factor method is that the annual corrosion rate only depends on the alkalinity of the concrete. Alkalinity, which is a measure of acid solubility, is not the only parameter to consider. Acid solubility represents the potential of the concrete to dissolve and neutralise a sulphuric acid environment and relates to the chemical composition of the concrete. A number of physical factors also influence the acid solubility of the concrete such as density, porosity, permeability, absorption, shape and size of siliceous aggregate particles and physical quality of calcareous aggregates. Such factors determine the structural integrity of the concrete that is, the dissolution rate of the concrete in a sulphuric acid environment.

The acid insolubility test (SANS 6242, 2002) employed in South Africa to gauge alkalinity gives no indication of concrete performance in acidic environments. Acid insolubility measured depends on the chemical composition of the concrete and only measures the capacity of the concrete to neutralise an acidic environment. Acid insolubility is calculated as the percentage of insoluble material remaining after a finely ground portion of the concrete is boiled in a concentrated hydrochloric acid solution for approximately 60 minutes. Grinding destroys the physical characteristics of the concrete and the boiling in the concentrated hydrochloric acid solution is significantly more corrosive than acidic environments in sewers.

Available laboratory tests to assess the resistance of concrete to sulphuric acid solutions fail to consider the influence of certain parameters, which are of significant importance to the attack mechanisms in sewers. Specimens prepared for testing are often not representative of the concrete intended for use in the sewer structure. Specimens are not prepared in a manner similar to that of the corresponding sewer pipes or mortar and paste specimens are used, which neglect the influence physical properties on acid resistance of the concrete (Ehrich et al, 1999). Some tests determine resistance of concrete in solutions of concentrations either significantly lower (Ehrich et al, 1999) or higher (Krüger, 1990) than the acidic environments in sewers. Attack on concrete in concentrated sulphuric acid solutions ($pH < 0,0$) is not representative of that in sewer environments ($pH > 0,0$). Attack in dilute solutions ($pH > 2,0$) fail to illustrate the deterioration of concrete in more corrosive environments commonly encountered in sewers throughout South Africa ($pH = 1,0$).

A test that accounts for the above parameters neglects to assess the quantitative influence of the calcium sulphate layer on the sulphuric acid attack mechanism (De Belie, Monteny and Taerwe, 2002). Calcium sulphate is sparingly soluble in aqueous solutions and saturation in sulphuric acid solutions is rapid. After saturation, the calcium sulphate precipitates onto the surface of the concrete specimens forming a gypsum layer, the physical properties of which depend on the concentration of the sulphuric acid solution.

A stable solid gypsum layer forms in solutions at concentrations of around 0,1 mol/ℓ, which are similar to that in sewer environments (Rombèn, 1979). Such a layer isolates the concrete from the sulphuric acid solution slowing and eventually stifling the attack (Pavlik, 1994). Attack at such concentrations is a function of the layer (formation rate, thickness and diffusion coefficients of the ions) and not on the chemical and physical properties of the concrete, which determines acid resistance (structural integrity and neutralisation capacity) of the concrete. A highly soluble concrete forms a layer at a faster rate, which slows and stifles the attack quicker than a concrete of lower solubility that is, the former appears more resistant to the sulphuric acid solution.

Another critical aspect to consider is that a pasty layer rather than a solid layer forms in sewers located in flat hot areas such as those common to Australia (Thistlethwayte, 1972) and South Africa (Kelly and Krüger, 1996). Such a pasty layer allows the sulphuric acid generated to penetrate sustaining the attack on the concrete substrate. Acidic conditions in the layer prevent the formation of ettringite, which commonly occurs in the concrete substrate behind the solid layer (Thistlethwayte, 1972). A pasty layer easily dissolves, particularly at the average daily sewage level region where the flowing sewage continuously removes the products of corrosion exposing the concrete substrate to the sulphuric acid environment. Severe attack occurs due to the run-off of the sulphuric acid generated on the sewer walls above the sewage level region.

Assessing resistance of sewer pipe concrete to such severely corrosive environments requires a robust laboratory test without the formation of the solid calcium sulphate layer. Allowing the layer to develop introduces too many variables and fails to reflect the worst-case scenario that is, the attack at the average daily sewage level region. A layer masks the influence of the physical and chemical properties on the attack mechanism prohibiting accurate determination of the differences in acid resistance namely in concrete containing different mineral extenders, chemical additives and calcareous aggregates. A representative test requires the manufacture of concrete samples in a similar manner to sewer pipes and a mineral acid solution of similar properties to the severely corrosive environments.

Availability of the experimental section at Virginia was crucial to the research. Assessing the nature of attack, particularly at the average daily sewage level region depicts the conditions (acid type and strength) required to formulate a laboratory test procedure representative of that in severely corrosive sewer environments common to South Africa. Such a test is essential in sewer design and allows for the development of a suitable concrete mixture to withstand the severely corrosive conditions of concern to concrete pipe manufactures in South Africa. Severe conditions are destructive to calcareous aggregate concrete (Kelly and Krüger, 1996) that normally give good performance in corrosive sewer environments (Stutterheim, 1954). Concrete requires modifications to improve structural integrity in severe conditions.

An investigation to assess attack on concrete samples in the environment at Virginia further illustrated the robustness of the laboratory test developed. Such an investigation forms part of the future research that aims to model the sewer corrosion process. Assessing attack in a sewer environment indicates the influence of the concrete on the activity of the thiobacillus colony, which assists with the correlation of the mineral acid to the biological sulphuric acid attack and allows for the development of a robust biological laboratory test suited to conditions in South Africa.

A laboratory method for measuring the resistance of concrete in a biologically induced sulphuric acid environment similar to that in sewers exists (Ehrich et al, 1999). Concrete specimens, prepared or cut from sewer structures, are preconditioned and seeded with thiobacillus thiooxidans. Specimens are then inserted into a bacterial chamber controlled at a constant temperature (37 °C) and relative humidity (100 %) to give optimum growth of the thiobacillus thiooxidans. Hydrogen sulphide gas (10 ppm) and a salt solution containing minerals essential for the growth of the thiobacillus thiooxidans are continuously fed into the chamber. Growth of the thiobacillus thiooxidans are sustained on the concrete specimens for a period of a year. Attack on the specimens is then assessed and compared to other concretes tested in a similar manner.

Another laboratory method that aims to assess the biogenic sulphuric acid attack involves immersing concrete specimens prepared or cut from sewer structures into a solution containing thiobacillus bacteria, sulphur and mineral salts essential for the growth of the bacteria (De Belie et al, 2004). Specimens are then incubated in a hydrogen sulphide chamber to further develop the growth of the thiobacillus bacterial colony after which the seeded specimens are subjected to a number of test cycles (10). A cycle consists of immersing the specimens into a salt solution capable of supporting the growth of the thiobacillus bacterial colony for 10 days. Sulphuric acid generated by the bacteria in the solution attacks the concrete. Specimens are removed and rinsed in water for 2 days and then dried for a further 2 days to simulate the wetting and drying action of the flowing sewage at the average daily sewage level.

Simulating the attack in sewers is complex and both the methods above are not entirely suited to conditions such as those encountered in Virginia. Attack monitored in the environment of the first test is representative of that in sewers but far less aggressive than that encountered in areas such as Virginia. A hydrogen sulphide level of 10 ppm maintained in the test atmosphere is significantly lower compared to the 40 ppm to 200 ppm in the sewer atmosphere at Virginia. Attack in the second test is less representative of that in sewers. Attack occurs in a sulphuric acid solution generated by a thiobacillus bacterial colony and fails to simulate the attack from sulphuric acid which is directly excreted from the thiobacillus bacteria onto the concrete substrate in sewers. A representative investigation was the monitoring of attack on concrete pipe sections in the experimental section at Virginia (Kelly and Krüger, 1996). Amount of data collected was insufficient to formulate an explanation into the difference in attack mechanisms and rates on concrete mixtures investigated.

A model such as the life factor method is invaluable in sewer design. Applying the life factor model proves successful in areas where sewer design is relatively straightforward and allows for accurate estimations of parameters used in the calculations. Application of the model is misleading in low-lying areas with an undulating topography and warm climate throughout the year. Sewers in such areas require storage tanks, rising mains, bends and drops all of which lead to the adverse conditions in the sewage responsible for the generation of sulphide and sulphuric acid. Owing to the changing conditions along the line accurate prediction of the parameters used in the calculations are not possible. A current investigation forming part of the overall research into the sewer corrosion problem by the University of Cape Town and related industries aims to standardise the model to conditions monitored in the experimental section at Virginia.

2.9 Conclusion

A review of the literature provided a comprehensive understanding of the sewer corrosion problem and illustrated the importance of a laboratory test to study the factors relating to the sulphuric acid attack mechanism on the sewer pipe concrete. A test to measure the acid resistance needs to consider the structural integrity and neutralisation capacity of sewer pipe concrete in severely corrosive environments commonly encountered in South Africa and to address the worst-case scenario that is, attack at average daily sewage level region. Such a test is crucial to assist with the formulation of a comprehensive model, which accounts for all the aspects of sewer corrosion such as sulphide generation and emission, sulphuric acid generation and corrosion rate of the concrete.

Accurate assessment of the annual corrosion depends not only on the alkalinity of the concrete but also on the ability of the concrete to neutralise and withstand sulphuric acid environments and stifle the growth of the thiobacillus bacteria. Acid resistance gives a good indication of the neutralisation capacity and structural integrity of a concrete in a sulphuric acid environment and is an appropriate material factor for use in a corrosion rate equation. A factor to account for the toxicity of the concrete towards the thiobacillus bacterial colony requires further research as it is not completely addressed in this thesis. Such research is long-term and needs to correlate the attack mechanisms in existing laboratory test methods to the sulphuric acid attack mechanism in sewer environments and modify the life factor method to conditions in South Africa. A model relating the sulphide generation, sulphide emission into the sewer atmosphere and sulphuric acid generation to the concrete substrates in a given sewer is needed to ensure development of a robust life factor method. Such a holistic approach is essential in predicting the service life of concrete pipes in sulphuric acid environments.

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CHAPTER 3

EXPERIMENTAL METHODOLOGY - ESTABLISHING THE MINERAL ACID TEST

3.1 Introduction

Successful design of a concrete pipe mixture for use in corrosive sewer environments requires a laboratory test to measure the acid resistance of the concrete. Acid resistance determines the ability of the sewer pipe concrete to withstand and neutralise sulphuric acid generated in sewers. Calcareous aggregate concrete aims to neutralise the acidic environment arising from auto-oxidation of hydrogen sulphide and sulphuric acid generated biologically effectively deterring and slowing the development of the acid-loving thiobacillus thiooxidans responsible for the severe attack. Success depends on the integrity and neutralisation capacity of the concrete in the acid environment. Cement binders and calcareous aggregate particles need to dissolve at a slow and equal rate neutralising the acidic conditions.

A laboratory test needs to:-

- be conducted on concrete that is representative of that actually used in sewer pipes
- measure resistance of concrete in an acid medium of strength similar to that in sewers
- illustrate the integrity of concrete components in the acid medium
- determine neutralisation capacity of the concrete
- assess the worst case scenario, that is attack at the average daily sewage level

The objective of this chapter is to document and discuss the experimental methodology employed to develop a mineral acid resistance test. Conception of the study arose from literature, sewer inspections and consultations with persons experienced in the sewer corrosion problem. A preliminary investigation assessed the feasibility of using a sulphuric acid solution as a test medium. A series of experiments was done on siliceous aggregate concrete prior to sourcing dolomite aggregate materials traditionally used for manufacture of sewer pipes. These experiments were used to:-

- assess attack mechanisms in dilute and concentrated sulphuric acid solutions
- determine strength of a sulphuric acid solution to sustain attack through the calcium sulphate layer forming on the test specimens, thus simulating the attack occurring at the crown of sewer pipes
- assess performance of a rig designed to minimise the calcium sulphate precipitate on the test specimens thus simulating the attack occurring at the average daily sewage level region of sewer pipes

After sourcing dolomite aggregate materials, a preparation method was developed to compact concrete test specimens in a manner similar to the roller suspension method used for the manufacture of sewer pipes. An investigation was done to determine the effectiveness of the sulphuric acid solution tests in measuring the resistances of dolomite aggregate concrete as a function of mass loss and hydrogen ion consumption with time:-

- static tests in which specimens remain stationary allowing calcium sulphate to accumulate and assess attack at the crown of sewer pipes
- dynamic tests in which specimens are continuously rotated and brushed to inhibit accumulation of calcium sulphate and assess attack at the average daily sewage level region of sewer pipes

Attack on the dolomite aggregate concrete was significantly different from that on the siliceous aggregate concrete. Saturation of the solutions with calcium sulphate depends on the solubility of the dolomite aggregates. Aggregate solubility differences led to variations in the sulphuric acid attack mechanisms making mass loss and hydrogen ion consumption unreliable measures to compare acid attack of sewer pipe concrete. An investigation to minimise the differences in solubility on the attack mechanism led to the formulation of the mineral acid solution test procedure:-

- sulphuric acid tests to ascertain the point at which the calcium sulphate saturation affects mass loss and hydrogen ion consumption rates
- sulphuric acid tests to ascertain the frequency of solution renewals to minimise the saturation effect and accumulation of calcium sulphate on concrete, simulating attack at the average daily sewage level region of sewer pipes
- hydrochloric acid tests to replace sulphuric acid renewal tests
- comparison of the sulphuric acid renewal tests with hydrochloric acid tests to validate using a hydrochloric acid solution as test medium
- standardisation of a hydrochloric acid test procedure

3.2 Sulphuric acid concentration tests

The aim of this experiment was to assess the nature of attack on concrete in concentrated and dilute sulphuric acid solutions and to establish whether the attack in concentrated solutions is representative of that in sewers. Attack on concrete in solutions of higher concentrations is accelerated giving measurements with which to determine acid resistance within a shorter period, which is desirable for a test procedure if the mechanism of attack is representative of that in sewer environments.

3.2.1 Specimen preparation

Cylindrical concrete specimens (80 × 150 mm) were prepared from a mixture containing 13/9 mm granite stone (stone/cement ratio of 3,00), mainly siliceous dune sand (sand/cement ratio of 1,59) and ordinary portland cement (OPC) with a water/cement ratio of 0,36. Specimens were compacted into cylindrical steel moulds in five layers (25 strokes per layer) using a tamping rod with a square base (20 × 20 mm). Specimens were then steam cured in the moulds at 50 °C for 4 hours to simulate curing during the manufacture of concrete pipes. After removal from the moulds, the specimens were stored in water at 23 °C for 5 days prior to testing in the sulphuric acid solutions.

3.2.2 Experimental method

Six sulphuric acid solutions each of a different concentration were prepared (Table 3.1). The concentration range was chosen to monitor attack on concrete in sulphuric acid solutions (0,98 - 49,09 g/ℓ) of strengths similar to those in sewers associated with severe corrosion common in areas throughout South Africa, and to establish the viability of using concentrated sulphuric acid solutions (73,56 – 196,16 g/ℓ) to assess attack in such areas. A single concrete specimen was immersed into each of the solutions (approximately 5 ℓ). Specimens were removed, cleaned (under running water with a stiff nylon brush) and weighed (in grams to one decimal place) once every 24 hours for a period of 5 days. Specimen mass losses (%) were calculated and recorded with time.

Table 3.1 Sulphuric acid solutions to establish concentration range appropriate for testing

Solution	**H_2SO_4**		**H^+ ion**	**pH**
	(g/ℓ)	(mol/ℓ)	(mol/ℓ)	
1	0,98	0,01	0,02	1,7
2	24,52	0,25	0,50	0,3
3	49,09	0,5	1,00	0,0
4	73,56	0,75	1,50	-
5	98,08	1,00	2,00	-
6	196,16	2,00	4,00	-

3.2.3 Results and discussion

Specimens in each of the solutions lost mass over the first 24 hours of testing (Figure 3.1). After 24 hours, specimens in solutions 2 to 6 lost mass at an increasing rate whereas the mass of the specimen in solution 1 remained constant.

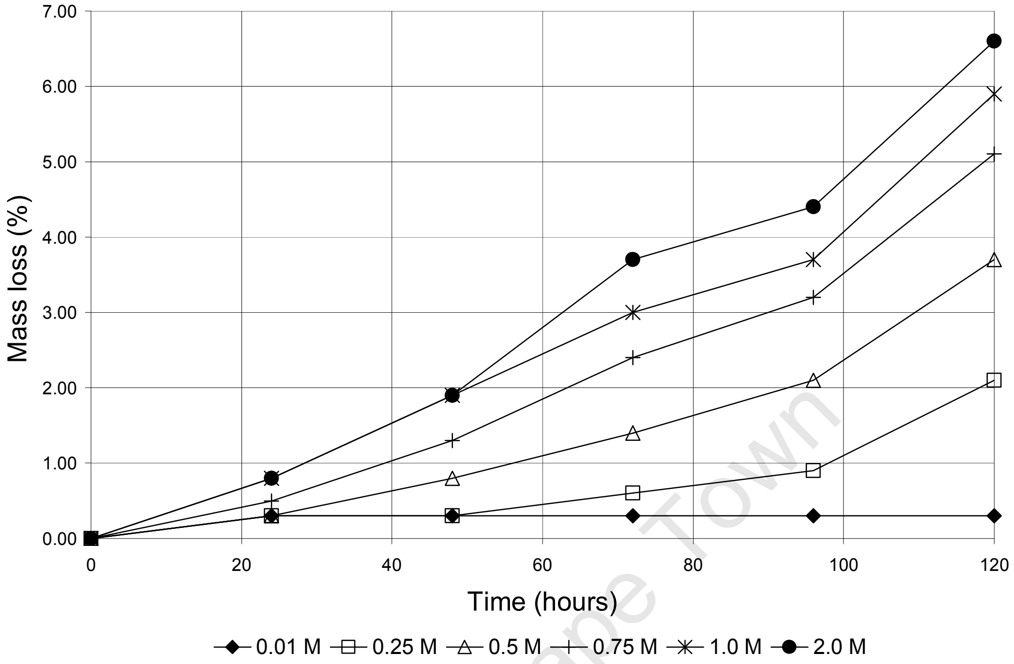

Figure 3.1 Specimen mass loss with time in the sulphuric acid solutions

Amount and rate of mass loss of the specimens directly relates to the concentration of the sulphuric acid solutions. A higher concentration leads to a higher mass loss with time. Stability of the acid-soluble compounds in the cement binder is dependent on the hydrogen ion concentration of the solutions. An increase in hydrogen ion concentration increases the dissolution potential of the solution, the dissolution rate of the acid-soluble compounds, and destabilises the compounds of lower solubility.

The rate of mass loss of the specimen in solution 1 was negligible after 24 hours due to the rapid neutralisation of the hydrogen ions, which decreases the aggressiveness of the solution towards the concrete and the nature of the calcium sulphate layer that formed. A tenacious dense layer, which resisted brushing under running water, formed on the surface of the specimen. The layer offered greater resistance to the diffusion of ions involved in the attack mechanism than the porous layers, which disintegrated easily during the handling and brushing of the specimens in solutions 2 to 6.

Calculation of hydrogen ion consumptions from the specimen mass losses confirms that the aggressiveness of solution 1 substantially decreased with time compared with that of solutions 2 to 6 (Table 3.2). Consumptions in solutions 2 to 6 were substantially higher but changes in the aggressiveness were minimal due to the abundance of hydrogen ions available. Calculations assume that mass losses were entirely due to the disintegration of the mortar portion of the specimens as no stone particle fall-out was noticed, and that the calcium oxide (CaO) content of the cement represents the portion consuming the hydrogen ions (H^+) in the solutions. For example, consider specimen in solution 1:-

After 24 hours, the mass loss of the specimen in solution 1 = 6,0 g

Since the mortar portion = 39 % cement + 61 % sand (Section 3.2.1)
$\therefore$ 6 g of mortar = 2,34 g of cement + 3,66 g of sand

Since OPC contains approximately 65 % CaO (Fulton, 1986)
∴ 2,34 g of OPC contains 1,52 g of CaO

Moles of CaO = mass of CaO (g) / molar mass of CaO (56,08 g/mol) (Ebbing, 1984)
∴ 6 g of mortar contains 0,027 moles of CaO

Since 1 mole of CaO reacts with 2 moles of H^+ i.e. 1 mole of H_2SO_4 (Equation 3.1) (Ebbing, 1984):-

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O \qquad (3.1)$$

∴ 0,027 moles of CaO reacts with or consumes 0,054 moles of H^+
∴ Consumption of H^+ in solution 1 = 0,054 mol / 5 ℓ = 0,011 mol/ℓ
∴ Concentration of H^+ in solution 1 = 0,02 – 0,011~ 0,01 mol/ℓ

This is consistent with results measured (Table 3.2). Approximately half the hydrogen ions in solution 1 were consumed within 24 hours and thus did not change up to 120 hours.

Table 3.2 Amount of hydrogen ions remaining in sulphuric acid solutions after 120 hours

Solution	**H^+ initial** (mol/ℓ)	**H^+ final** (mol/ℓ)	**H^+ reduction** (%)
1	0,02	0,01	50
2	0,50	0,46	8
3	1,00	0,87	13
4	1,50	1,32	12
5	2,00	1,79	10
6	4,00	3,75	6

3.2.4 General discussion

Calculating the amount of calcium ions liberated from the specimens indicates that the solutions become saturated with respect to calcium sulphate within 24 hours. Consider the specimen in solution 1, which reflects the least mass loss or amount of calcium ions liberated into the solutions within the initial 24 hours of testing:-

As calculated above, the amount of CaO dissociating after 24 hours = 0,027 moles

Since 1 mole of CaO dissociates to give 1 mole of Ca^{2+}
∴0,027 moles of CaO dissociates to give 0,027 moles of Ca^{2+}
∴Concentration of Ca^{2+} i.e. $[Ca^{2+}]$ in solution 1 after 24 hours = 0,027 mol/5 ℓ = 0.0054 mol/ℓ

Amount of Ca^{2+} required to saturate solution 1 is calculated from the solubility product of calcium sulphate, which is a function of the calcium ion ($[Ca^{2+}]$) and sulphate ion ($[SO_4^{2-}]$) concentrations (Equation 3.2) (Ebbing, 1984):-

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] \text{ where } K_{sp} = 2,4 \times 10^{-5} \text{ mol}^2/\ell^2 \qquad (3.2)$$

∴ $[Ca^{2+}] = 2,4 \times 10^{-5} \text{ mol}^2/\ell^2 / [SO_4^{2-}]$

Since 1 mole of H_2SO_4 dissociates to give 1 mole of SO_4^{2-}
∴ A H_2SO_4 concentration of 0,01 mol/ℓ gives $[SO_4^{2-}]$ of 0,01 mol/ℓ
∴ $[Ca^{2+}]$ required to saturate solution 1 = $2,4 \times 10^{-5}$ mol²/ℓ² / 0.01 mol/ℓ = 0,0024 mol/ℓ

However, the amount of Ca^{2+} in solution after 24 hours = 0,0054 mol/ℓ (see above)

∴ Solution 1 becomes saturated with respect to $CaSO_4$ within the initial 24 hours of testing

Solutions 2 to 6 were saturated at faster rates as the increase in sulphate ion concentrations substantially reduces the amounts of calcium ions required for saturation (Table 3.3) and the significantly higher mass losses measured imply more calcium ions were liberated into the solution over the initial 24 hours of testing.

Table 3.3 Calcium ions required for saturation of sulphuric acid solutions

Solution	**SO_4^{2-}**	**Ca^{2+}**	
	(mol/ℓ)	(mol/ℓ)	(g/5 ℓ)
1	0,01	$2,4 \times 10^{-3}$	$4,8 \times 10^{-1}$
2	0,25	$9,6 \times 10^{-5}$	$1,9 \times 10^{-2}$
3	0,5	$4,8 \times 10^{-5}$	$9,6 \times 10^{-3}$
4	0,75	$3,2 \times 10^{-5}$	$6,4 \times 10^{-3}$
5	1,0	$2,4 \times 10^{-5}$	$4,8 \times 10^{-3}$
6	2,0	$1,2 \times 10^{-5}$	$2,4 \times 10^{-3}$

The sulphuric acid attack mechanism significantly alters after calcium sulphate saturation of the solutions. Dissociation of the calcium ions from the acid-soluble compounds of the cement binder is opposed due to the common-ion effect (Ebbing, 1984) and any calcium ions that dissociate precipitate on the specimens and hinder the movement of the ions involved in the attack mechanism. Saturation influences the attack in solution 1 significantly more than that in solutions 2 to 6. The high hydrogen ion concentrations in solutions 2 to 6 vigorously attack the acid-soluble compounds and result in the formation of the porous calcium sulphate layers observed on the specimen surfaces. The abundance of hydrogen ions in the solutions provides the driving force to overcome the common-ion effect opposing the dissociation of the calcium ions into the solutions, which sustains the attack on the concrete.

In solution 1, the acid-soluble compounds dissolve at a significantly slower rate due to the low concentration of hydrogen ions, and the effective consumption of the hydrogen ions, which significantly reduces the aggressiveness of the solution. Calcium ions slowly dissociate and precipitate to form a compact calcium sulphate layer after saturation. Diffusion of the ions involved in the attack mechanism through the layer is slow and after a certain thickness the attack appears stifled as the mass of acid-soluble compounds dissociating counteracts that of calcium sulphate precipitating.

3.2.5 Conclusion

Accelerating attack on concrete by using concentrated sulphuric acid solutions such as solutions 2 to 6 fails to assess the resistance of concrete to the sulphuric acid environments developing in sewers with time in weaker sulphuric acid environments (pH greater than 1,00 and less than 2,00). Any improvements in the concrete to resist the less aggressive sulphuric acid environments and those initially developing on the concrete sewer walls from auto-oxidation of the hydrogen sulphide or lesser acid-tolerant thiobacillus bacterial species may not be detected (Section 2.4). Acid-soluble compounds in the concrete that potentially resist the initial weaker sulphuric acid environment and prolongs the deterioration of the concrete which create sites for growth of the corrosive thiobacillus thiooxidans rapidly disintegrate at the high hydrogen ion concentrations of solutions 2 to 6.

A weaker solution such as solution 1 is more representative of the attack in sewers but rapid consumption of the hydrogen ions fails to sustain a constant rate of attack through the calcium sulphate layer forming. A constant replenishment of the hydrogen ions is required to ensure an adequate concentration gradient to provide the driving force for the diffusion of hydrogen ions through the layer to dissociate the acid-soluble compounds in the concrete behind the layer and encourage diffusion of the ions through the layer thereby sustaining acid attack.

3.3 Sulphuric acid strength test

The aim of this experiment was to determine the strength of a sulphuric acid solution which sustains acid attack through the calcium sulphate layer that forms and is representative of that in sewers. An adequate and constant supply of hydrogen ions ensures a high concentration gradient that provides the driving force for the diffusion of hydrogen ions and promotes the dissolution and diffusion of acid-soluble compounds through the layer to generate mass loss and hydrogen ion consumption trends with time with which to assess acid resistance of the concrete.

3.3.1 Experimental method

A siliceous aggregate concrete specimen (Section 3.2.1) was immersed into a sulphuric acid solution (ca. 50 ℓ) maintained at a pH of 2,0. After 23 days, the strength of the solution was increased; initially to a pH of 1,50 maintained for 8 days and then a pH of 1,00 maintained for 27 days. Over the initial 10 days of testing, the specimen was removed once every 24 hours after which removals were at random intervals. After removals, the specimen was cleaned (under running water using a stiff bristle nylon brush) and weighed. Mass loss and hydrogen ion consumption were recorded with time (Appendix A). Hydrogen ion concentration (pH) of the solution was determined by method of titration using a sodium hydroxide solution (0,1 mol/ℓ), according to Equation 3.3.

$$2NaOH + H_2SO_4 \rightarrow 2Na^+ + SO_4^{2-} + 2H_2O \qquad (3.3)$$

3.3.2 Results and discussion

Specimen mass loss and hydrogen ion consumption rates were constant over the initial 3 days of testing after which the rates decreased substantially with time (Figure 3.2). Specimen mass loss decreased at a significantly higher rate becoming negligible after 6 days whereas the hydrogen ion consumption rate became negligible after 23 days.

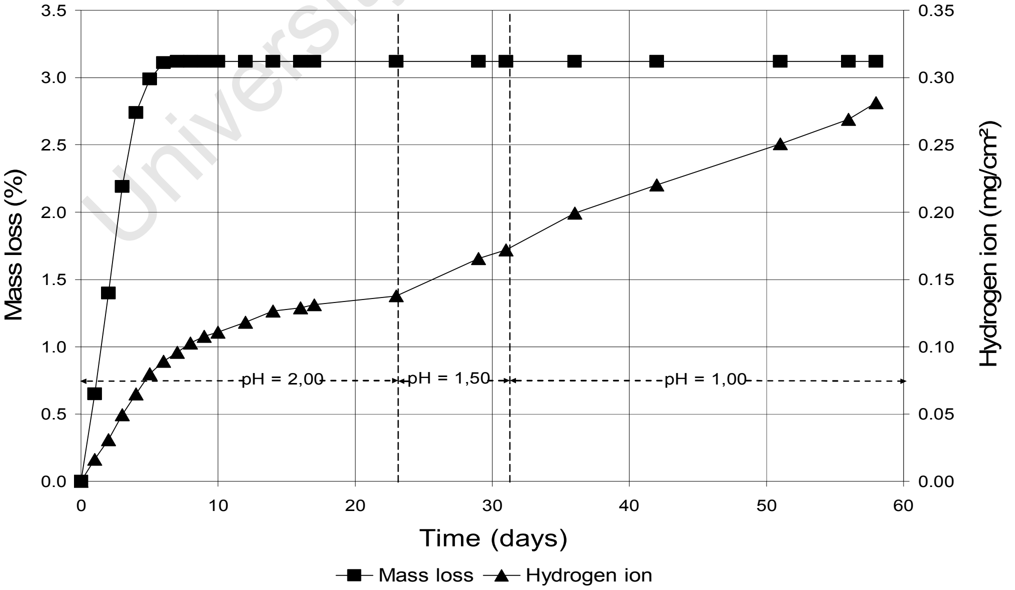

Figure 3.2 Specimen mass loss and hydrogen ion consumption with time in a sulphuric acid solution maintained at a pH of 2,00 for 23 days, 1,50 for 8 days and 1,00 for 27 days

Similar trends in hydrogen ion consumption and mass loss over the initial 6 days of testing is due to the hydrogen ions reacting with the acid-soluble compounds in the cement binder, which results in the disintegration of the mortar portion responsible for specimen mass loss. A constant rate of attack occurs prior to the saturation of the solution with calcium sulphate. After approximately 3 days, sufficient calcium ions (0,24 moles or 9,62 g) dissociate to saturate the solution (Section 3.2.4). Calcium sulphate precipitates onto the specimen, acting as a barrier against the diffusion of the ions involved in the sulphuric acid attack mechanism slowing the attack rate, which then decreases with the thickness of the layer. After 6 days, the layer slows the diffusion of hydrogen ions to such an extent that any mass loss arising from the diffusion of ions into the solution is compensated for by the calcium sulphate that precipitates. After 23 days, the thickness of the layer stops the flux of hydrogen ions effectively stifling the acid attack.

A decrease in pH to 1,50 increases the hydrogen ion consumption rate (Figure 3.2). A decrease in pH represents a substantial increase in hydrogen ion concentration, which provides a driving force for hydrogen ion diffusion through the calcium sulphate layer. After a further 8 days, the hydrogen ion consumption rate starts to decrease, which indicates that the hydrogen ion concentration was not sufficient to sustain a constant rate of attack. A decrease in pH to 1,00 revives the hydrogen ion consumption and sustains a constant rate of consumption. A corresponding increase in mass loss with hydrogen concentration was not evident. As the solution is saturated, any calcium ions that dissociate precipitates directly onto the specimen as calcium sulphate, which counteracts the dissolution and diffusion of other ions such as aluminium and iron into the solution. Attack remains effectively stifled by the calcium sulphate layer, which due to its stability in the sulphuric acid solution pacifies the surface of the specimen.

3.3.3 Conclusion

A sulphuric acid solution maintained at a pH of 1,00 sustains a constant rate of hydrogen ion consumption through the calcium sulphate layer and establishes adequate trends with which to assess the resistance of sewer pipe concrete at the crown of a sewer pipe where a calcium sulphate layer forms. A pH of 1,00 is an ideal strength for testing as it is similar to that of sulphuric acid environments generated by the thiobacillus thiooxidans species, which are responsible for degradation of sewer pipe concrete. A shortcoming of the test procedure is that it fails to assess the resistance of the sewer pipe concrete at the average daily sewage level region where the calcium sulphate layer disintegrates into the flowing sewage. Such a test procedure requires the removal of the calcium sulphate. This requirement led to the development of a rig to limit and remove the precipitate, and is discussed below.

3.4 Assessing attack at the average daily sewage level

The aim of the experiment was to assess the performance of a rig designed to remove the calcium sulphate precipitate on concrete specimens in the sulphuric acid solution maintained at a pH of 1,00. A robust test procedure to determine the resistance of concrete in a sulphuric acid environment encountered in sewers requires the removal of the calcium sulphate, which in many cases represents the worse case scenario that leads to the collapse of sewer pipes.

3.4.1 Apparatus

A pilot rig was designed to remove the calcium sulphate precipitate. It consisted of a poly-vinyl chloride (PVC) tank with a 72 ℓ maximum capacity (Figure 3.3). Two rubberised steel rollers positioned approximately 50 mm apart at the bottom-centre and a soft PVC-bristle brush supported at the top-centre on two stainless steel pins spanned the compartment length. A motor driving a rubber belt over pulleys attached to the steel axle on the outside of the compartment rotated the rollers at approximately 16 rev/min.

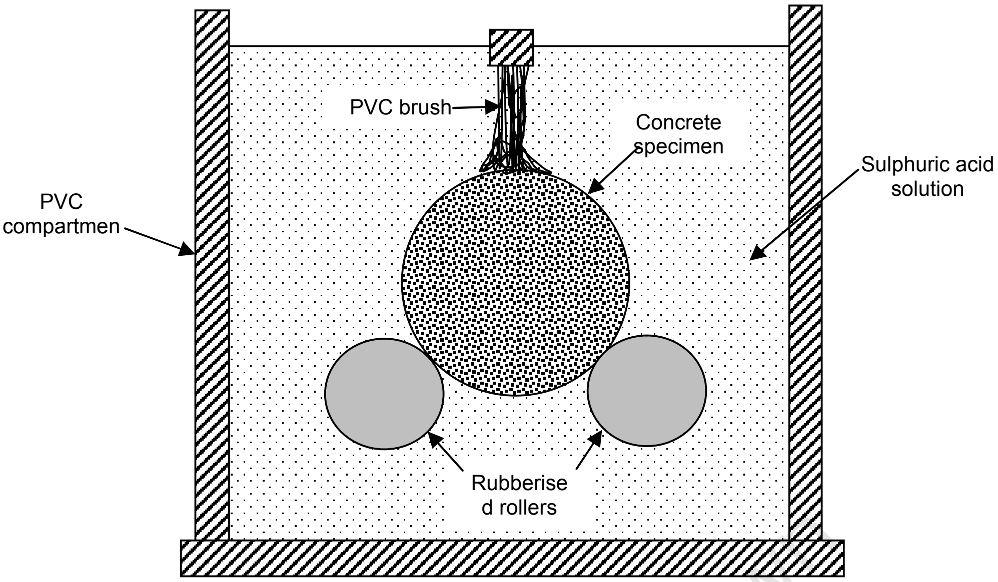

Figure 3.3 Cross-section of rig to test specimens in a sulphuric acid solution while removing the calcium sulphate precipitating (rubberised rollers rotate at 16 rev/min)

3.4.2 Experimental method

One of the siliceous aggregate concrete specimens previously prepared (Section 3.2.1) was positioned on the rollers and rotated in a sulphuric acid solution (50 ℓ) maintained at a pH of 1,00 for 105 days. Specimens were continuously brushed with the soft PVC bristles during rotation. Specimens were removed, cleaned (under running water using a stiff nylon brush) and weighed at random intervals, recording the mass loss and hydrogen ion consumption with time. After 71 days, the sulphuric acid solution was renewed to dissolve the calcium sulphate responsible for stifling the attack.

3.4.3 Results and discussion

Specimen mass loss and hydrogen ion consumption rates steadily decreased with time becoming negligible after 56 days of testing (Figure 3.4). A marked increase in the rates occurred with the solution renewal at 71 days after which the rates again steadily decreased with time.

The significantly higher mass loss and hydrogen ion consumption rates over the first 4 hours were due to the high rate of attack that occurs directly after the immersion of the specimen into the sulphuric acid solution. Acid-soluble compounds readily destabilise as the solution contains a substantial amount of hydrogen ions and is free of calcium ions. The continual decrease in the mass loss and hydrogen ion consumption rates after the initial 4 hours of testing was due to the saturation of the solution with calcium sulphate, which precipitates onto the specimen and decreases the rate of attack. As calculated above (Section 3.2.4), a sulphate ion concentration of 0,05 mol/ℓ requires 0,024 moles of calcium ions for saturation, which equates to a specimen mass loss of 0,18 % that occurs within the initial 4 days of testing.

The ongoing mass loss after saturation of the solution indicates that brushing during the rotation of the specimen diminishes the effect of the calcium sulphate layer on the rate of attack. The constant brushing inhibits precipitation of calcium sulphate and removes loosely bound corrosion debris. The negligible mass loss and hydrogen ion consumption after 56 days was due to the eventual formation of a dense calcium sulphate layer (Figure 3.5). Such a dense layer forms due to the continuous removal of the loose corrosion debris and acts as a barrier against the diffusion of the hydrogen ions, which stifles the attack. The sharp increase in the rate of attack at 71 days is due to dissolution of calcium sulphate into the fresh solution. Saturation again occurs shortly after the re-immersion of the specimen resulting in the steady decrease in the rate of attack with time.

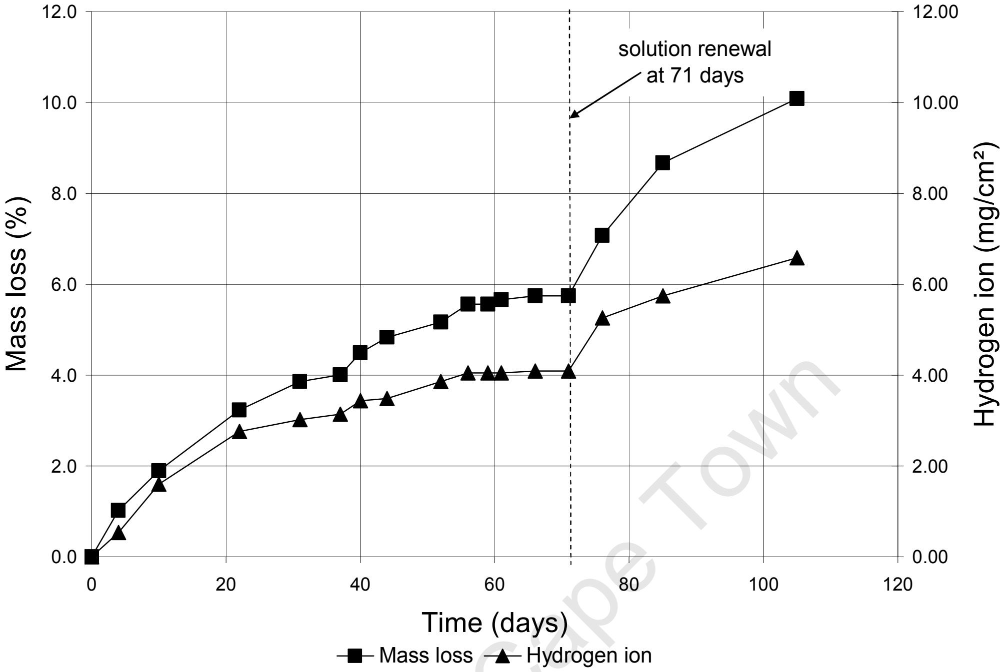

Figure 3.4 Specimen mass loss and hydrogen ion consumption with time in rig designed to remove calcium sulphate precipitate in a sulphuric acid solution maintained at a pH of 1,00

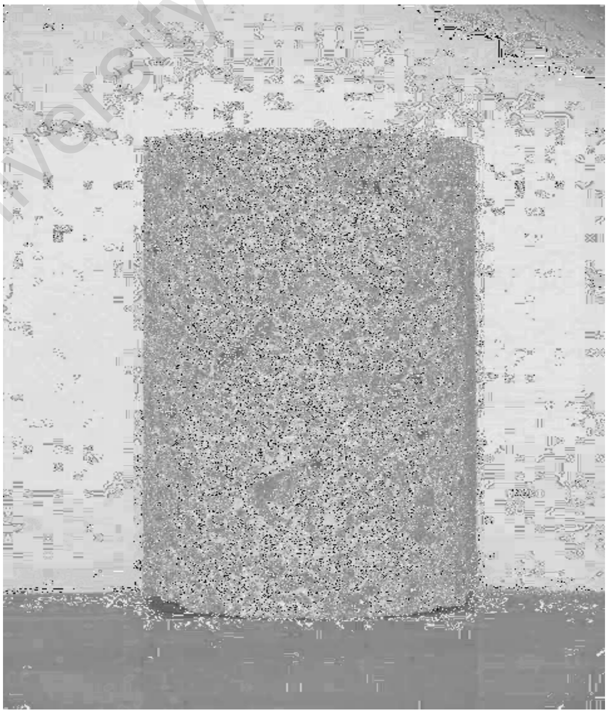

Figure 3.5 Concrete specimen showing the build-up of the calcium sulphate layer between the aggregate particles, which occurs in sulphuric acid solutions at a pH of 1,00

3.4.4 General discussion

Significantly lower mass loss after 6 days in the solution at a pH of 1,00 (1,2 % compared to 3,1 % in the solution at a pH of 2,00 - Section 3.3.2, Figure 3.2) relates directly to the calcium sulphate saturation rates of the solutions. Saturation of the solution at a pH of 2,00 is three times slower implying the attack on the specimen remains unimpeded for a significantly longer period. A steady decrease in the mass loss rate after saturation of the solution at a pH of 1,00 compared to the sudden decrease in the solution at a pH of 2,00 indicates that continual brushing removes corrosion debris and calcium sulphate accumulating on the specimen surface. Specimen mass loss was sustained for 56 days compared to 6 days in the respective solutions.

Significantly higher hydrogen ion consumption after 6 days in the solution at a pH of 1,00 (0,54 mg/cm^2 compared to 0,09 mg/cm^2 at a pH of 2,00) does not correlate with the differences in mass loss. Substantially higher hydrogen ion concentration at a pH of 1,00 (0,1 mol/ℓ compared to 0,01 mol/ℓ at a pH of 2,00) leads to a faster attack rate accounting for the higher consumption and rapid saturation of the solution. Calcium sulphate precipitating on the surfaces counteracts the corrosion debris removed with the continuous brushing giving the lower mass loss. Consumption continues as the high concentration ensures the driving force for diffusion of the hydrogen ions through the layer.

After the saturation of the solution and precipitation of calcium sulphate, the mechanism of attack involves the diffusion of hydrogen ions and sulphate ions through the layer towards the region of lower concentration at the fresh concrete surface. Sulphate ions diffuse at a significantly slower rate due to their bulky nature. Hydrogen ions attack the acid-soluble compounds in the fresh concrete surfaces behind the layer releasing the calcium ions and other ions such as aluminium and iron, which diffuse out towards the solution. The mobility of the calcium ions is significantly slower due to the saturation of the solution allowing calcium sulphate to precipitate directly onto the fresh surface or within the existing layer (Figure 3.5).

The indirect relationship between mass loss and hydrogen ion consumption illustrates the significant effect of calcium sulphate saturation on the sulphuric acid attack mechanism. Based on mass loss, the attack in stronger solutions, which are more destructive to acid-soluble compounds in the concrete, appears less severe than that in weaker solutions. Solubility of the concrete, which determines the saturation rate of the solution, affects the relationship between mass loss and hydrogen ion consumption and influences reliability of the measurements in determining acid resistance.

Overall, the continual rotation and brushing of the specimen in the sulphuric acid solution at pH of 1,00 was successful. Significant mass loss and hydrogen ion consumption with time allows for easier interpretation of acid resistance. A direct relationship between mass loss and hydrogen consumption exists and removal of corrosion products resembles the scenario at the average daily sewage level region. A concern is the interrelationship between the acid attack mechanism, solubility of the concrete and saturation rate of the solution. Solubility of the concrete affects the attack. A concrete having a higher solubility saturates the solution at a faster rate allowing the calcium sulphate layer to build-up sooner and stifle the attack quicker. As a result, concrete of a higher solubility may appear to resist the sulphuric acid attack better requiring a test procedure incorporating regular solution renewals to minimise the effect of calcium sulphate saturation on the attack mechanism.

3.4.5 Conclusion

An improvement in the mass loss and hydrogen ion consumption trends with time for the siliceous aggregate concrete specimens was achieved using the rig with rotating rollers. The continuous rotation and brushing inhibits and removes corrosion products from the surface of the specimen, sustaining mass loss and hydrogen ion consumption for a significantly longer period, making the rig more suited to assess the resistance of concrete to attack at the average daily sewage level region of sewer pipes. The sulphuric acid solution maintained at pH of 1,00 ensures the diffusion and consumption of hydrogen ions is sustained through the layer of corrosion products that accumulates.

Although mass loss and hydrogen ion consumptions were sustained for significantly longer using the rig, the calcium sulphate saturation remains a major factor to consider in determining the resistance of sewer pipe concrete to a sulphuric acid solution. Sewer pipe concrete containing dolomite aggregate for example is capable of saturating the sulphuric acid solution quicker. Calcium carbonate in the dolomite readily dissolves into the solution increasing the tendency for calcium sulphate to precipitate, which may make the inhibition and removal of the corrosion products from the surface more difficult. A further investigation was therefore required to assess the manner in which highly soluble concrete such as dolomite aggregate concrete affects the sulphuric acid attack mechanism and to develop a procedure to decrease the influence of the calcium sulphate further and simulate the attack at the average daily sewage level region better.

3.5 Static and dynamic sulphuric acid solution tests

The aim of the investigation was to determine the feasibility of measuring the acid resistance of sewer pipe concrete containing dolomite aggregates in a sulphuric acid solution at a pH of 1,00, on specimens remaining stationary allowing calcium sulphate to accumulate (static testing) and on specimens continuously rotated and brushed thus inhibiting the accumulation of calcium sulphate (dynamic testing).

3.5.1 Concrete mixture proportions

Concrete specimens were prepared from sewer pipe mixtures (Table 3.4) and raw materials sourced from commercial concrete pipe factories (Olifantsfontein, Wadeville and Roodepoort factories situated in Gauteng Province and the Kuilsriver and Blackheath factories situated in Western Cape Province). All mixtures contained dolomite stone and dolomite crusher sand. Olifantsfontein, Wadeville and Roodepoort dolomite aggregates were sourced from different quarries. Kuilsriver and Blackheath dolomite aggregate was sourced from the same quarry. Roodepoort, Kuilsriver and Blackheath mixtures also contained a siliceous fine aggregate sourced from the respective areas. Standard tests (sieve analysis of the aggregates (SANS method 201, 2002), acid insolubility of the aggregates (SANS method 6242, 2002) and chemical analysis of the rapid hardening portland cements (SANS method 50196 – 2, 2006) were done to compare the quality of the raw materials.

Table 3.4 Sewer pipe mixture proportions based on ratio of raw materials to cement content

Factory	**Ratio of Materials**				
	Dolomite stone	Dolomite sand	Siliceous sand	Cement	Total aggregate
Olifantsfontein	2,28	2,28	-	1,00	4,56
Wadeville	2,90	1,72	-	1,00	4,62
Roodepoort	3,06	1,48	0,39	1,00	4,93
Kuilsriver	2,47	1,41	1,00	1,00	4,88
Blackheath	3,45	1,32	0,53	1,00	5,30

3.5.2 Specimen preparation and standard testing

Aggregates were air dried for 30 days prior to mixing. Water was added to each mixture to achieve a similar consistency giving a w/c ratio of 0,36 for all mixtures. Cylindrical concrete specimens (80 × 150 mm) were prepared from the respective dolomite aggregate mixtures using a preliminary method formulated from compaction trials done on a siliceous aggregate mixture (Appendix B - Section B.2.1). Specimens (20) were steam-cured 4 hours after compaction in a chamber maintained at 50 °C for 4 hours. Specimens were then air-cured in a conditioning room at a temperature of 26 °C and relative humidity of 60 % for 28 days.

Some of the steam-cured specimens (6) were water-cured at a temperature of 23 °C for 28 days.

Standard tests were done on the air-cured specimens to assess the physical and chemical properties of the concrete to compare with measurements done on respective sewer pipes, to assess the reliability of the compaction method:-

- compressive strength (SANS method 5863, 2006)
- relative density (SANS method 6251, 1994)
- acid insolubility (SANS method 6242, 2002)
- durability index - oxygen permeability and water sorptivity (Alexander et al, 1999)

Compressive strength tests were done on the air and water-cured specimens to assess the effectiveness of the steam curing and compaction. Acid insolubility, relative density and durability index tests were only done on the air-cured specimens and respective pipe sections.

Cylindrical specimens (80 × 80 mm for concrete specimens and 40 × 40 mm for pipe sections, six per mixture and six per pipe section) were prepared for strength tests (Appendix B – Section B.2.1). Disc specimens (80 × 25 mm for concrete specimens and 80 × 40 mm for pipe sections, six per mixture and six per pipe section) were prepared for relative density and durability index tests (Appendix B– Section B.2.1). Acid insolubility measurements (average of six determinations) involved grinding a portion of concrete (300 g) into a powder (600 µm). A representative portion (50 g) of the powder was ground further to obtain a fine powder (150 µm). Specimens (5 g) of the fine powder were digested in a concentrated hydrochloric acid solution at a temperature of 100 °C for 60 minutes after which the solution was filtered to collect the insoluble material remaining.

Durability index tests characterise the transport properties of the concrete, which are critical parameters controlling potential durability that is, resistance to corrosive environments. Acid insolubility measures the potential of the concrete to dissolve and neutralise an acidic environment.

3.5.3 Experimental method

Specimens (two from each mixture cured in air for 28 days) were immersed into separate sulphuric acid solutions (20 ℓ solutions for the static tests and 50 ℓ solutions for the dynamic tests) maintained within a pH range of 1,00 to 1,50. Static test specimens remained stationary whereas dynamic test specimens were continuously rotated and brushed with the soft PVC-bristle brush. An additional testing rig consisting of four compartments similar to that designed for the testing of the siliceous aggregate specimens (Figure 3.3) was constructed for the dynamic investigation. Specimens were removed (at random intervals) and cleaned under running water using a stiff bristle nylon brush prior to weighing and measuring of dimensions. Hydrogen ion concentrations were determined by method of titration (Appendix A). Static test solutions were renewed after 14 days and dynamic test solutions after 12 and 31 days to disintegrate the layer of calcium sulphate on the specimen surfaces and revive attack. Mass losses (%) and hydrogen ion consumptions (mg/cm^2) of the specimens were recorded for 68 days.

3.5.4 Results and discussion

Standard testing of materials

Particle size analysis of the dolomite stone indicated that the maximum particle size was less than 19,0 mm (Figure 3.6). Stone from Blackheath was coarser containing more particles larger than 13,2 mm than the Olifantsfontein and Kuilsriver stone with the Wadeville and Roodepoort stone containing the least amount of this size. Stone from Wadeville contained more particles larger than 9,5 mm than the Olifantsfontein, Roodepoort and

Blackheath stone, the Kuilsriver stone containing the least. Stone from the Western Cape Province contained more particles smaller than 6,7 mm and 4,75 mm than the stone from the Gauteng Province.

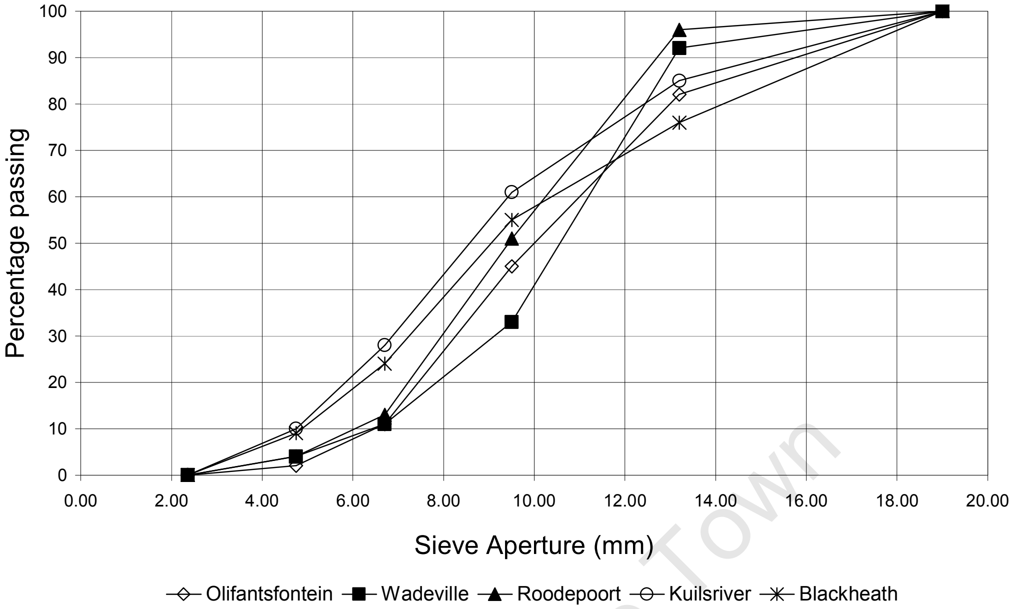

Figure 3.6 Particle size analysis of dolomite stone from Gauteng and Western Cape (standard sieve sizes: 19,0 mm; 13,5 mm; 6,5 mm; 4,75 mm and 2,36 mm)

Olifantsfontein dolomite crusher sand was the coarsest (Figure 3.7). Sand from Kuilsriver was coarser compared to those from Wadeville and Blackheath, which contained similar amounts of particles larger than 0,6 mm, the latter with more particles finer than 0,6 mm. Sand from Roodepoort was overall the finest despite the fact that the sand from Blackheath contained more particles smaller than 0,15 mm.

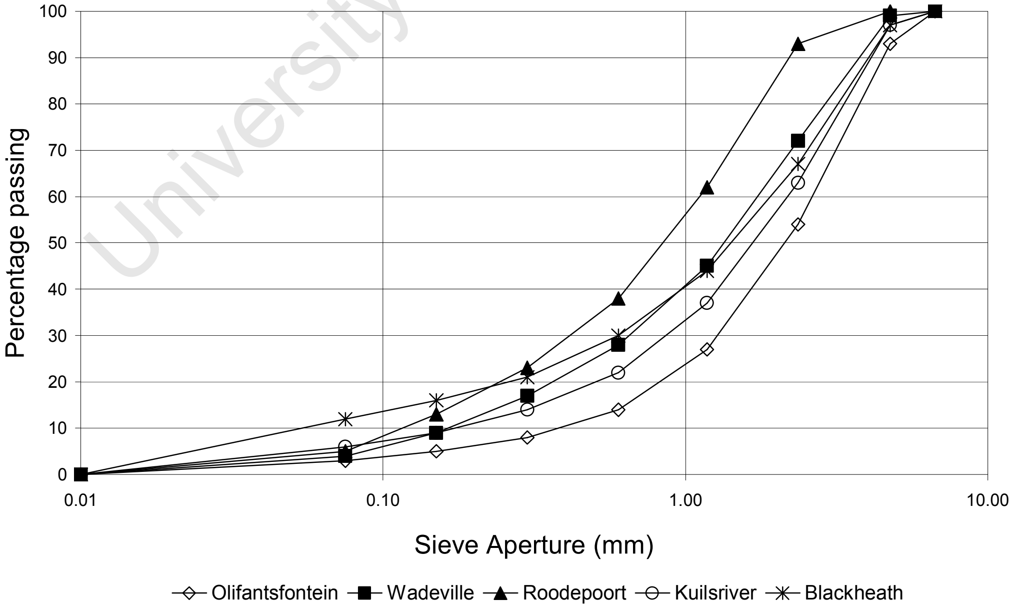

Figure 3.7 Particle size analyses of dolomite crusher sands from Gauteng and Western Cape (standard sieve sizes: 6,7 mm; 4,75 mm; 2,36 mm; 1,18 mm; 0,6 mm; 0,3 mm; 0,15 mm and 0,075 mm)

Siliceous filler sands (naturally occurring weathered sands) were finer than the crushed dolomite sands. Sand from Kuilsriver was the coarsest with approximately 50 % of the particles larger than 0,6 mm (Figure 3.8). Sand from Blackheath was coarser than that from Roodepoort.

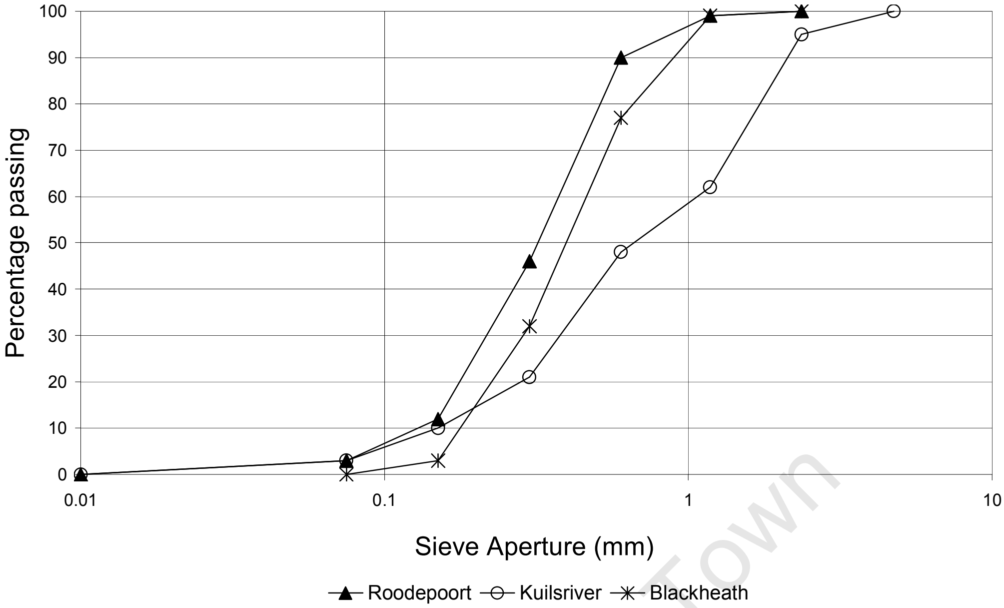

Figure 3.8 Particle size analyses of siliceous sands from Gauteng and Western Cape (standard sieve sizes: 6,7 mm; 4,75 mm; 2,36 mm; 1,18 mm; 0,6 mm; 0,3 mm; 0,15 mm and 0,075 mm)

Siliceous filler sands from the Roodepoort and Blackheath factories contained significantly more fines than the filler sand from the Kuilsriver factory, which contained a similar amount of fines to the dolomite crusher sand from the Roodepoort factory (Table 3.5). Crusher sands from the Olifantsfontein, Kuilsriver, Wadeville and Blackheath factories contained a significantly lower portion of fines.

Table 3.5 Fineness moduli of crusher and filler sands from Gauteng and Western Cape

Factory	**Fineness Modulus**	
	Dolomite crusher sand	Siliceous filler sand
Olifantsfontein	3,99	-
Wadeville	3,30	-
Roodepoort	2,71	1,53
Kuilsriver	3,58	2,64
Blackheath	3,25	1,89

Acid insolubility of the dolomite stones and dolomite crusher sands was predictably low (Table 3.6) indicating the aggregates possess a good acid neutralisation capacity. Solubility of the stones was higher than that of the respective crusher sands. Olifantsfontein and Roodepoort aggregates were more soluble than the Wadeville stone, Wadeville crusher sand, Kuilsriver stone and Blackheath stone. Kuilsriver and Blackheath dolomite sands were of a significantly lower solubility. Sands processed in the Western Cape were not to the specification required for manufacture of concrete pipes. Sands were a by-product from a lime manufacturing plant, which allows more fine clay material to come through during processing. Siliceous sands from Roodepoort and Kuilsriver were of a higher acid insolubility than the sand from Blackheath, which contained an acid-soluble calcareous fraction derived from the presence of broken seashells.

Cement analysis: Chemical compositions of the rapid hardening portland cements were similar (Table 3.7). Cements from the Western Cape contained more iron and sodium oxides, and less magnesium, aluminium and potassium oxides. Olifantsfontein, Wadeville and Roodepoort cements were finer, indicating that these cements were rapid hardening cements, compared with the Kuilsriver and Blackheath cements.

Table 3.6 South African Bureau of Standards (SABS) acid insolubility of coarse and fine aggregates from Gauteng and Western Cape

Factory	**Acid insolubility (%)**		
	Dolomite stone	Dolomite sand	Siliceous sand
Olifantsfontein	4,18	6,28	-
Wadeville	8,45	9,62	-
Roodepoort	4,83	5,87	93,90
Kuilsriver	9,07	13,76	96,44
Blackheath	7,01	15,24	70,02

Table 3.7 Chemical compositions and Blaine fineness of ordinary portland cements from Gauteng and Western Cape

Oxides	**Olifantsfontein**	**Wadeville**	**Roodepoort**	**Kuilsriver**	**Blackheath**
	(%)	(%)	(%)	(%)	(%)
SiO_2	22,1	22,0	22,1	21,8	22,5
Al_2O_3	4,0	4,0	4,0	3,2	3,3
Fe_2O_3	2,5	2,5	2,6	4,2	4,2
TiO_2	0,3	0,3	0,3	0,2	0,2
CaO	64,4	64,2	64,0	64,2	64,9
MgO	4,2	4,2	4,1	1,1	1,06
P_2O_5	0,3	0,3	0,3	0,0	0,0
SO_3^-	2,0	2,0	2,4	2,3	2,6
Cl^-	0,0	0,0	0,01	0,01	0,01
K_2O	0,64	0,65	0,6	0,47	0,48
Na_2O	0,13	0,13	0,14	0,28	0,28
Blaine Fineness (cm^2/g)	4480	4450	4780	3080	3100

Specimen preparation and standard testing

Specimen preparation: All five mixtures compacted well. Siliceous filler sand from Kuilsriver increased the workability of the mixture making compaction easier. Dolomite stone particles from the Western Cape Province fractured significantly more on compaction than those from Gauteng Province. Some of the stone particles from Kuilsriver crumbled into a powder on heavy tamping.

Compressive strengths: Steam curing was effective as strengths of the steam plus air and water-cured specimens were similar (Table 3.8). Strengths of the Roodepoort, Kuilsriver and Blackheath pipes compared favourably to the strengths of the respective laboratory specimens. Olifantsfontein and Wadeville pipe strengths were notably lower than the strengths of the respective laboratory specimens.

Strengths of Western Cape concretes (ca. 45 MPa) were significantly lower than strengths of Gauteng concretes (ca. 65 MPa). Such lower strengths result from the excessive fracturing of Western Cape dolomite stone particles during compaction and differences in the cement fineness. Cracks act as stress raisers and rapidly propagate through the concrete causing premature failure. Visual inspection of the failure surface showed cracks propagating through the fractured dolomite stone particles in the Western Cape concrete whereas cracks in the Gauteng concrete propagated through the cement binder and around the dolomite stone particles.

Table 3.8 Compressive strengths (coefficient of variation less than 5 %) of concrete specimens and respective sewer pipe sections at 28 days

Factory	Pipe section (MPa)	Air-cure spec. (MPa)	Water-cure spec. (MPa)
Olifantsfontein	67,2	76,4	78,3
Wadeville	56,4	65,1	69,8
Roodepoort	66,4	65,9	73,7
Kuilsriver	43,6	42,0	51,2
Blackheath	50,7	47,6	52,1

Relative density: Specimen densities were similar to the respective pipe densities (Table 3.9). Wadeville and Blackheath pipe concretes were of a lower density.

Table 3.9 Relative densities (coefficient of variation less than 5 %) of concrete specimens and respective sewer pipes

Factory	Relative density (g/cm^3)	
	Pipe	*Specimen*
Olifantsfontein	2,57	2,51
Wadeville	2,38	2,47
Roodepoort	2,59	2,51
Kuilsriver	2,53	2,51
Blackheath	2,40	2,44

Acid insolubility: Specimen acid insolubilities compared favourably to the respective pipe acid insolubilities (Table 3.10). Roodepoort, Wadeville and Blackheath pipe insolubilities were higher than the respective specimen insolubilities. Such differences are due to inconsistencies in the mixture contents as pipes from the relevant factories were manufactured using different batches of raw materials.

Table 3.10 SABS acid insolubilities (coefficient of variation less than 5 %) of concrete specimens and respective sewer pipes

Factory	Acid insolubility (%)	
	Pipe	*Specimen*
Olifantsfontein	6,89	6,03
Wadeville	11,87	8,60
Roodepoort	15,25	9,98
Kuilsriver	25,41	24,02
Blackheath	16,60	13,19

All five mixtures were reasonably acid soluble indicating good neutralisation capacities. Acid insolubility of the Olifantsfontein concrete was noticeably lower than that of the Wadeville, Roodepoort and Blackheath concrete. Acid insolubility of the Kuilsriver concrete was significantly higher.

Acid-soluble dolomite aggregate (Table 3.6) in the Olifantsfontein mixture results in the low insolubility value measured. Siliceous filler sands in the Kuilsriver, Blackheath and

Roodepoort mixtures (Table 3.4) account for the higher acid insolubilities. Kuilsriver mixture contains the most siliceous sand explaining the poorer solubility compared to the Blackheath mixture that contains less sand of which a portion is acid-soluble, and the Roodepoort mixture that contains the least sand and a dolomite aggregate of good solubility.

Durability index tests: Oxygen permeability index (OPI) values indicate that concrete specimens and pipes were impermeable and of good quality (Table 3.11). Specimens were of a significantly lower permeability than the respective pipes (a difference of half a unit is large as the OPI values are logarithmic). Water sorptivity values indicate that the specimens and pipes were dense and of low sorptivity. Sorptivity of the pipes compared favourably to that of the respective specimens. OPI and porosity values of the Wadeville pipe are the only exception. Sections of pipe tested were from rejects leading to the inconsistency in the values.

Table 3.11 Oxygen permeability index (coefficient of variation less than 5 %), water sorptivity (coefficient of variation less than 10 %) and porosity (coefficient of variation less than 10 %) measurements of five different concrete specimens and pipe sections

Factory	**OPI**		**Water sorp. (mm/√hr)**		**Porosity (%)**	
	Pipe	*Specimen*	*Pipe*	*Specimen*	*Pipe*	*Specimen*
Olifantsfontein	10,01	10,63	4,92	7,48	6,1	6,5
Wadeville	9,84	10,65	5,20	7,99	12,3	8,0
Roodepoort	10,37	10,79	4,89	4,75	8,2	8,2
Kuilsriver	10,06	10,58	4,75	4,17	8,6	8,9
Blackheath	10,20	10,42	6,69	5,29	10,6	10,4

The results for the standard tests and durability index tests indicated that the laboratory compaction method achieves concrete of a similar quality, often somewhat improved quality to that of the roller-suspension compaction method used for the manufacture of sewer pipes. Specimen concretes of a better quality indicate that the compaction of the preparation method was possibly more forceful than that of the roller suspension method.

A concern was the fracturing of the dolomite stone during compaction, particularly the severe fracturing of the Western Cape stone. Such fracturing does not negatively affect the transport properties of the concrete as much as it does compressive strength. Compaction crushes the stone into smaller particles that are free of cracks, which do not necessarily result in concrete of a poor quality. Cracking does however affect certain characteristics of the concrete. Surface areas of the stone significantly increase effectively exposing more of the dolomite aggregate to a corrosive environment such as an acidic solution.

Standard tests on dolomite stone from the five factories (namely relative density - SANS method 5844, 2006) to assess porosity and aggregate crushing (10 % Fines Aggregate Crushing Test (i.e. 10 % FACT) - SANS method 5842, 2006) to assess strength revealed that the stone from the Western Cape was of a poorer quality than the stone from Gauteng (Appendix B – Section B.3.2). Stone from the Western Cape was of a comparable relative density to stone from Gauteng but of substantially lower 10 % FACT values (Table 3.12).

Size of the stone particles (9,5 mm to 13,2 mm) crushed to determine the 10 % FACT are nominally the same as that in the sewer pipe mixtures making the values a representative measure of the stone strengths. Aggregates with low crushing values such as those from the Western Cape are not a problem in standard concrete mixtures. However, such aggregates are not desirable in high performance mixtures and those intended for heavy mechanical compaction. Quality of the Western Cape stone was poor as the processing of the stone does not comply with specifications required for manufacture of concrete pipes. Stone was a by-product from a lime processing plant.

Table 3.12 Relative density and 10 % FACT values of dolomite stone sourced from factories in Gauteng and Western Cape

Factory	Relative density (g/cm^3)	10 % FACT (kN)
Olifantsfontein	2,87	354
Wadeville	2,81	235
Roodepoort	2,86	246
Kuilsriver	2,79	160
Blackheath	2,79	130

An investigation into the fracturing of the stone during compaction indicated that the specimen preparation method was significantly more destructive than the roller suspension method (Appendix B – Section B.3). Specimens and pipes were compacted using the same mixture. A grading analysis of the mixture was done prior to compaction and directly after specimen and pipe compaction to determine extent of stone particle fracturing. Specimen compaction fractured twice the amount of large stone particles (13,2 mm) than the roller suspension compaction used to manufacture pipes, which significantly alters the concrete matrix of the specimens. Cracks effectively increase the area of the dolomite aggregate, which increases the dissolution/reactivity of the dolomite stone and affects the performance of the concrete in acidic environments.

Specimen compaction was subsequently modified to reduce fracturing of the stone particles (Appendix B – Section B.4) and simulate the fracturing occurring during the compaction of pipes. A circular steel compaction rod with flat ends (32 mm in diameter) replacing the rod with the square base (20 × 20 mm) significantly decreased fracturing of the stone particles during specimen compaction, thus better simulating the fracturing during roller suspension compaction. A method statement (Appendix B – Section B.5), based on the modified compaction procedure, was developed for the preparation of future specimens to investigate the acid resistance of sewer pipe concrete.

Sulphuric acid solution tests

Static tests: Specimen mass loss (average of two determinations) and hydrogen ion consumption decreased progressively with time (Figure 3.9 and 3.10). After 10 days, mass loss became negligible and hydrogen ion consumption remained constant. Sharp increases in mass loss occurred with solution renewals at 14 days, after which the mass loss rate decreased again, becoming negligible after 50 days. Hydrogen ion consumption rate only increased slightly, then decreased and remained constant after 39 days. After 68 days, the Kuilsriver specimens (2,3 %) lost more mass than the Olifantsfontein (2,1 %), Roodepoort (1,9 %), Blackheath (1,8 %) and Wadeville (1,6 %) specimens. Olifantsfontein specimens (3,10 mg/cm^2) consumed more hydrogen ions than the Roodepoort (2,95 mg/cm^2), Blackheath (2,92 mg/cm^2), Kuilsriver (2,83 mg/cm^2) and Wadeville (2,69 mg/cm^2) specimens.

According to the mass loss/hydrogen ion consumption ratios calculated after 68 days, the Kuilsriver specimen (0,81) was of a significantly poorer acid resistance than the Olifantsfontein (0,68), Roodepoort (0,66), Blackheath (0,62) and Wadeville (0,59) specimens. A high ratio indicates that the mass loss of the specimen is relatively high and hydrogen ion consumption relatively low, which is not favourable in sewer environments. Such a concrete disintegrates at a faster rate and neutralises sulphuric acid generated to a lesser extent. A concrete with a low mass loss and a high neutralisation capacity is more effective in acidic sewer environments.

Dynamic tests: Specimen mass loss (average of two determinations) and hydrogen ion consumption decreased with time and became negligible after 4 days (Figure 3.11 and 3.12). Sharp increases in the rates occurred after the solution renewals at 12 and 31 days, after which the rates decreased again and became negligible after a further 7 days. After 68 days, the Kuilsriver specimens (10,5 %) lost more mass than the Roodepoort (9,6 %), Blackheath (9,1 %), Olifantsfontein (8,6 %) and Wadeville (8,5 %) specimens. Wadeville specimens (9,10 mg/cm^2) consumed more hydrogen ions than the Roodepoort (8,92 mg/cm^2), Olifantsfontein (8,68 mg/cm^2), Blackheath (7,94 mg/cm^2) and Kuilsriver (7,85 mg/cm^2) specimens.

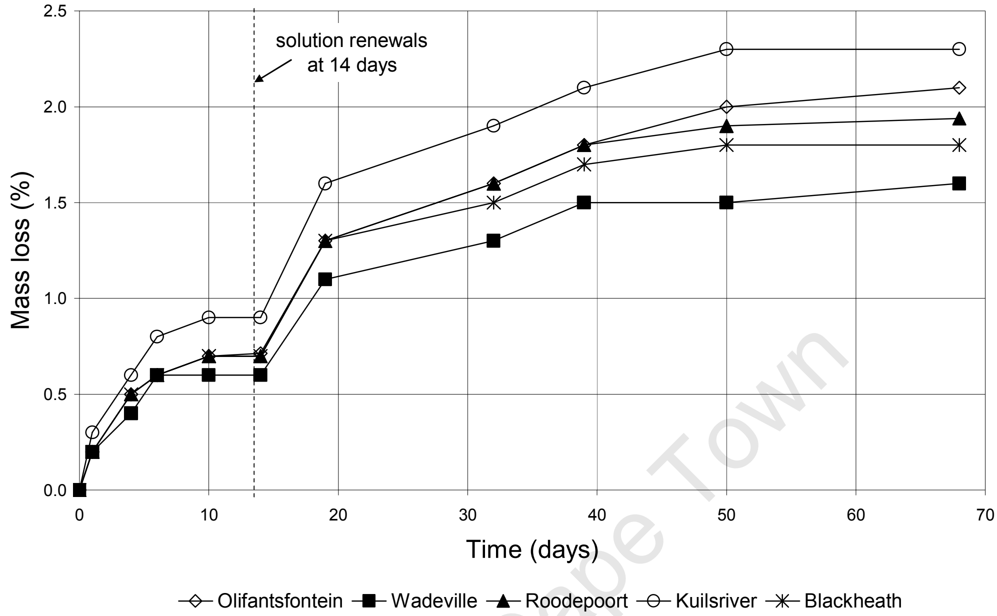

Figure 3.9 Mass losses with time of dolomite aggregate concrete specimens in sulphuric acid solutions maintained at pH 1,00 to 1,50 using the static method

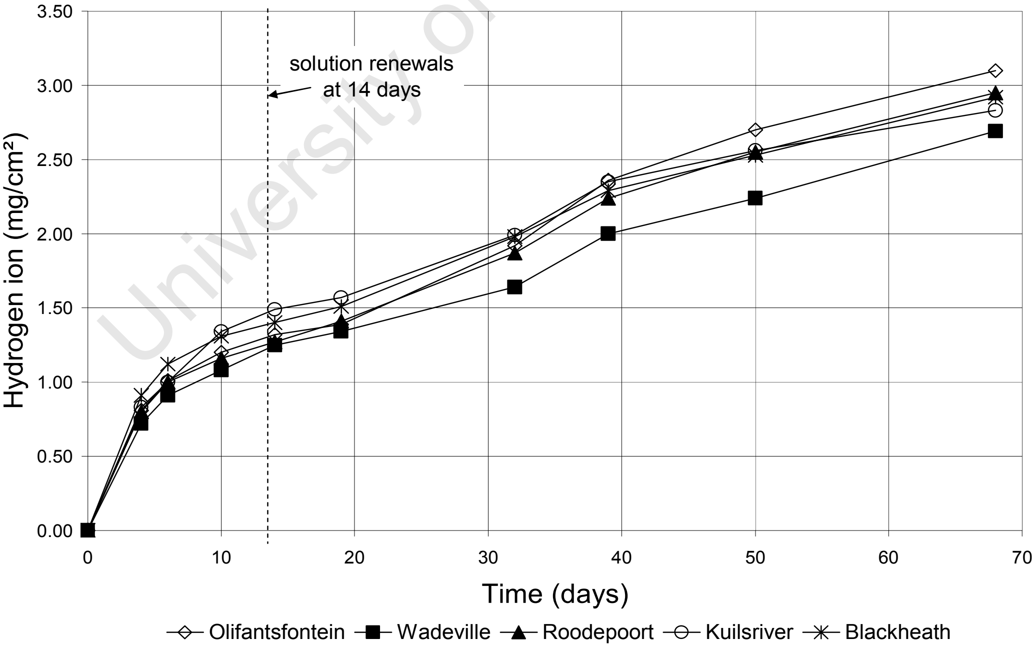

Figure 3.10 Hydrogen ion consumptions with time of dolomite aggregate concrete specimens in sulphuric acid solutions maintained at pH 1,00 to 1,50 using the static method

According to the mass loss/hydrogen ion consumption ratios calculated after 68 days, the Kuilsriver specimen (1,34) again was of a significantly lower resistance. Wadeville (0,93) and Olifantsfontein (0,99) specimens were more resistant than the Roodepoort (1,08) and

Blackheath (1,15) specimens. Ratios in the dynamic tests were significantly higher to those in the static tests as the solutions were renewed twice in the dynamic test and only once in the static test. Solution renewal tends to reflect a significantly higher mass loss in comparison to hydrogen ion consumption as the calcium sulphate layer, which accumulates on the specimens, dissolves without consuming hydrogen ions.

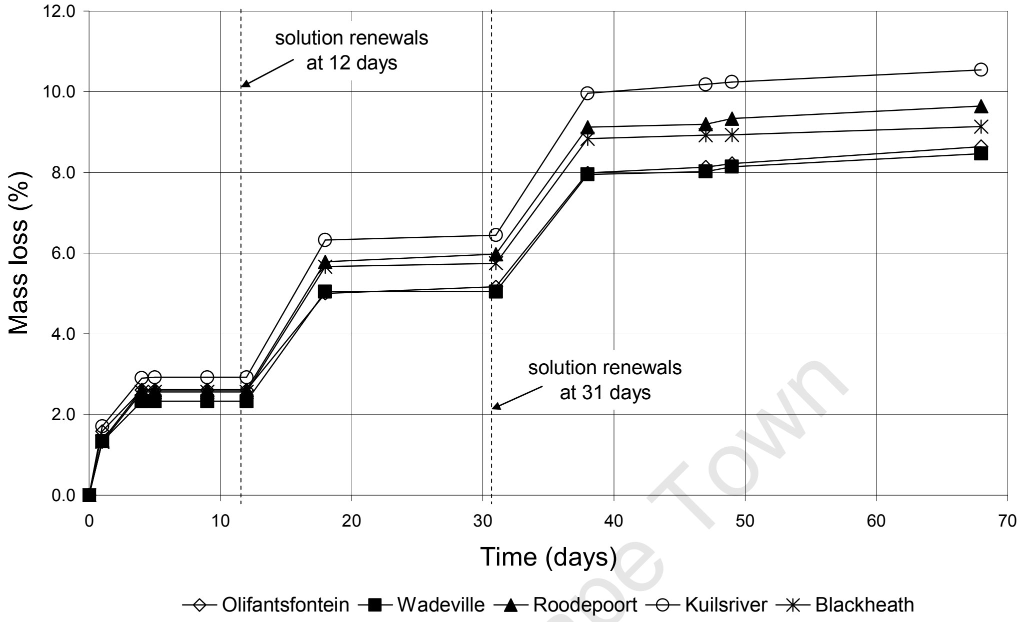

Figure 3.11 Mass losses with time of dolomite aggregate concrete specimens in sulphuric acid solutions maintained at pH 1,00 to 1,50 using the dynamic method

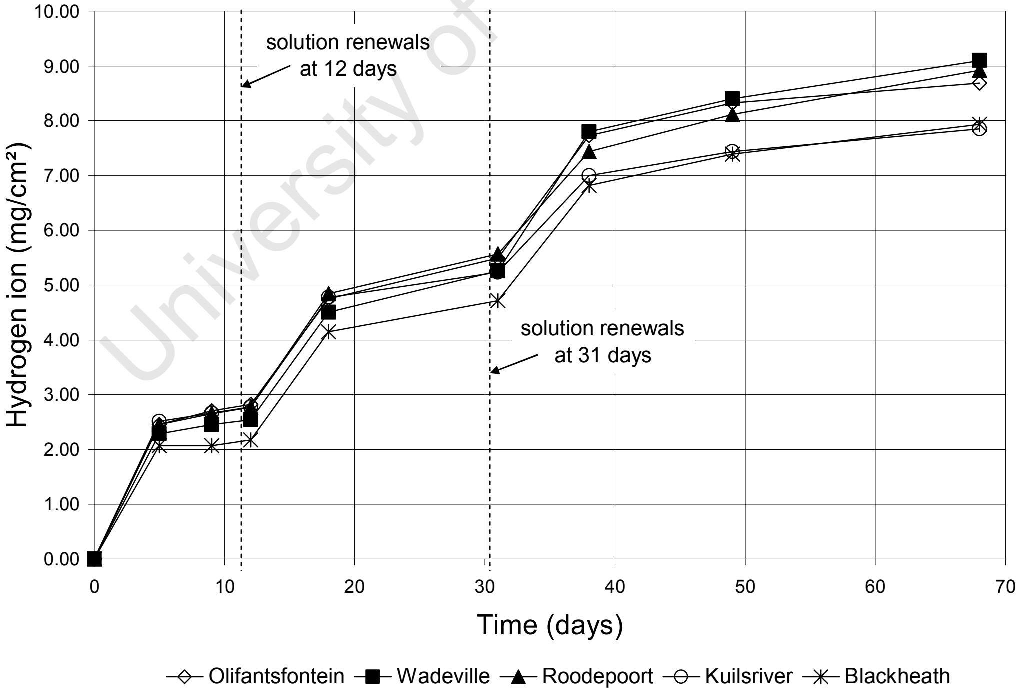

Figure 3.12 Hydrogen ion consumptions with time of dolomite aggregate concrete specimens in sulphuric acid solutions maintained at pH 1,00 to 1,50 using the dynamic method

Attack on the specimens in the static and dynamic tests depends on solubility of the concrete in the sulphuric acid solution, which largely depends on the dissolution of the dolomite aggregate. Surface area exposed to the sulphuric acid solutions mostly consists of dolomite, which contains acid-soluble calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) compounds that completely dissociate in acidic solutions (Equation 3.4 and 3.5) to release carbon dioxide (CO_2).

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \tag{3.4}$$
$$MgCO_3 + H_2SO_4 \rightarrow Mg^{2+} + SO_4^{2-} + H_2O + CO_2 \tag{3.5}$$

Similar mass loss and hydrogen ion consumption rates on the Olifantsfontein, Roodepoort and Wadeville specimens relate directly to their similar compositions (Table 3.4) and the similar acid solubility of the dolomite aggregates (Table 3.6) and consequently the concretes (Table 3.10). Siliceous sand fall-out accounts for the slightly higher mass loss to hydrogen ion consumption ratio of the Roodepoort specimens in the dynamic test. Sand fall-out does not significantly affect mass loss as the content is low and the particles are fine.

Similar mass loss of the Western Cape specimens to the Gauteng specimens relates to the siliceous sand contents of the former mixtures and the severe fracturing of the dolomite aggregate during the compaction of the former mixtures. Sand particle fall-out affects mass loss of the Western Cape specimens more so than that of the Roodepoort specimens, as the contents in the former mixtures were significantly higher and the particles significantly coarser. Slightly higher mass loss of the Kuilsriver specimens compared to the Blackheath specimens relates directly to the higher siliceous sand content and coarser sand particles in the Kuilsriver mixture. Severe fracturing, which increases the surface area of the dolomite aggregate allows for faster dissolution of the poorer acid soluble aggregate giving the Western Cape specimens comparable hydrogen ion consumption rates to the Gauteng specimens.

3.5.5 General discussion

Acid resistance of the dolomite aggregate specimens in the static and dynamic tests is drastically influenced by the saturation of the solutions with calcium sulphate. Saturation of the solutions results in low mass loss and hydrogen ion consumption rates of no substantial difference. The rates also decrease with the increase in thickness of the calcium sulphate layer. Attack depends on the concrete composition prior to saturation. After saturation, it depends on the diffusion of the ions involved in the attack mechanism through the calcium sulphate layers. Attack now depends on the composition and thickness of the layer and not on the chemical and physical compositions of the concrete making mass loss and hydrogen ion consumption rates an inaccurate measure of acid resistance.

Calculation of the amount of concrete to saturate the static and dynamic solutions from the calcium ions required for saturation of the respective solutions and the composition of the concrete indicates saturation occurs within the first day of testing. (The amount of calcium ions required for saturation is calculated from solubility product of calcium sulphate, K_{sp} as done above (Section 3.2.4)).

Static solutions require 0,38 g of calcium ions for saturation, and the dynamic solutions 0,96 g which results from the dissolution of CaO and $CaCO_3$ (dissolution of other acid-soluble compounds in the concrete such as $MgCO_3$ the sulphates formed such as the $MgSO_4$ are readily soluble in the sulphuric acid solution and negligibly influence the attack mechanism)

Assuming the concrete consist of 18 % cement which contains 65 % CaO, and 82 % dolomite which contains 50 % $CaCO_3$

$\therefore$ 1 g of concrete = 0,18 g of cement + 0,82 g of dolomite
$\therefore$ 1 g of concrete contains 0,12 g of CaO (56,08 g/mol) and 0,41 g of $CaCO_3$ (100,09 g/mol)
$\therefore$ 1 g of concrete contains 0,002 moles of CaO and 0,004 moles $CaCO_3$
Assuming CaO and $CaCO_3$ completely dissociate in the solutions

$\therefore$ 1 g of concrete liberates 0,006 moles or 0,25 g of Ca ions (40,08 g/mol) into the solutions

∴ Amount of concrete to saturate the static solution is 1,53 g and the dynamic solution is 3,87 g

After 1 day, approximately 8 g of concrete dissolves into the static solution and 64 g of concrete dissolves into the dynamic solution that is, five and sixteen times that required to saturate the respective solutions with calcium sulphate.

Mass loss and hydrogen ion consumption rates in the static tests were significantly lower compared to those in the dynamic tests, despite the faster saturation of the dynamic solutions, which stifles attack after 4 days compared to 10 days in the static solutions. Attack rates partly increase due to the larger solution volumes in the dynamic test allowing dissolution of more calcium ions. Significant increases directly relate to the continuous brushing, limiting precipitation of calcium sulphate on the specimens and forcing calcium sulphate to remain suspended in the solution or precipitate onto the floor of the container.

Static and dynamic tests fail to give sufficiently sensitive measurements to determine differences in acid resistances of dolomite aggregate concrete. Stifling of the attack prohibits useful measurements of mass loss and hydrogen ion consumption to predict acid resistances within a short period (5 days). Attack accelerates with sulphuric acid solution renewals, which result in the sharp increases in mass losses and hydrogen ion consumptions. Sustaining the attack requires frequent renewals to prevent the formation of a layer, which only partially disintegrates liberating sufficient calcium ions into the fresh solutions for saturation and immediately stifling any further attack.

Slower stifling of the mass loss and hydrogen ion consumption in the static test solution relates to the increase in reactivity in the dynamic test solution and the continuous brushing, which removes any loose corrosion debris accumulating on the surfaces of the specimens and generates a denser calcium sulphate layer. Accumulation on the specimen surfaces of any insoluble corrosion debris such as fine siliceous sand particles infers porosity allowing easier diffusion of ions and prolonging hydrogen ion consumption. Some of the insoluble particles dislodge during brushing of the static test specimens prior to their weighing explaining the longer period of mass loss.

3.5.6 Conclusion

Olifantsfontein, Wadeville and Roodepoort specimens exhibit better resistance to sulphuric acid solutions than the Blackheath and Kuilsriver specimens. The good quality of the dolomite aggregate from Gauteng gives the concrete a better integrity whereas the good acid solubility of the aggregate infers a better neutralisation capacity. The fracturing of the Western Cape dolomite aggregate allows for a faster dissolution of the aggregate particles decreasing the structural integrity of the concrete. Fall-out of the coarse siliceous sand particles further decreases the integrity of the concretes.

Assessing the acid resistance of dolomite aggregate concrete used for the manufacture of sewer pipes is not successful using either the static or the dynamic methods. The rapid saturation of the test solutions with calcium sulphate and consequent formation of the layer isolates the specimens from the sulphuric acid solutions giving low measurements of mass loss and hydrogen ion consumption, which were not significantly different and not functions of the chemical and physical composition of the concrete.

Acid resistance of the dolomite aggregate concretes are better assessed using the dynamic test procedure than the static test procedure. Attack rates in the dynamic test are significantly higher than those in the static tests (mass loss rates and hydrogen ion consumption rates in the dynamic test are respectively 5 times and 3 times those in the static test). Although the dynamic testing procedure proves more suited to assess the acid resistance of the dolomite aggregate concrete, reliable mass loss and hydrogen ion consumption measurements were only possible with regular solution renewals, which exposes the fresh concrete to the sulphuric acid solution minimising the effect of the calcium sulphate layer on the attack mechanism. Such renewals also simulate the worse case scenario, that is attack at the average daily sewage level, which is of prime importance. Attack at the crown is a secondary consideration and static tests to simulate conditions at the crown require exceptionally long testing times, which fail to predict the corrosion rates in the area that leads to the potential collapse of the pipe.

3.6 Sulphuric acid solution test to investigate calcium sulphate saturation

The aim of this investigation was to ascertain the effect of calcium sulphate saturation on the attack mechanism with time on dolomite aggregate concrete specimens immersed in a sulphuric acid solution.

3.6.1 Experimental method

Blackheath specimens (two of the air-cured specimens prepared for the static and dynamic tests – Section 3.5.2) were immersed in a sulphuric acid solution (50 ℓ) at a pH of 1,00, which increased over the 66 hour test period to a pH of 1,30. Specimens were continuously brushed during rotation using the soft-PVC-bristle brush. Specimens were removed and cleaned with a stiff bristle nylon brush under running water once every 2 hours for the first 12 hours and then at random time intervals prior to weighing and measuring the dimensions. Hydrogen ion concentration of the solution was determined by titration prior to re-immersing the specimens. Mass losses and hydrogen ion consumptions of the specimens were recorded with time.

3.6.2 Results and discussion

Specimen mass loss rate (average of two specimens) and hydrogen ion consumption rate decreased with time (Figure 3.13). Over the initial 24 hours of testing, the mass loss and hydrogen ion consumption (3,1 % and 2,39 mg/cm^2 respectively) were significantly higher compared to those over the following 24 hours (0,8 % and 0,74 mg/cm^2 respectively).

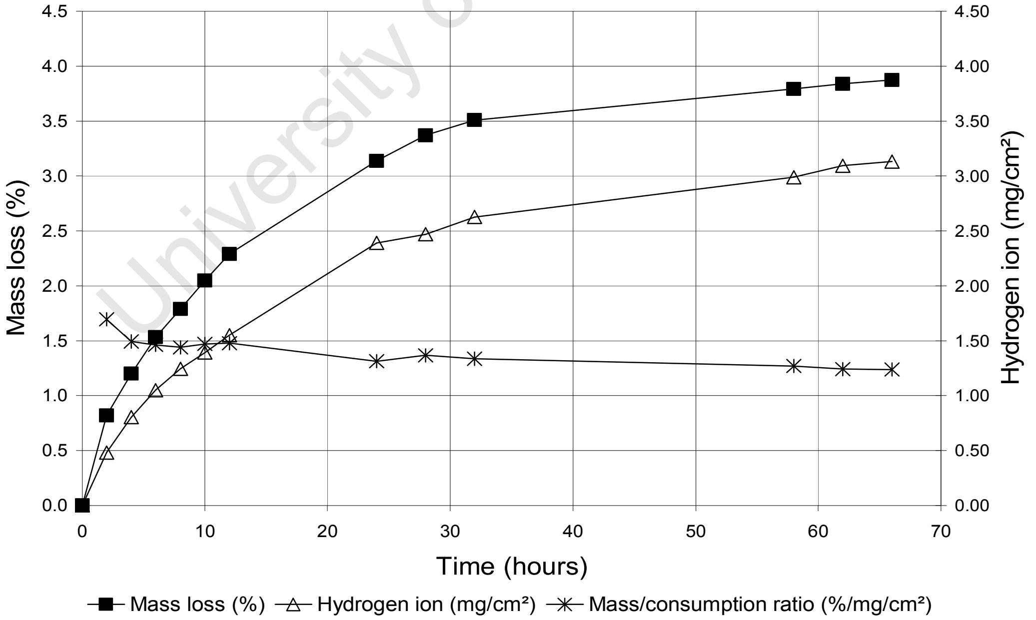

Figure 3.13 Mass losses, hydrogen ion consumptions and mass/consumption ratios with time of Blackheath concrete specimens in a sulphuric acid solution maintained at pH 1,00 to 1,30

The rate of attack was high directly after immersion of the specimens. Acid-soluble compounds destabilise at a fast rate due to the high hydrogen ion concentration (100,8 mg/ℓ) and there is a rapid spontaneous dissociation of the acid-soluble compounds into the fresh solution. Attack rate decreases shortly after immersion. Saturation of the solution with calcium sulphate occurs within the initial 2 hours of testing slowing the dissolution of the calcium oxide and calcium carbonate. Approximately 23 g of concrete dissolves into the solution after 2 hours, which liberates significantly more calcium ions than the 3,87 g of concrete required to liberate the amount of calcium required to saturate the 50 ℓ solution with calcium sulphate (refer to calculations in Section 3.5.4).

After saturation, the calcium sulphate precipitating onto the specimens significantly slows the attack resulting in the continuous decrease in hydrogen ion consumption and corresponding mass loss rates. Such a direct relationship between the mass loss and hydrogen ion consumption (see ratio on Figure 3.13) indicates that the calcium sulphate layer inhibits the diffusion of hydrogen ions. Concentration of hydrogen ions behind the layer decreases as the thickness increases with time slowing the dissolution of the acid-soluble compounds from the fresh concrete. After about 30 hours, the layer reaches a thickness that virtually stifles the attack.

A slow but steady decrease in the mass loss to hydrogen ion consumption ratio with time (1,70 to 1,24, Figure 3.13) indicates that the mass loss rate decreases at a faster rate than the hydrogen ion consumption rate, which is due to the mass gain from the precipitation of the calcium sulphate.

3.6.3 Conclusion

A dolomite aggregate concrete rapidly saturates the sulphuric acid test-solution with calcium sulphate, which decreases the mass loss and hydrogen ion consumption rates substantially within the first 24 hours of testing. Sustaining the attack on the concrete requires frequent renewals of the solution. Solution renewals at least once every 24 hours are required to sufficiently disintegrate the calcium sulphate layer and expose the fresh concrete thereby ensuring the attack remains a function of the physical and chemical properties of the concrete.

Accelerating the attack with solution renewals generates useful trends of mass loss and hydrogen ion consumption with time. Constant exposure of the concrete to the sulphuric acid solution ensures mass loss directly relates to hydrogen ion consumption, which is useful in predicting the ability of the dolomite aggregate concrete to resist and neutralise a biologically induced sulphuric acid environment. A practical solution renewal frequency to minimise the saturation effect and generate such a relationship is required in order to measure the acid resistance of the sewer pipe concrete reliably, since continuous renewals to eliminate the saturation effect are not feasible.

3.7 Sulphuric acid solution renewal tests

The aim of this investigation was to assess the feasibility of sulphuric acid solution renewals to determine acid resistances of dolomite aggregate concrete using the dynamic rig.

3.7.1 Experimental methods

Specimens (two of the air-cured Roodepoort and two of the air-cured Blackheath specimens prepared for the static and dynamic tests – Section 3.5.2) were immersed, each specimen in separate sulphuric acid solutions (50 ℓ) maintained at a pH of 1,00 to 1,05. Two of the solutions (one containing a Roodepoort specimen and one containing a Blackheath specimen) were renewed every 24 hours and the remaining two solutions each containing one of the respective specimens were renewed every 8 hours for a period of 5 days. Specimens were continuously brushed during rotation with the soft-PVC-bristles. Specimens were removed every 24 and 8 hours respectively, that is at times coinciding with the solution renewals. Specimens were cleaned under running water with a stiff nylon brush, weighed and their dimensions measured prior to re-immersion into the fresh solutions. Mass loss and hydrogen ion consumption of the specimens were recorded with time.

3.7.2 Results and discussion

Solution renewals every 24 hours: Mass loss and hydrogen ion consumption of the Roodepoort specimen and the Blackheath specimen were similar with time (Figure 3.14). After 120 hours (5 days), mass loss and hydrogen ion consumption of the Blackheath specimen (17,4 % and 12,88 mg/cm^2) were fractionally higher compared to those of the Roodepoort specimen (17,1 % and 12,27 mg/cm^2).

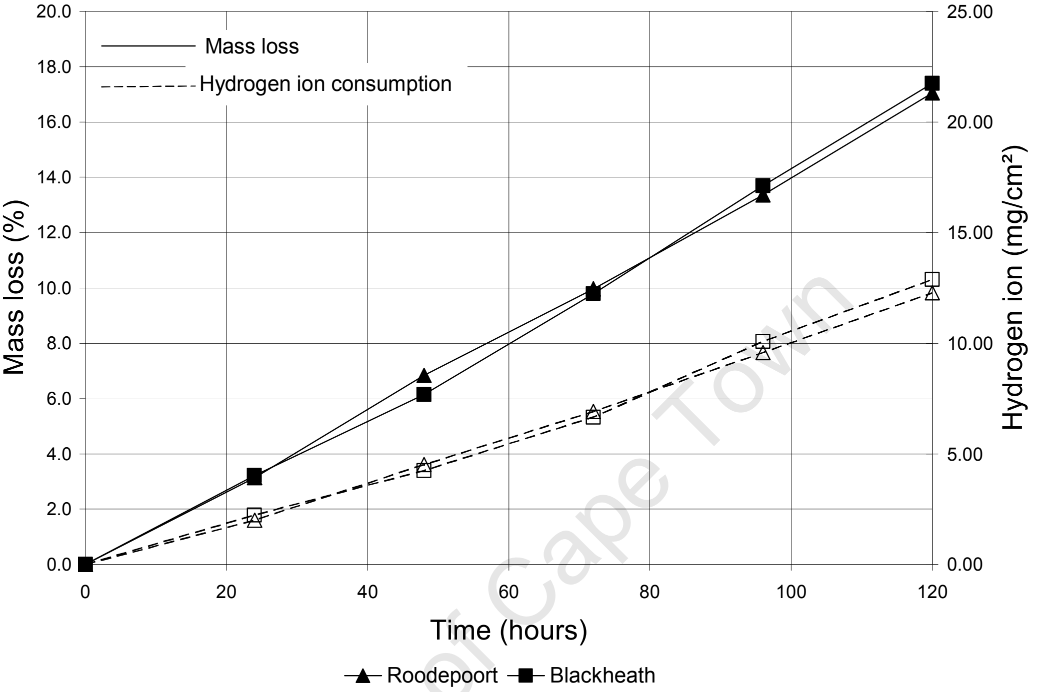

Figure 3.14 Mass loss and hydrogen ion consumption with time of Roodepoort and Blackheath concrete specimens in sulphuric acid solutions renewed every 24 hours

Solution renewals every 8 hours: Mass loss and hydrogen ion consumption of the Blackheath specimen were significantly higher compared to those of the Roodepoort specimen with time (Figure 3.15). After 120 hours (5 days), the mass loss and hydrogen ion consumption of the Blackheath specimen (27,5 % and 22,56 mg/cm^2) were substantially higher compared to those of the Roodepoort specimen (19,1 % and 14,36 mg/cm^2).

Solubility of the concretes in the sulphuric acid solution caused the significant differences in mass loss and hydrogen ion consumption between the specimens in the 8-hour renewal test. The resulting build-up rate of the calcium sulphate layer on the specimens led to the similar mass loss and hydrogen ion consumption in the 24-hour renewal test (Figure 3.14). Mass loss and hydrogen ion consumption measurements in the 8-hour test clearly indicate that the Blackheath concrete dissolves at a faster rate than the Roodepoort concrete. As a result, the calcium sulphate layer builds up at a faster rate on the Blackheath specimen than the Roodepoort specimen, which reduces mass loss and hydrogen ion consumption of the Blackheath specimen at a faster rate than that of the Roodepoort specimen causing the similar mass loss and hydrogen ion consumption measurements after 24 hours (Figure 3.16).

Constant mass loss and hydrogen ion consumption rates in the 24-hour and 8-hour renewal tests with time were due to the measurements coinciding with the solution renewals. Attack in each of the solutions prior to renewal is similar. Similar amounts of concrete and/or calcium sulphate dissolve into each of the respective fresh solutions giving similar mass loss and hydrogen ion consumption resulting in the constant cumulative rates measured in the 24-hour and 8-hour renewal tests.

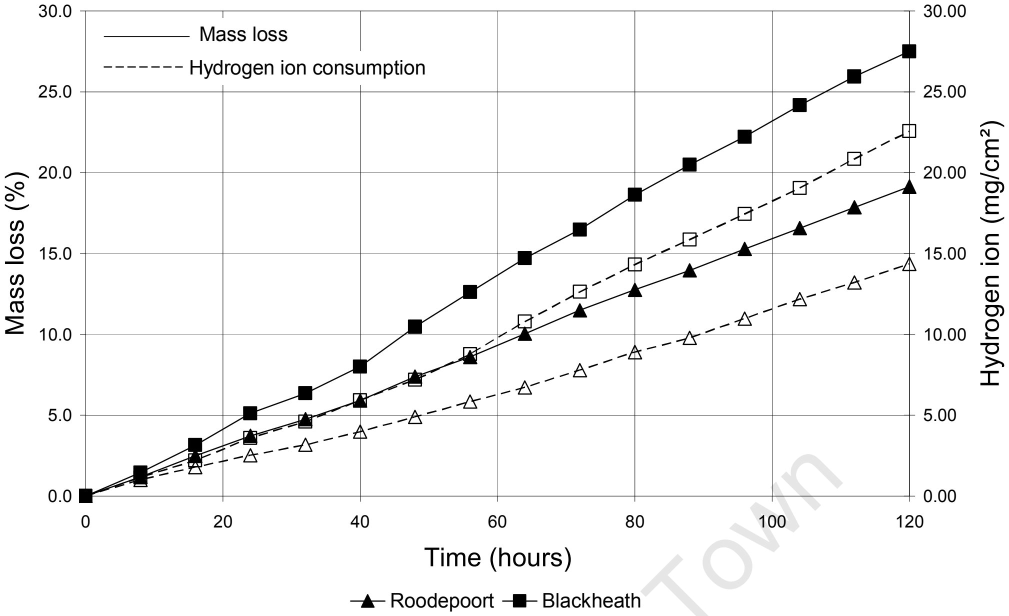

Figure 3.15 Mass loss and hydrogen ion consumption with time of Roodepoort and Blackheath concrete specimens in sulphuric acid solutions renewed every 8 hours

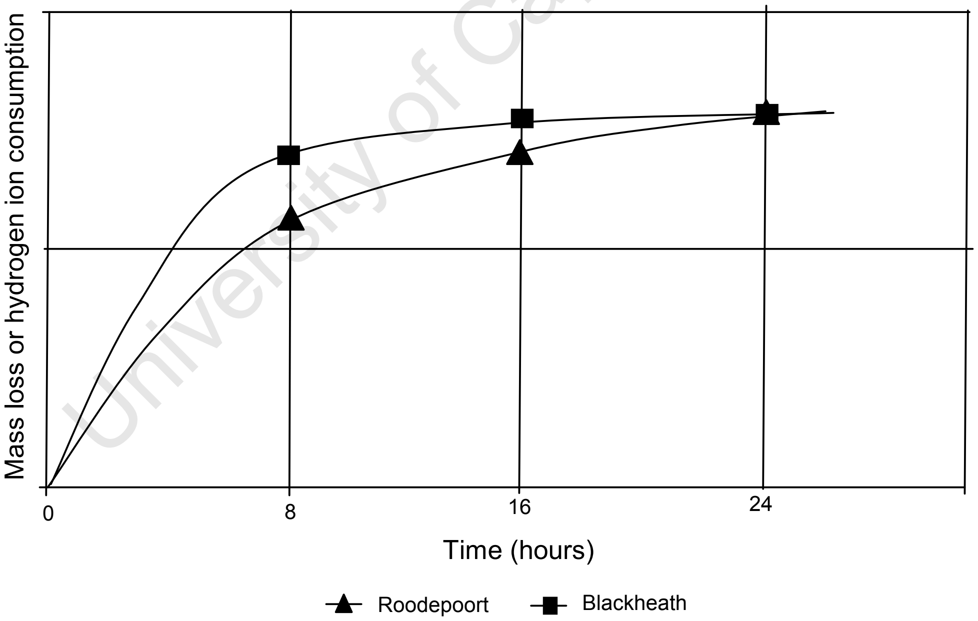

Figure 3.16 Schematic illustrating the difference in the rates at which mass loss or hydrogen ion consumption decrease with time in a sulphuric acid solution at a pH of 1,00 for a Roodepoort specimen and a Blackheath specimen

A need for a representative test that accounts for the manner in which the physical and chemical properties influence the acid solubility of concrete is evident from the sulphuric acid renewal tests. An acid insolubility test such as the SABS test indicates that the Roodepoort concrete is more soluble than the Blackheath concrete (Table 3.10). The substantially lower mass loss and hydrogen ion consumption of the Roodepoort specimen in the 8-hour renewal test clearly indicates the concrete is capable of resisting an acidic environment better, that is it resists dissolution better in the form of a composite material.

The similar attack rates of the specimens in the 24-hour renewal tests compared to the significant differences in the 8-hour renewal tests confirm the impact of the calcium sulphate layer on the sulphuric acid attack mechanism. Calcium sulphate accumulates and stifles the attack on more soluble concrete at a faster rate. Compensating for the differences in solubility requires frequent solution renewals to minimise the stifling effect of the layer on the attack mechanism. In the absence of the layer, provided the formation of the layer can be prevented or minimised, the measurements of mass loss and hydrogen ion consumption are dependant on the concrete properties and allow for the determination of acid resistance.

3.7.3 General discussion

Solution renewals every 8 hours compensate for the higher solubility of the Blackheath concrete and allow for successful determination of the differences in acid resistance between the Roodepoort and Blackheath concrete. A more soluble concrete requires more frequent solution renewals to determine the differences in acid resistance. Such renewals are labour-intensive, time consuming and require a separate investigation to determine the renewal frequency. Obtaining sufficient mass loss and hydrogen ion consumption trends requires testing over several days, and to achieve representative results more than one specimen of each concrete needs testing, which requires numerous solution renewals.

However, sulphuric acid solution renewals fail to completely eradicate the influence of calcium sulphate on the attack mechanism, as saturation occurs soon after immersion of the dolomite aggregate concrete specimens. Continuous renewals to eliminate the saturation effect and simulate attack at the average daily sewage level of concrete sewer pipes are not viable. Therefore, simulating attack requires an acid solution such as a hydrochloric acid solution, which possesses similar attack properties but forms soluble reaction products.

Sulphuric and hydrochloric acids both completely dissociate in an aqueous solution. As a result, solutions prepared to contain an equal amount of hydrogen ions possess the ability to attack the concrete to the same extent. Calcium dissolving into the hydrochloric acid solution does not precipitate out as calcium chloride ($CaCl_2$), since it is readily soluble in an aqueous solution (solubility > 0,1 mol/ℓ) whereas calcium sulphate is sparingly soluble (solubility of 0.01 – 0,1 mol/ℓ) (Ebbing, 1984).

A solubility of greater than 0,1 mol/ℓ implies that more than 0,1 mol/ℓ of Ca^{2+} is required to saturate the hydrochloric acid solution (Equation 3.6).

$$CaCl_2 \rightarrow Ca^{2+} + 2Cl^- \qquad (3.6)$$

$\therefore$ In a 50 ℓ hydrochloric acid solution, more than 5 moles or 200,4 g of $CaCl_2$ is required for saturation.

As calculated previously (Section 3.5.4), 1 g of dolomite aggregate concrete dissolving liberates 0,25 g of Ca^{2+} into an aqueous acid solution.

$\therefore$ More than 802 g of dolomite aggregate concrete are required to saturate a 50 ℓ hydrochloric acid solution with $CaCl_2$, which is substantially higher than the 3,87 g of dolomite aggregate concrete (Section 3.5.4) required to saturate the 50 ℓ sulphuric acid solution with $CaSO_4$.

Other salts such as magnesium, aluminium and iron chlorides involved in the attack are present in far lesser amounts and are also readily soluble (solubility > 0,1 mol/ℓ) and cannot saturate the hydrochloric acid solution. Therefore, owing to the absence of the sulphate ion and the soluble nature of the salts that form, the concrete remains exposed to a hydrochloric acid solution.

3.7.4 Conclusion

Concrete containing the dolomite aggregate from the Blackheath factory is of poorer acid resistance to that containing the dolomite aggregate from the Roodepoort factory. The higher solubility of the Blackheath dolomite compared to the Roodepoort dolomite is directly related to the differences in physical properties between the aggregates, which determine the dissolution rates of the particles in the dynamic test. Acid insolubility measurements clearly indicate the Blackheath dolomite is chemically of a lower solubility, which implies the faster dissolution of the aggregate particles in the sulphuric acid solution is due to factors such as higher porosity and cracks that are inflicted during the specimen compaction.

Assessing acid resistance in sulphuric acid solutions using the dynamic rig is not practical as frequent solution renewals are required to minimise the effect of the calcium sulphate layer on the attack mechanism and ensure measurements of mass loss and hydrogen ion consumption remain functions of the physical and chemical properties of the concrete, rather than of the solution. Assessing attack at the average daily sewage level, which represents the worst-case scenario, requires a test medium in which the reaction products are completely soluble to prevent formation of a tenacious corrosion layer on the concrete specimens.

3.8 Assessing attack on concrete in a hydrochloric acid solution

The aim of this investigation was to assess the feasibility of using a hydrochloric acid solution of similar strength to the sulphuric acid solution in the dynamic rig to measure the acid resistance of sewer pipe concrete specimens as functions of mass loss and hydrogen ion consumption.

3.8.1 Experimental method

A Roodepoort and a Blackheath specimen (air-cured specimens prepared for the static and dynamic tests – Section 3.5.2) were each immersed in a hydrochloric acid solution (50 ℓ) at a pH of 1,00. Solution pH was allowed to vary for 24 hours after which the pH was re-adjusted to 1,00 to ensure control within a range of 1,00 to 1,50. Specimens were rotated and continuously brushed with the soft-PVC-bristle brush to remove loose corrosion debris. Specimens were removed and cleaned (under running water using a stiff nylon brush) once every 8 hours for 104 hours. Specimens were weighed, dimensions measured and hydrogen ion concentration of the solutions determined prior to re-immersion. Mass loss and hydrogen ion consumption were recorded with time.

3.8.2 Results and discussion

After 104 hours, the mass loss and hydrogen ion consumption of the Blackheath specimen (43,2 % and 35,68 mg/cm^2) were significantly higher than that of the Roodepoort specimen (37,0 % and 26,53 mg/cm^2) (Figure 3.17). Mass loss rate of the Roodepoort specimen remained constant with time whereas that of the Blackheath specimen increased somewhat after 24 hours. Hydrogen ion consumption rates of both specimens increased continuously with time but that of the Blackheath specimen increased at a faster rate than that of the Roodepoort specimen.

The significantly higher and continuous mass loss and hydrogen ion consumption of the specimens with time in the hydrochloric acid solution compared to those in the sulphuric acid solution indicate that the corrosion products formed do not precipitate out of the hydrochloric acid solution to stifle the acid attack mechanism. Calcium, magnesium, aluminium, potassium and sodium chlorides that form during the dissolution reaction are readily soluble (solubility > 0,1 molℓ) in the hydrochloric acid solution (Ebbing, 1984).

For example, the amount of calcium ions (the most abundant of the ions in the dolomite aggregate concrete) liberated from the Blackheath concrete specimen (the most attacked) after 104 hours is substantially lower than that required for calcium chloride saturation:-

Amount of concrete dissolving after 104 hours into the solution = 648,9 g

Since 1 g of dolomite aggregate concrete contains 0,25 g of Ca^{2+} (Section 3.5.4)
∴648,9 g of dolomite aggregate concrete contains 162,2 g of Ca^{2+}
∴162,2 g / 40,08 g/mol = 4 moles of calcium is liberated from the Blackheath concrete specimen into the 50 ℓ hydrochloric acid solution after 104 hours

∴Concentration of the calcium ion after 104 hours is approximately 0,08 mol/ℓ, which is less than that required for saturation (greater than 0,1 mol/ℓ)

(Note: A rough estimation of the amount of calcium chloride to saturate an aqueous solution is evident from the SABS acid insolubility test where a saturated solution of calcium chloride is required to condition the test specimen. An excess of 500 g was required to saturate a litre of de-ionised water, which equates to a solubility of more than 4,5 mol/ℓ.)

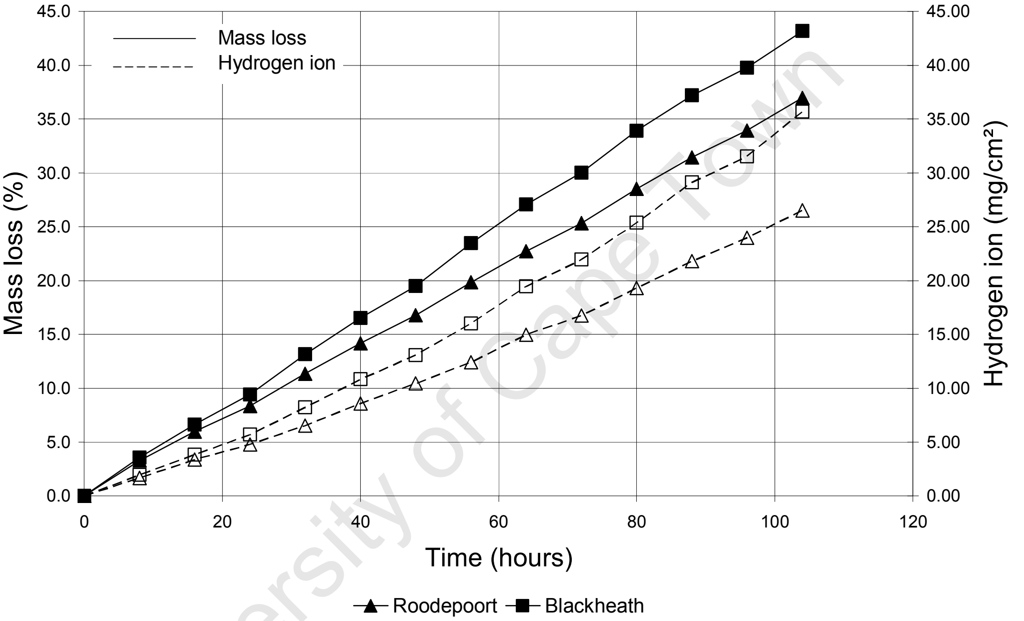

Figure 3.17 Mass loss and hydrogen consumption of Roodepoort and Blackheath concrete specimens with time in a hydrochloric acid solution maintained at pH of 1,00 to 1,50

As a result, only a porous layer of corrosion debris consisting of acid-insoluble particles remains on the specimen surfaces in the hydrochloric acid solution. The ions involved in the attack freely move through the layer and are easily removed with the brushing of the specimens under running water offering little interference. The constant exposure of the fresh concrete to the acid solution ensures the mass loss and hydrogen ion consumption measurements are a function of the chemical and physical properties of the concrete, and allows for an accurate comparison of acid resistance between the Blackheath and Roodepoort specimens.

An increase in the hydrogen ion consumption rate with time directly relates to the exposure and dissolution of the dolomite aggregate stone particles. As the attack front progresses, the amount of dolomite stone exposed to the solution increases whereas that of the cement binder portion decreases. Amount of calcium carbonate and magnesium carbonate in a portion of dolomite (80 to 90 %) is significantly higher compared to the amount of calcium oxide in a similar portion of cement (65 %). Therefore, an equivalent amount of dolomite neutralises substantially more hydrogen ions (Equations 3.1, 3.4 and 3.5) without necessarily reflecting a corresponding increase in mass loss.

Stone particles in the Blackheath concrete specimen were noticeably more soluble compared to those in the Roodepoort concrete specimen and dissolved at a faster rate than the cement binder portion to leave cavities on the attacked surface of the Blackheath specimen (Figure 3.18). The exposure of the faster dissolving Blackheath stone as the attack front progresses with time accounts for the increase in the mass loss rate with time and contributes to the higher mass loss and hydrogen ion consumption of the Blackheath specimen in comparison to the Roodepoort specimen. SABS measurements show that, chemically, the Blackheath stone is of a significantly lower acid solubility (Table 3.5). This implies the faster dissolution must relate to a physical property of the stone such as the fracturing of the particles during compaction, which results in the preferential dissolution of the stone. As a result, an increase in hydrogen ion consumption rate with time occurs as the Blackheath dolomite stone particles are exposed, causing the increase in mass loss rate after 24 hours.

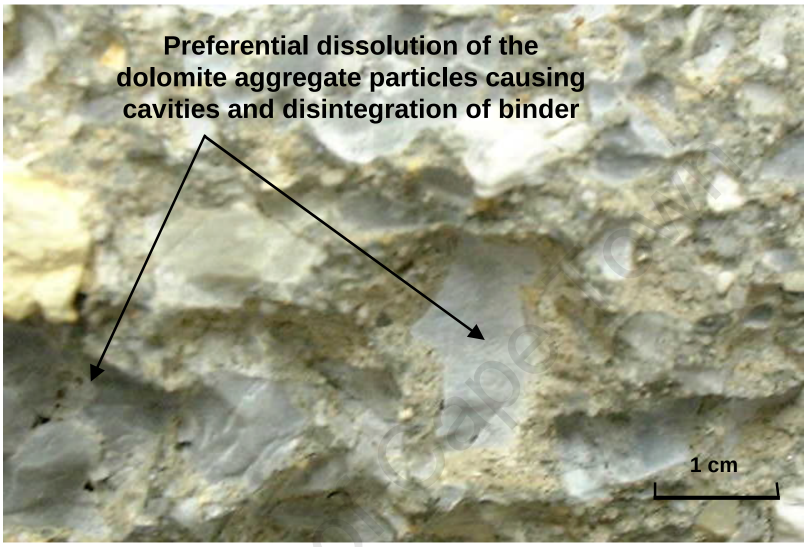

Figure 3.18 Blackheath specimen exposed to a hydrochloric acid solution maintained at a pH of between 1,00 and 1,50 for 104 hours

3.8.3 General discussion

The absence of a tenacious corrosion layer accounts for the significantly higher attack rate in the hydrochloric acid solution compared to that in the sulphuric acid solution renewed every 8 hours. After 104 hours, mass loss and hydrogen ion consumption for the Blackheath (43,2 % and 35,68 mg/cm^2) and Roodepoort (37,0 % and 26,53 mg/cm^2) specimens in the hydrochloric acid solution were approximately twice those of the Blackheath (24,2 % and 19,05 mg/cm^2) and Roodepoort (16,6 % and 12,18 mg/cm^2) specimens in the sulphuric acid solution. Solubility of the Blackheath concrete is noticeably higher than that of the Roodepoort concrete in the hydrochloric acid solution as corrosion debris accumulating on the specimens affects the attack mechanism far less than the calcium sulphate layer accumulating in the sulphuric acid solutions.

The similar mass loss to hydrogen ion consumption ratios of the Blackheath and Roodepoort specimens in the hydrochloric acid solution (1,21 and 1,39 respectively) compared to those in the sulphuric acid solution (1,27 and 1,36 respectively) indicates the nature of attack is similar in both mediums. The lower ratio of the Blackheath specimen implies the concrete possesses a better neutralisation capacity than the Roodepoort concrete, albeit that the mass loss is substantially higher. Dissolution of the Blackheath specimens was however at the expense of the dolomite aggregate particles giving the concrete a noticeably poorer integrity and resistance to an acid environment.

3.8.4 Conclusion

Mass loss and hydrogen ion consumption measurements in the hydrochloric acid solution clearly indicate that the acid solubility of the Blackheath concrete is substantially higher than that of the Roodepoort concrete. The soluble nature relates to the faster dissolution of the Blackheath dolomite aggregate particles, which destroys the integrity of the concrete giving the concrete a poorer acid resistance than that of the Roodepoort concrete.

Acid resistances of sewer pipe concrete are suitably assessed from mass loss and hydrogen ion consumption measurements on specimens in a hydrochloric acid solution using the dynamic rig. Measurements are a function of the chemical and physical properties of the concrete specimens and illustrate the capacity of the concrete to neutralise an acidic environment. Obtaining representative measurements with which to assess acid resistances are less time consuming and labour intensive than in sulphuric acid solution renewal tests.

3.9 Assessing the reliability of testing in a hydrochloric acid solution

The aim of this investigation was to compare mass loss and hydrogen ion consumption measurements of the dolomite aggregate concretes in a hydrochloric acid solution to those in a sulphuric acid solution to:-

- assess the reliability of testing in the hydrochloric acid solution
- determine the control of variables necessary to develop a robust procedure for testing in a hydrochloric acid solution
- formulate a standard test method to measure acid resistance as functions of chemical and physical properties of sewer pipe concrete

3.9.1 Sample preparation and standard testing

Concrete specimens were prepared from sewer pipe mixtures (Table 3.4) and a new batch of raw materials sourced from the Olifantsfontein, Wadeville, Roodepoort, Kuilsriver and Blackheath factories. Sieve analysis and acid insolubility were done on the coarse and fine aggregates. Chemical compositions of the cements were not measured, and were assumed similar to those determined for the static and dynamic testing (Table 3.7). Cements were from the same sources, which maintain strict quality control.

Specimens were prepared using the standard method (Appendix B – Section B.6). Aggregates were air-dried prior to mixing. A w/c ratio of 0,36 was used to achieve the desired consistency for compaction of the mixtures. Acid insolubility, relative density, oxygen permeability, water sorptivity and porosity were measured on steam-cured specimens after air curing them for 28 days in a conditioning room maintained at 25 °C and 60 % relative humidity. Compressive strengths were measured on steam-cured specimens after water curing them at 23 °C for 28 days.

3.9.2 Experimental methods

Specimens (eight from each mixture) were immersed, four each separately in a hydrochloric acid solution at a pH of 1,00, and four each separately in a sulphuric acid solution at a pH of 1,00. The pH of the hydrochloric acid solutions was re-adjusted to 1,00 every 24 hours to ensure control within a range of 1,00 to 1,50. The pH of the sulphuric acid solutions was maintained within a range of 1,00 to 1,05 by the solution renewals every 8 hours to reduce the effect of the calcium sulphate saturation on the attack mechanism. Specimens were continuously brushed during rotation. Specimens were removed once every 8 hours and cleaned under running water prior to weighing. Hydrogen ion concentrations of the solutions were determined and sulphuric acid solution renewals were done prior to re-immersion of the specimens. Hydrochloric acid solutions were renewed after 48 hours to determine the effect of fresh solutions on the mass loss and hydrogen ion consumption rates. Dimensions of the specimens were determined once every 24 hours. Specimen mass loss and hydrogen ion consumption rates were recorded for 96 hours.

3.9.3 Results and discussion

Analyses of raw materials

Sieve analysis: Stone particles from Olifantsfontein, Wadeville, Roodepoort and Blackheath factories were less than 19,0 mm in size (Figure 3.19). Stone from the Kuilsriver factory contained a small amount of particles greater than 19,0 mm. Stone from the Kuilsriver and Roodepoort factories contained more particles greater than 13,2mm than that from the Olifantsfontein, Blackheath and Wadeville factories. Stone particles from Olifantsfontein and Roodepoort factories were all greater than 6,7 mm in size. Stone from Wadeville, Blackheath and Kuilsriver factories contained particles smaller than 6,7 mm and 4,75 mm.

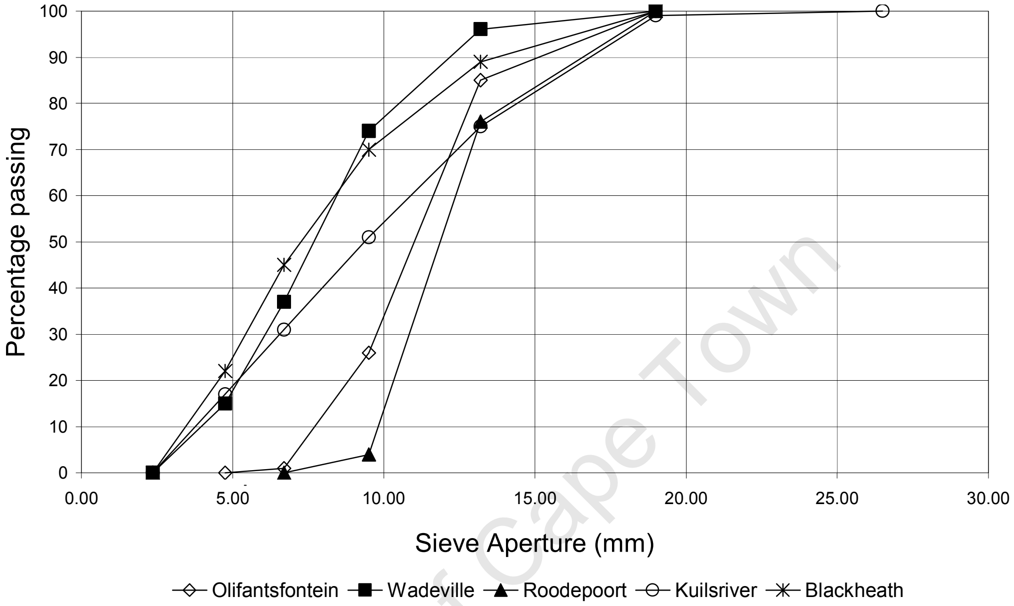

Figure 3.19 Particle size analyses of dolomite stone from Gauteng and Western Cape (standard sieve sizes: 19,0 mm; 13,5 mm; 6,5 mm; 4,75 mm and 2,36 mm)

Dolomite crusher sand from the Blackheath factory contained more particles greater than 0,6 mm in size than that from the Olifantsfontein and Wadeville factories (Figure 3.20). Sand from the Kuilsriver factory contained significantly less particles greater than 0,6 mm in size and that from the Roodepoort factory the least. Sand from the Kuilsriver factory contained the largest fraction of particles smaller than 0,6 mm in size. Sands from Kuilsriver and Roodepoort contained a significantly higher portion of fines than the sands from Blackheath, Olifantsfontein and Wadeville (Table 3.13).

Siliceous filler sand from the Kuilsriver factory was substantially coarser than that from Roodepoort and Blackheath factories (Figure 3.21). Sands from Roodepoort and Blackheath contained significantly more fines than the sand from the Kuilsriver factory (Table 3.13).

Acid insolubility: Acid insolubility of the dolomite stone and crusher sand from the Olifantsfontein factory and the dolomite crusher sand from the Roodepoort factory was lower than that of the dolomite stone from the Roodepoort, Blackheath and Wadeville factories and the dolomite crusher sand from the Wadeville factory (Table 3.14). Acid insolubility of the dolomite crusher sand from the Blackheath factory and the dolomite stone from the Kuilsriver factory was significantly higher and that of the dolomite crusher sand from Kuilsriver substantially higher. Acid insolubility of the dune sand from the Blackheath factory was substantially lower than that of the siliceous filler sands from the Roodepoort and Kuilsriver factories due to the calcareous seashell fraction in the dune sand.

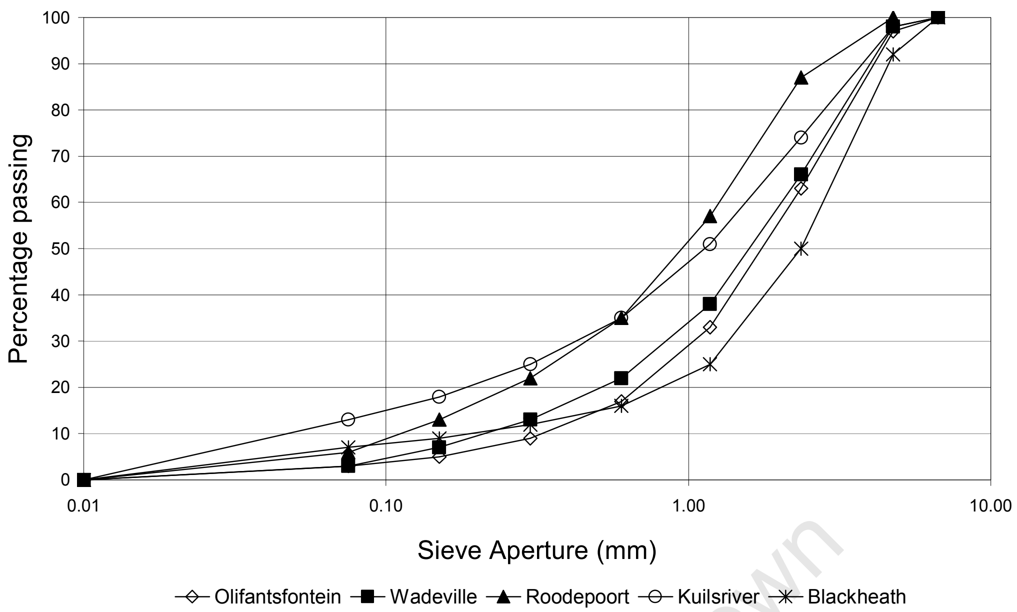

Figure 3.20 Particle size analyses of dolomite crusher sands from Gauteng and Western Cape (standard sieve sizes: 6,7 mm; 4,75 mm; 2,36 mm; 1,18 mm; 0,6 mm; 0,3 mm; 0,15 mm and 0,075 mm)

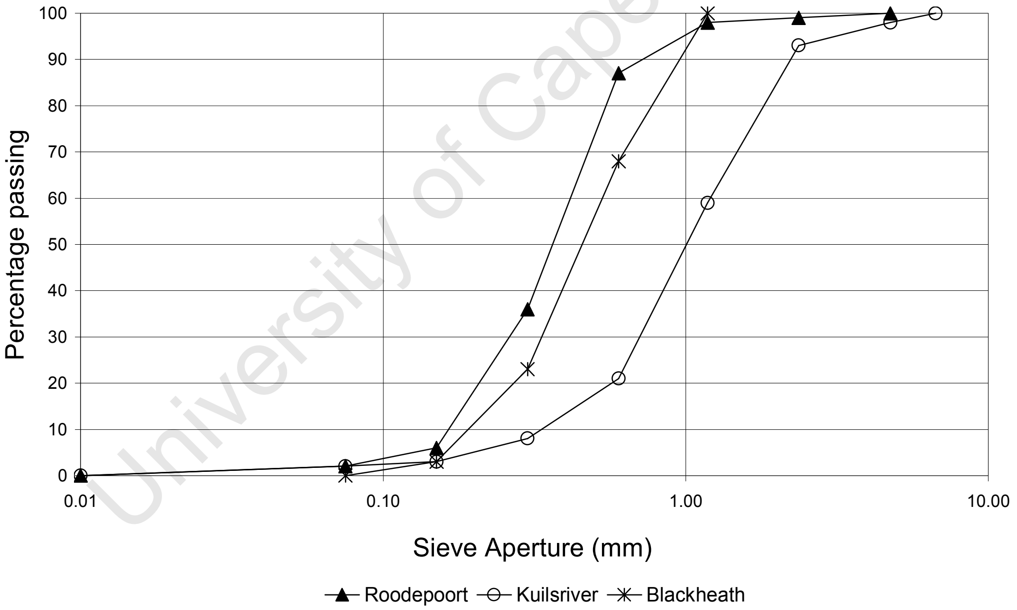

Figure 3.21 Particle size analyses of siliceous filler sands from Gauteng and Western Cape (standard sieve sizes: 6,7 mm; 4,75 mm; 2,36 mm; 1,18 mm; 0,6 mm; 0,3 mm; 0,15 mm and 0,075 mm)

Specimen preparation

The compaction method fractured and crushed some of the dolomite stone and crusher sand particles from the Western Cape. Soft particles, which pulverise into a powder on compaction, were present. Compaction of the Kuilsriver mixture was difficult due to the higher workability arising from the siliceous filler sand, which gave excessive movement.

Table 3.13 Fineness moduli of crusher and filler sands from Gauteng and Western Cape

Factory	Fineness Modulus	
	Dolomite crusher sand	Siliceous filler sand
Olifantsfontein	3,76	-
Wadeville	3,56	-
Roodepoort	2,86	1,74
Kuilsriver	2,99	3,18
Blackheath	3,96	2,06

Table 3.14 SABS acid insolubility (coefficient of variation less than 5 %) of coarse and fine aggregates from Gauteng and Western Cape

Material	Acid insolubility (%)		
	Dolomite stone	Dolomite sand	Siliceous sand
Olifantsfontein	5,89	5,23	-
Wadeville	8,15	9,83	-
Roodepoort	9,39	6,55	95,81
Kuilsriver	14,48	23,36	97,10
Blackheath	9,00	15,69	70,72

Standard testing of concrete specimens

Compressive strengths of the Olifantsfontein and Roodepoort specimens were higher than those of the Wadeville specimens, the reason for which is unclear (Table 3.15). Strengths of the Kuilsriver and Blackheath specimens were substantially lower due to the fracturing of the dolomite stone on compaction. Cracks result in premature failure during compression of the specimen. Strengths of the Olifantsfontein, Wadeville and Roodepoort specimens were higher compared to those of the respective pipe concretes (Table 3.8). Strengths of Kuilsriver and Blackheath specimens were similar to those of the respective pipe concretes.

Table 3.15 Relative density (coefficient of variation less than 5 %), acid insolubility (coefficient of variation less than 5 %), oxygen permeability (coefficient of variation less than 5 %), water sorptivity (coefficient of variation less than 10 %), porosity (coefficient of variation less than 10 %) and compressive strength (coefficient of variation less than 5 %) of the concrete specimens

Material	Relative Density (g/cm^3)	Acid insol. (%)	Oxygen Perm. (Index)	Water sorp. (mm/√hr)	Porosity (%)	Compr. Strength (MPa)
Olifantsfontein	2,48	5,93	10,39	6,66	9,12	84,2
Wadeville	2,44	9,44	10,16	5,90	9,72	66,2
Roodepoort	2,47	11,20	10,51	5,62	9,03	80,3
Kuilsriver	2,46	20,48	10,01	4,93	10,87	38,6
Blackheath	2,44	14,27	9,48	5,57	9,09	39,2

Relative density, oxygen permeability index, water sorptivity and porosity of the specimens were relatively similar and typical of good quality concretes (Table 3.15). The exception was the lower oxygen permeability of the Blackheath specimen, which could result from the fracturing of the stone particles. All values indicate the specimens were dense, impermeable and of low sorptivity. Similar values for specimen concrete and respective pipe concrete (Table 3.9 and 3.11) indicate the specimen compaction is similar to the roller suspension compaction. Similarity in the values with those of the specimens prepared for the static and dynamic tests (Table 3.9 and 3.11) illustrate the specimen compaction method was repeatable, consistent and reliable.

Acid insolubility of the specimens was low indicative of concrete soluble in acidic mediums (Table 3.15). Acid insolubility of the Olifantsfontein specimens was the lowest due to the soluble nature of the dolomite aggregates. Acid insolubility of the Wadeville specimens was lower than that of the Roodepoort specimens containing acid-insoluble siliceous filler sand. Acid insolubility of the Blackheath specimens was higher due to the poorer solubility of the dolomite crusher sand and siliceous sand content. Acid insolubility of the Kuilsriver specimens was the highest due to the poor acid solubility of the dolomite aggregates and large siliceous filler sand content. Acid insolubility values of the concrete specimens were similar to those of the respective pipe concretes (Table 3.9).

Hydrochloric acid solution tests

Mass loss of the specimens (average of four determinations) increased at a constant rate with time. After 96 hours, mass loss of the Blackheath (36,9 %), Kuilsriver (35,8 %) and Olifantsfontein (34,3 %) specimens were significantly higher than that of the Wadeville (31,8 %) and Roodepoort (31,3 %) specimens (Figure 3.22).

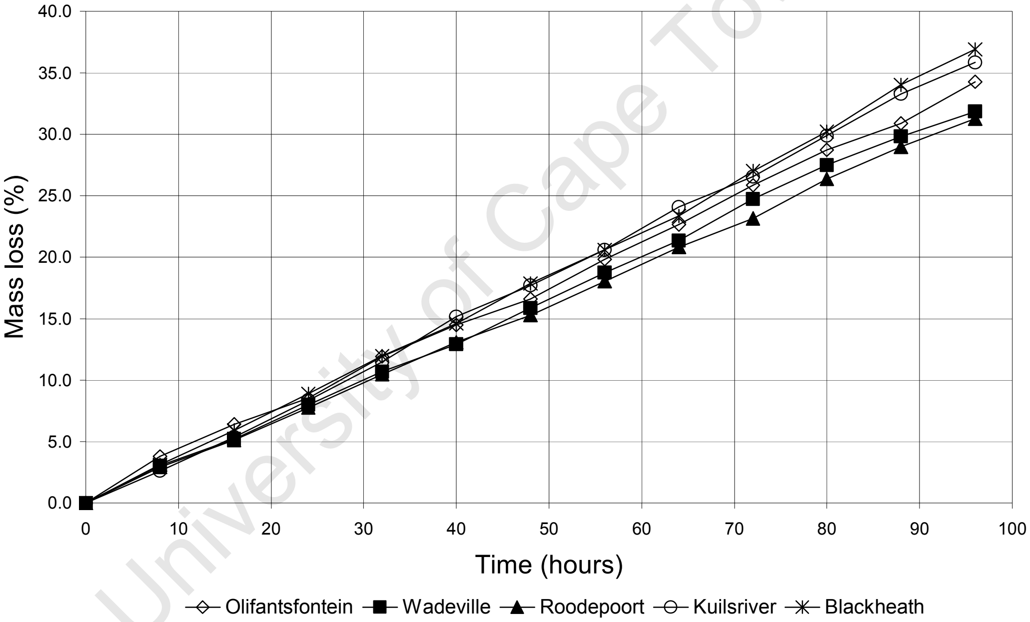

Figure 3.22 Mass loss with time of dolomite aggregate concrete specimens in hydrochloric acid solutions maintained at pH 1,00 to 1,50

Hydrogen ion consumption rates (average of four determinations) increased with time (Figure 3.23). Consumptions of the Olifantsfontein and Blackheath specimens increased at higher rates than those of the Kuilsriver, Wadeville and Roodepoort specimens. After 96 hours, consumptions of the Olifantsfontein (31,27 mg/cm^2) and Blackheath (29,54 mg/cm^2) specimens were significantly higher than those of the Kuilsriver (26,82 mg/cm^2), Wadeville (25,77 mg/cm^2) and Roodepoort (25,47 mg/cm^2) specimens.

The continuous mass loss and hydrogen ion consumption with time was due to the absence of a corrosion layer precipitating on the specimens in the hydrochloric acid solutions. The increase in the hydrogen ion consumption rate was due to the increase in exposed area of dolomite stone, which is of a higher neutralisation capacity, and corresponding decrease of area of cement binder exposed to the hydrochloric acid solution as the attack front progresses with time. Hydrogen ion consumption of the Olifantsfontein specimens was highest and increased at a faster rate due to the higher acid solubility of the dolomite aggregate (Table 3.14), which also accounts for the higher mass loss of the specimens compared to that of the Wadeville and Roodepoort specimens.

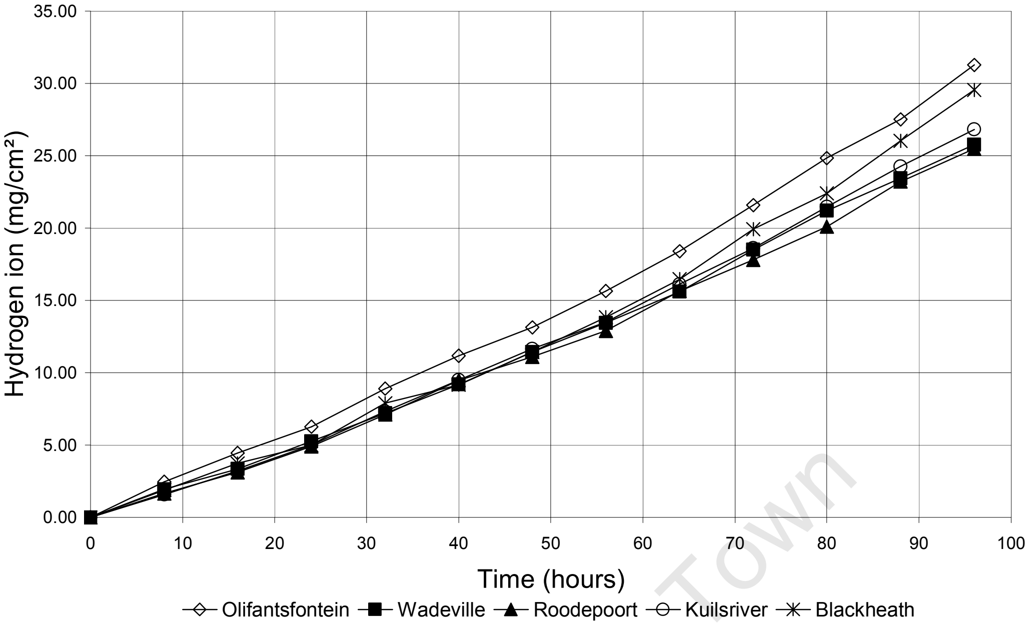

Figure 3.23 Hydrogen ion consumption with time of dolomite aggregate concrete specimens in hydrochloric acid solutions maintained at pH 1,00 to 1,50

Mass loss of the Blackheath specimens was higher than that of the Olifantsfontein specimens due to the faster dissolution of the Western Cape dolomite stone resulting from the fracturing during compaction. Mass loss of the Kuilsriver specimens was similar to that of the Blackheath specimens due to fracturing of the dolomite stone and fall-out of the siliceous sand particles. Fall-out of the sand particles and the lower acid solubility of the dolomite stone (Table 3.14) results in the lower hydrogen ion consumption of the Kuilsriver specimens compared to the Blackheath specimens. Hydrogen ion consumption of the Blackheath specimens and Olifantsfontein specimens, which were more acid-soluble (Table 3.15) and that of the Kuilsriver specimens and the more acid-soluble Wadeville and Roodepoort specimens (Table 3.15) were similar due to the fracturing of the Western Cape dolomite stone.

According to mass loss to hydrogen ion consumption ratios, the Olifantsfontein concrete (1,09) is more efficient in resisting and neutralising an acidic environment than the Roodepoort (1,23) and Wadeville (1,23) concrete. The Blackheath concrete (1,25) appears as efficient as the latter two Gauteng concretes but is so at the expense of the preferential dissolution of the dolomite aggregate particles giving the concrete poorer resistance in the acid environment. The Kuilsriver concrete (1,33) is significantly less efficient in resisting and neutralising an acid environment due to the fall-out of the coarse siliceous sand particles, which decreases the integrity of the concrete and as a result the neutralisation capacity.

After 96 hours, the difference in mass loss between the Blackheath and Roodepoort specimens (5,6 %) was comparable to that (5,9 %) measured in the preliminary hydrochloric acid solution test (Section 3.8.3) whereas the difference in hydrogen ion consumption (4,07 mg/cm^2) was almost half that previously measured (7,55 mg/cm^2). The significant difference in the hydrogen ion consumption measurements is directly related to the differences in the dissolution rates of the different dolomite stone batches received from the Blackheath and Roodepoort factories in the hydrochloric acid solution. The Roodepoort stone from the previous batch consumed less hydrogen ions in its physical state albeit that the stone was of a significantly lower acid insolubility (4,83 % compared to 9,39 %) whereas the Blackheath stone in the previous batch consumed more due to the lower acid insolubility of the stone (7,01 % compared to 9,00 %). Hydrogen ion consumption depends not only on the chemical potential of the stone to dissolve but also on properties such as structural and chemical composition, shape, size, porosity and strength and these differences result in the different consumptions of the Roodepoort stone in its physical state.

As a result, the Roodepoort specimen tested here consumes more hydrogen ions (25,47 mg/cm^2 compared to 23,97 mg/cm^2) but loses less mass, which makes the concrete more efficient in neutralising an acid environment compared to that in the previous batch (i.e. a mass loss to hydrogen ion consumption ratio of 1,22 compared to 1,44 respectively). In contrast the Blackheath specimen tested here consumes more (29,54 mg/cm^2 compared to 31,52 mg/cm^2) and loses more mass, as a result making the concrete as efficient in neutralising an acid environment as that from the previous batch (i.e. a mass loss to hydrogen ion consumption ratio of 1,24 compared to 1,26).

Visual examination of specimens on completion of the tests clearly illustrates differences in attack mechanisms on the various sewer pipe concretes. Attacked surfaces of the Olifantsfontein and Wadeville specimens were smooth compared to those of the Roodepoort specimens, which appear rougher due to the slower dissolution of some dolomite stone particles that stand proud (Figure 3.24). Surfaces of the Kuilsriver and Blackheath specimens were substantially rougher in comparison (Figure 3.25). Cavities due to the preferential dissolution of the dolomite stone particles appear over the entire surface. Surfaces of the Kuilsriver specimens appear the roughest due to fall-out and protrusion of the coarse siliceous sand particles (Figure 3.26).

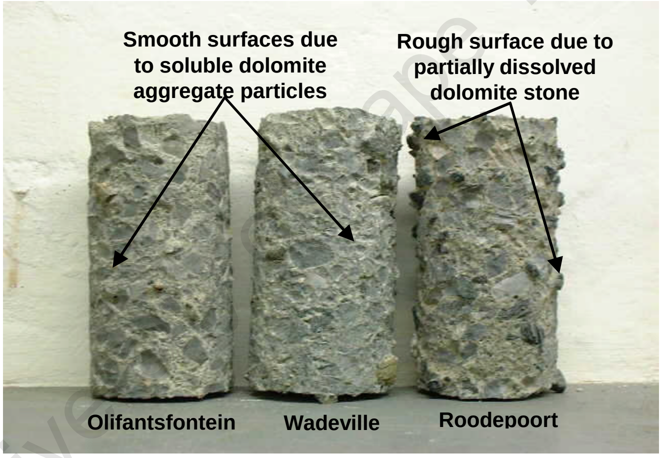

Figure 3.24 Olifantsfontein, Wadeville and Roodepoort specimens exposed to hydrochloric acid solutions maintained at a pH of 1,00 to 1,50 for 96 hours

Sulphuric acid solution renewal tests

Mass loss (average of four determinations) and hydrogen ion consumption (average of four determinations) of the specimens increased at a constant rate with time. After 96 hours, mass loss of the Blackheath (21,3 %), Kuilsriver (20,3 %) and Olifantsfontein (18,7 %) specimens was significantly higher than that of the Roodepoort (14,2 %) and Wadeville (13,4 %) specimens (Figure 3.27). Hydrogen ion consumption of the Blackheath (15,78 mg/cm^2) specimens was higher than that of the Olifantsfontein (13,85 mg/cm^2) and Kuilsriver (13,26 mg/cm^2) specimens, which was significantly higher than that of the Wadeville (8,72 mg/cm^2) and Roodepoort (8,56 mg/cm^2) specimens (Figure 3.28).

Calcium sulphate saturation and precipitation results in the substantially lower mass loss and hydrogen ion consumption of the specimens in the sulphuric acid solution compared to those in the hydrochloric acid solution. After 96 hours, the Wadeville and Roodepoort specimens reflected a 56 % lower mass loss and a 66 % lower hydrogen ion consumption in the sulphuric acid solution. Mass loss of the Olifantsfontein, Kuilsriver and Blackheath specimens was 43 % lower whereas hydrogen ion consumption of the Olifantsfontein specimens was 56 % lower and that of the Kuilsriver and Blackheath specimens 50 % and 46 % lower respectively.

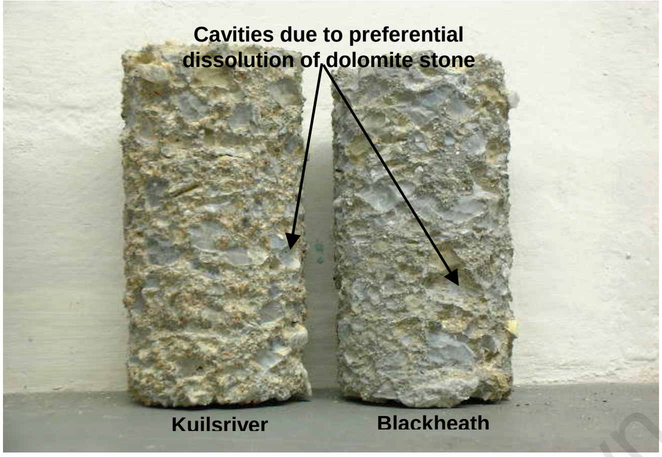

Figure 3.25 Kuilsriver and Blackheath specimens exposed to a hydrochloric acid solutions maintained at a pH of 1,00 to 1,50 for 96 hours

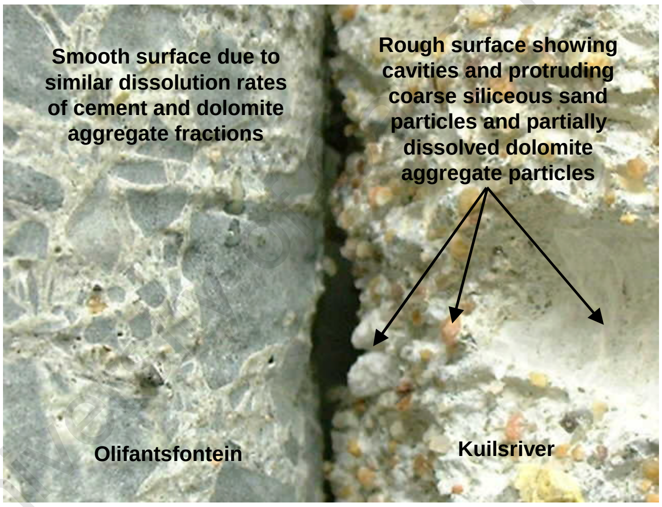

Figure 3.26 Olifantsfontein and Kuilsriver specimens exposed to hydrochloric acid solutions maintained at a pH of 1,00 to 1,50 for 96 hours

Similar rankings in mass loss between the specimens were obtained in the hydrochloric and sulphuric acid solutions whereas the hydrogen ion consumption rankings were different (Table 3.16). Consumption of the Blackheath specimens was significantly higher than that of the Olifantsfontein specimens in the sulphuric acid solutions, whereas in the hydrochloric acid solutions consumption of the Olifantsfontein specimens was higher than that of the Blackheath specimens. Consumption of the Olifantsfontein and Kuilsriver specimens was similar and significantly higher than that of the Wadeville and Roodepoort specimens in the sulphuric acid solutions, whereas consumption of the Kuilsriver, Wadeville and Roodepoort specimens was similar in the hydrochloric acid solutions.

Variations in the mass loss and hydrogen ion consumption between the specimens in the sulphuric acid and hydrochloric acid solutions, and the differences in the hydrogen ion consumption rankings, are related to the different saturation rates of the sulphuric acid solutions with calcium sulphate and the poorer control of pH in the hydrochloric acid solutions.

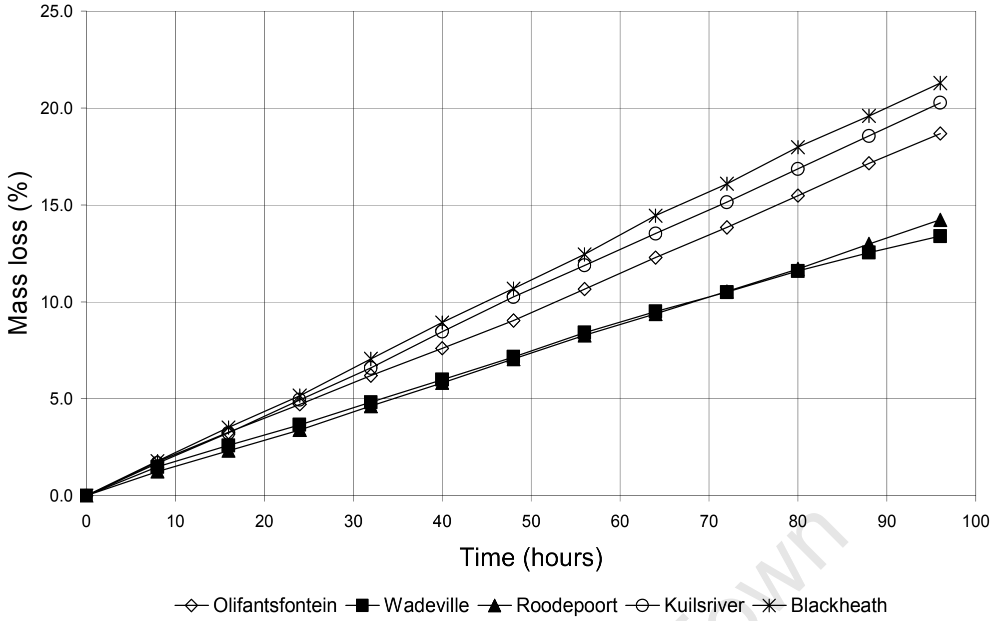

Figure 3.27 Mass loss with time of the dolomite aggregate concrete specimens in sulphuric acid solutions renewed once every 8 hours

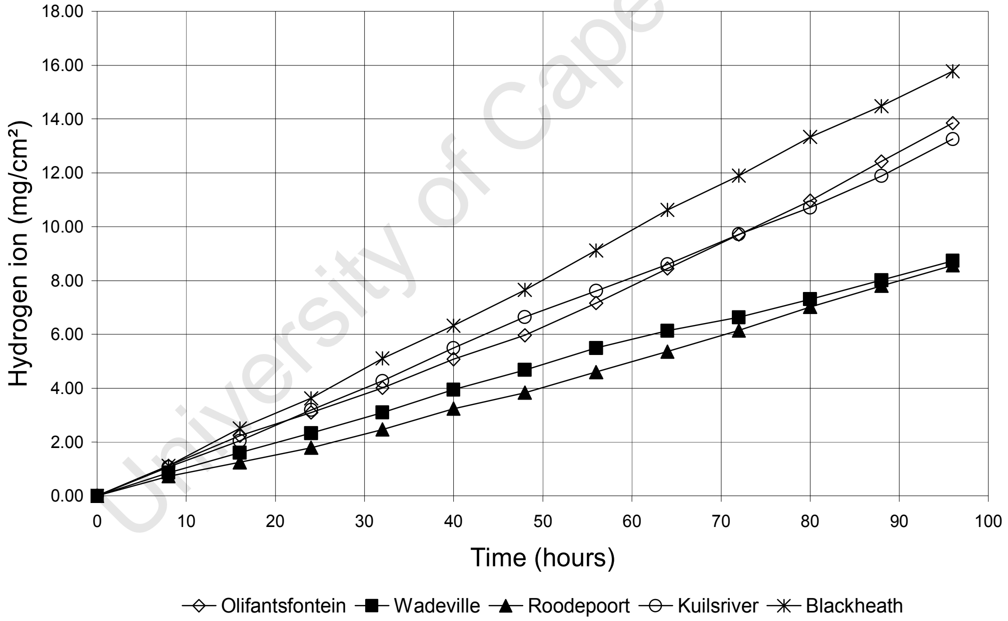

Figure 3.28 Hydrogen ion consumption with time of the dolomite aggregate concrete specimens in sulphuric acid solutions renewed once every 8 hours

Saturation rates of the sulphuric acid solutions depend on the solubility of the concrete. Concrete of a higher solubility saturates the solution quicker and allows faster build-up of the calcium sulphate layer, which influences the mass loss and hydrogen ion consumption more than concrete of a lower solubility. Saturation only affects the sulphuric acid solutions and not the hydrochloric acid solutions. A sufficient amount of concrete dissolves into the fresh solution within the initial two hours to release the calcium required for saturation (i.e. approximately 6 g dissolves as opposed to the 3,87 g required for saturation – Section 3.5.3). The amount of concrete dissolving into the hydrochloric acid solution within the 48 hours prior to renewal was substantially less than that required for the calcium chloride saturation of the solution with (i.e. approximately 350 g dissolves as opposed to the 802 g required for saturation - Section 3.7.3).

Table 3.16 Comparison between mass loss and hydrogen ion consumption for the specimens in the hydrochloric and sulphuric acid solutions after 96 hours

Material	**Mass loss** (%)		**Hydrogen** (mg/cm^2)	
	HCl	H_2SO_4	HCl	H_2SO_4
Olifantsfontein	34,3	18,7	31,27	13,85
Wadeville	31,8	13,4	25,77	8,72
Roodepoort	31,3	14,2	25,47	8,56
Kuilsriver	35,8	20,3	26,82	13,26
Blackheath	36,9	21,3	29,54	15,78

Another important consideration that significantly influences mass loss and hydrogen ion consumption measurements in the hydrochloric acid solution, which is also governed by the solubility of the concrete, was the rate at which the pH increased within the 24-hour period prior to re-adjusting. Allowing the pH to vary from 1,00 to 1,50 represents a substantial decrease in hydrogen ion concentration and corresponding aggressiveness of the solution. A concrete of a higher solubility decreases the pH of the solution at a faster rate over the 24-hour period than a concrete of a lower solubility, which effectively means the concrete of a higher solubility is exposed to less aggressive conditions than the concrete of a lower solubility. Acid resistances and neutralisation capacities of the more soluble concrete are underestimated as mass loss and hydrogen consumption rates decrease faster with time compared to those of the less soluble concrete.

Development of test procedure

A series of tests were done in the hydrochloric acid solution to develop a robust test procedure and establish pH control limits, brushing technique and solution renewal frequencies (Appendix C). Stricter control of pH ensures the aggressiveness of the hydrochloric acid solutions remain similar (Appendix C – Section C.2.2). A substantial decrease in the mass loss and hydrogen ion consumption rates with time results in allowing the pH to vary from 1,00 to 1,50, and this represents an exponential decrease in the hydrogen ion concentration (0,01 to 0,03 mol/ℓ) and aggressiveness of the solution. Strict control of the pH between 0,95 and 1,05 eliminates the variability in the measurements associated with the changes in hydrogen ion concentrations.

Solution renewals do not affect the rate of attack (Appendix C – Section C.2.2). Systematic solution renewals ensure accurate determination of the hydrogen ion concentrations. Solution renewals at least once every 24 hours eliminates the murky conditions arising from suspended material and dissolved ions, which make the colour change of the indicator difficult to detect and lead to inconsistencies in the detection of the titration end-point and variations in the hydrogen ion consumption measurements.

Specimens require continuous cleaning during rotation with the soft-PVC-bristle brush, and light cleaning under running water using a soft-nylon-bristle brush to remove any corrosion debris remaining prior to weighing (Appendix C – Section C.3.2). Such a competent cleaning/brushing technique allows similar and adequate removal of the corrosion debris and ensures specimens remain in constant contact with the hydrochloric acid solution.

On visual examination of the specimens tested in the sulphuric acid solutions, it is clear that the attack was similar to that in the hydrochloric acid solutions. Surfaces of the Gauteng specimens were smoother in comparison to those of the Western Cape specimens (Figure 3.29) illustrating the faster dissolution of the Western Cape dolomite. However, the substantially slower dissolution of the specimens in the sulphuric acid solution resulting from the calcium sulphate barrier prevents identifying factors such as cavities resulting from fast dissolving dolomite stone particles, potential fall-out of slower dissolving dolomite aggregate particles and fall-out of coarse siliceous sand particles that influence acid resistance. Quicker dissolution in the hydrochloric acid solution allows sufficient material loss to identify the influence of these factors on acid resistance and ensure mass loss and hydrogen ion consumption measurements are representative measures in determining the acid resistance of sewer pipe concrete. Achieving similar assessments in a sulphuric acid solution requires doubling the testing time or frequency of solution renewals, which are labour intensive, time consuming and fail to eradicate the influence of calcium sulphate on the attack mechanism.

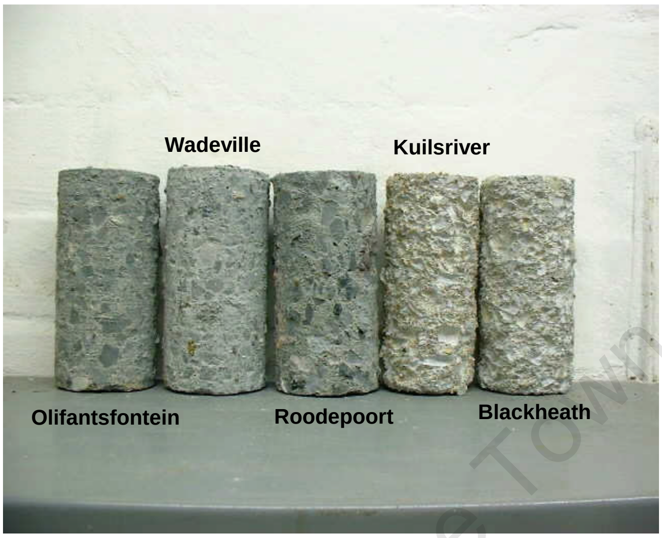

Figure 3.29 Olifantsfontein, Wadeville, Roodepoort, Kuilsriver and Blackheath specimens exposed to sulphuric acid solutions (pH of 1,00 to 1,05) renewed every 8 hours for 96 hours

3.9.4 Conclusion

Acid resistances of the Olifantsfontein, Wadeville and Roodepoort specimens from Gauteng were significantly better than those of the Kuilsriver and Blackheath specimens from the Western Cape. Mass loss and hydrogen ion consumption of the Western Cape specimens were comparable to those of the Gauteng specimens due to the faster dissolution of the Western Cape stone giving the concrete a poor integrity in an acidic environment. Olifantsfontein concrete was the most efficient in neutralising the acidic environments as specimens gave the lowest mass loss to hydrogen ion consumption ratio. Kuilsriver concrete was the least efficient due to the fall-out of the coarse siliceous sand particles giving the highest mass loss to hydrogen ion consumption ratio.

Assessing the acid resistance of sewer pipe concrete in a hydrochloric acid solution overcomes the problems encountered with testing in a sulphuric acid solution:-

- calcium chloride is soluble in a hydrochloric acid solution preventing saturation and development of a corrosion barrier such as the calcium sulphate layer that influences mass loss and hydrogen ion consumption of specimens in a sulphuric acid solution
- frequent solution renewals to avoid saturation, which are labour intensive and time consuming are not required
- mass loss and hydrogen ion consumption in the hydrochloric acid solution are reliable measures of the acid resistance and neutralisation capacity of the concrete and depend on the properties of the concrete and not on those of the calcium sulphate layer and its dissolution with sulphuric acid solution renewals
- testing in a hydrochloric acid solution simulates attack at the average daily sewage level region of a concrete sewer pipe, which represents the worse case scenario
- measurements in a hydrochloric acid solution are repeatable (standard deviation of mass loss (0,1 to 0,9 %) and hydrogen ion consumption (0,07 mg/cm^2 to 1,74 mg/cm^2) of the four specimens tested were low)

- robust measurements in a hydrochloric acid solution are obtainable with strict pH control to ensure constant strength, constant cleaning of the specimens to remove the corrosion debris and renewals of the solutions every 24 hours to avoid saturation and murky conditions and ensure accurate titration
- measurements to rank the acid resistances of concrete are obtained after a short time (96 hours)

Assessing resistance of sewer pipe concrete in a mineral acid solution is invaluable. A test such as the SABS acid insolubility test fails to reflect the influence of the dolomite aggregate on the acid resistance and neutralisation capacity of sewer pipe concrete. Sound dolomite aggregates dissolve at slow rates to neutralise an acid environment and maintain integrity of the concrete. Severe fracturing of dolomite stone effectively increases dissolution and neutralisation capacity at the expense of the integrity of the concrete. Visual examination of concrete specimens clearly illustrates the influence of such factors on the structural integrity of sewer pipe concrete.

3.10 References

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CHAPTER 4

ACID RESISTANCE OF MODIFIED SEWER PIPE CONCRETE

4.1 Introduction

A problem facing concrete pipe manufacturers in certain areas is the absence of acid-soluble stone such as dolomite and limestone, or acid-soluble stone of poor quality. Sewer pipe mixtures designed in such areas or in areas in which severely corrosive environments develop require modifications to improve the acid resistance of the concrete. Such concrete mixtures need to resist the sulphuric acid generated and/or stifle the growth of the thiobacillus bacterial colony.

Conventional mineral additives such as slag, fly-ash, silica fume and meta-kaolin generally improve the durability of concrete (Fulton, 1986). A pozzolanic reaction occurs between the calcium hydroxide in the hydrated cement and the mineral extender, which generates additional calcium silicate and calcium aluminate hydrates that seal and refine the pore structure of the cement binder (Regourd et al, 1983). A large amount of small pores that are uniformly dispersed throughout the binder forms decreasing the permeability of the concrete (Regourd, 1987). Absorption of aggressive solutions and the degradation of the concrete due to the leaching-out of the calcium hydroxide decreases.

Acid resistance of concrete with a calcium aluminate cement binder (CAC) is better than that with an ordinary portland cement binder (OPC). On hydration, the CAC binder does not form calcium hydroxide (De Belie et al, 1997), which readily leaches out of an OPC binder in an acidic environment. Compounds in the CAC binder are also more toxic towards thiobacillus bacteria (Ehrich et al, 1999), which slows the activity of the thiobacillus colony and prolongs the conditions favouring the growth of the thiobacillus thiooxidans responsible for the severe corrosion of sewer pipe concrete. At a pH of greater than 3, the high alumina content in the CAC allows for the precipitation of aluminium hydroxide (insoluble at pH greater than 3), which forms a alumina-gel layer that slows the attack more than the silica-gel layer forming on an OPC binder giving the CAC concrete a better resistance to these milder conditions.

The objective of the investigation was to assess the feasibility of modifying concrete mixtures to improve acid resistance. Acid resistances of modified mixtures were determined using the hydrochloric acid method developed and compared to acid resistances of corresponding standard mixtures. Scope of the investigation involved determining the acid resistances of:-

- a sewer pipe mixture containing a poor quality dolomite aggregate such as that from the Western Cape modified with conventional mineral additives and CAC
- a sewer pipe mixture containing a good quality dolomite aggregate such as that from Gauteng modified with conventional mineral additives and CAC
- a siliceous aggregate mixture containing different shapes and sizes of fine aggregate particles modified with silica fume
- special concrete mixtures used for the lining of sewer pipes, which have higher cement contents than standard sewer pipe mixtures and contain CAC and a dolomite or a synthetic calcium aluminate aggregate such as Alag™

4.2 Acid resistance of additive-modified Western Cape sewer pipe mixtures

The aim of this investigation was to assess the influence of conventional mineral extenders and calcium aluminate cement on the acid resistances of sewer pipe concrete containing poor quality dolomite aggregate such as that used in the Blackheath factory, which is readily soluble in the hydrochloric acid solution but fractures on compaction leading to preferential dissolution of dolomite stone particles.

4.2.1 Specimen preparation and standard testing

Six concrete mixtures were prepared using the Blackheath factory mixture design (Table 4.1). Additives (i.e. cement extenders) were used in quantities similar to those used in industry. A superplasticizer (1 % of the binder content) was added to the silica fume and meta-kaolin mixtures to assist with dispersion. CAC was used to replace OPC.

Table 4.1 Mixture proportions based on ratio to total binder content

Mixture	Dolomite Stone	Dolomite sand	Siliceous sand	Cement	Mineral Additives	w/b
OPC	3,45	1,32	0,53	1,0	-	0,36
Slag	3,45	1,32	0,53	0,5	0,5	0,36
Fly ash	3,45	1,32	0,53	0,7	0,3	0,36
Silica fume	3,45	1,32	0,53	0,9	0,1	0,32
Meta-kaolin	3,45	1,32	0,53	0,9	0,1	0,36
CAC	3,45	1,32	0,53	1,0	-	0,32

Standard raw materials such as the dolomite stone, dolomite crusher sand, siliceous filler sand and OPC were sourced from the factory. Additives and CAC were obtained in bags from the relevant suppliers. Particle size analysis and acid insolubility measurements were done on dolomite stone, dolomite crusher sand and siliceous filler sand to assess quality.

Specimens were prepared from each mixture using the standard method developed (Appendix B – Section B.6). Aggregates were air-dried. A water : binder ratio (w/b) of 0,36 was used to achieve the desired consistency for compaction in all the mixtures except the mixture containing the silica fume, which required less water giving a w/b ratio of 0,32.

Splitting tensile (SANS method 6253, 1994) and compressive strengths of each concrete were measured directly after steam curing (i.e. 8 hours after compaction) to assess the suitability of the modified mixtures in sewer pipe manufacture. Acid insolubility, relative density, oxygen permeability, water sorptivity and porosity measurements were done on steam-cured specimens after air-curing for a further 28 days in a conditioning room maintained at 25 °C and 60 % relative humidity. Compressive strengths were also measured on steam-cured specimens after water-curing at 23 °C for 28 days.

4.2.2 Experimental method

Mass loss and hydrogen ion consumption of concrete specimens (four from each mixture air-cured for 28 days) were recorded with time using the hydrochloric acid method (Appendix C - Section C.4). The standard procedure was modified to accommodate the high dissolution rate of concrete. Solutions were renewed once every 12 hours to ensure accurate measurement of the hydrogen ion concentration and a test period of 48 hours was used to establish reliable trends of mass loss and hydrogen ion consumption with time.

4.2.3 Results and discussion

Analysis of raw materials

Particle size: Stone particles were all less than 19,0 mm (Figure 4.1). Stone grading was finer compared to that of the batches sourced from the factory for the previous investigations (Section 3.5.3 and 3.9.3). Crusher sand particles were all less than 4,75 mm (Figure 4.2) with a fineness modulus of 3,34. Crusher sand grading was similar to that of the batches sourced from the factory for the previous investigations (Section 3.5.3 and 3.9.3). Siliceous sand particles were all less than 1,18 mm (Figure 4.2) with a fineness modulus of 1,73. The siliceous filler sand was finer than that sourced from the factory for the previous investigations (Section 3.5.3 and 3.9.3).

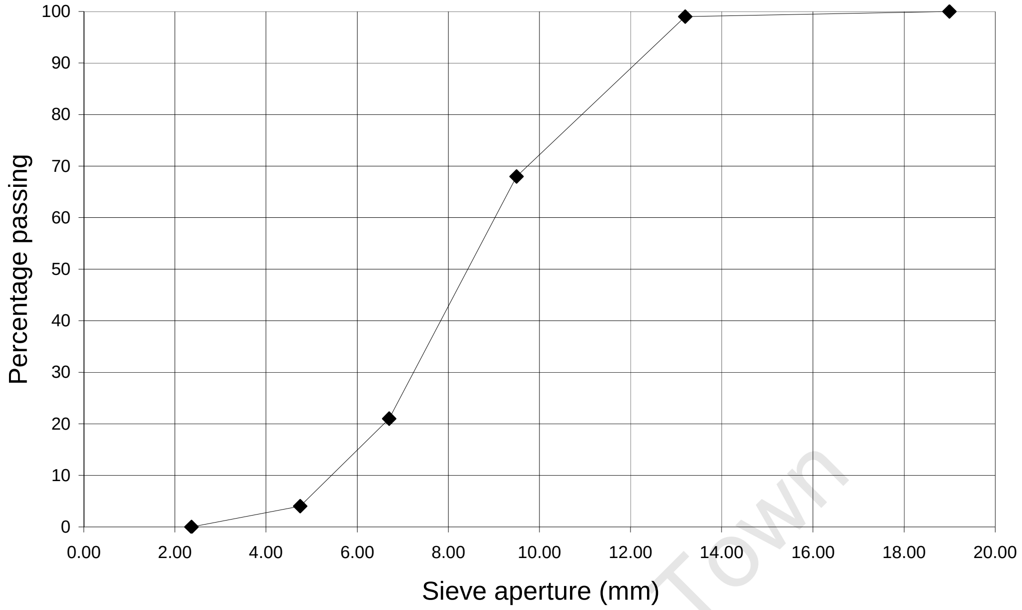


Figure 4.1 Particle size analysis of dolomite stone from Blackheath (standard sieve sizes 19 mm, 13,2 mm, 9,5 mm, 6,7 mm, 4,75 mm and 2,36 mm)

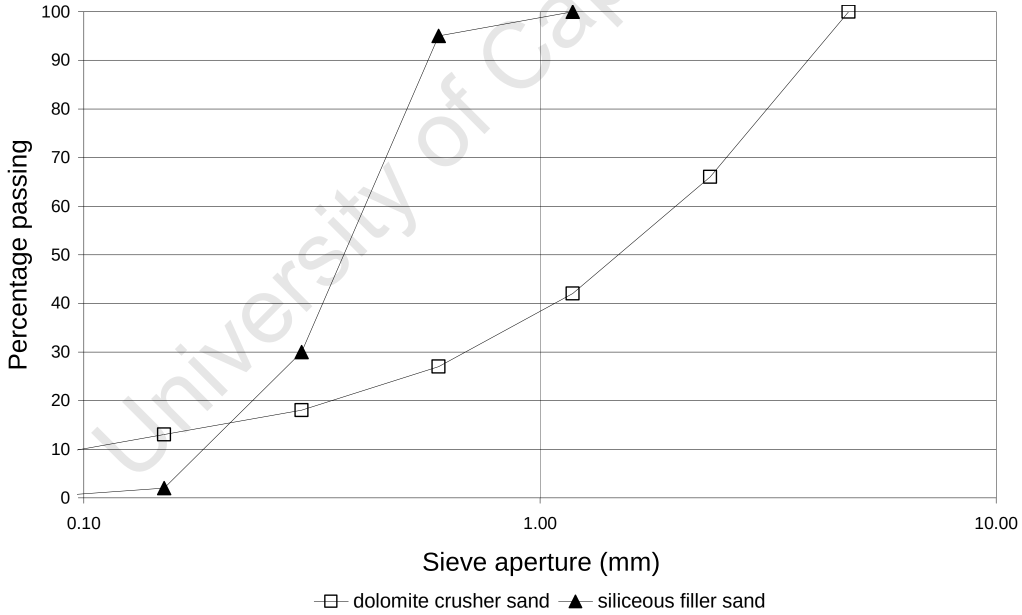


Figure 4.2 Particle size analyses of dolomite crusher and siliceous filler sands from Blackheath (standard sieve sizes 6,7 mm, 4,75 mm, 2,36 mm, 1,18 mm, 0,6 mm, 0,3 mm, 0,15 mm and 0,075 mm)

Acid insolubility: Acid insolubilities of the dolomite aggregates were low implying the aggregates readily dissolve to neutralise an acid environment. Acid insolubility of the dolomite stone (4,90 %) was significantly lower than that sourced from the Blackheath factory for the previous investigations (7,01 and 9,00 % respectively). Acid insolubility of the dolomite crusher sand was lower (11,3 % compared to 15,24 and 15,69 % respectively) and that of the siliceous filler sand higher (76,1 % compared to 70,20 and 70,72 % respectively).

Specimen compaction and standard testing of concrete

Compaction of the modified mixtures was similar to that of the standard mixture with the exception of the silica fume mixture, which compacted easier due to the higher workability of the mixture.

Specimen strengths: Splitting tensile strengths at 8 hours (average of six determinations - Table 4.2) of the silica fume (3,0 MPa) specimens were higher compared to those of the meta-kaolin (2,7 MPa), CAC (2,5 MPa) and OPC (2,4 MPa) specimens. Splitting strengths of the slag (1,9 MPa) and fly ash (1,7 MPa) specimens were significantly lower. Compressive strengths at 8 hours (average of six determinations – Table 4.3) of the CAC specimens (49,0 MPa) were significantly higher compared to those of the silica fume (36,9 MPa) and meta-kaolin (34,3 MPa) specimens, which themselves were notably higher compared to those of the OPC specimens (30,5 MPa). Strengths of the slag (19,1 MPa) and fly ash (23,6 MPa) specimens were significantly lower.

Table 4.2 Splitting tensile strengths at 8 hours and compressive strengths at 8 hours and 28 days of standard and modified Blackheath concrete specimens

Concrete	**Strengths** (MPa)		
	Splitting tensile	Compressive	
	(8 hours)	(8 hours)	(28 days)
OPC (0,36)	2,4	30,5	55,8
Slag (0,36)	1,9	19,1	53,1
Fly ash (0,36)	1,7	23,6	40,9
Silica fume (0,32)	3,0	36,9	64,9
Meta kaolin (0,36)	2,7	34,3	51,4
CAC (0,36)	2,5	49,0	53,2

Slower strength development of slag and fly ash concrete was due to the slower rate of hydration of the binders in comparison to the OPC binder (Lea, 1970). At early ages (7 days), slag concrete gains strength slower than fly ash concrete (Mantel, 1991). A 50 % slag concrete achieves a compressive strength of 25 % less than OPC concrete at 7 days and a 30 % fly ash concrete 20 % less. A lower early-strength conceivably leads to problems such as cracking and failure on the de-moulding of sewer pipes directly after steam curing (i.e. 8 hours after manufacture). Silica fume, meta-kaolin and CAC concrete mixtures were more suited to the method of sewer pipe manufacture. Compressive strength of the CAC concrete is highest due to faster rate of hydration of the CAC compared to OPC (Lea, 1970). Silica fume concrete gains compressive strength at a faster rate than the OPC concrete (Mantel, 1991). A 10 % silica fume concrete achieves a compressive strength of at least 5 % more than OPC concrete at 7 days.

Compressive strengths determined at 28 days (average of six determinations – Table 4.2) of the CAC (53,2 MPa), slag (53,1 MPa) and meta-kaolin (51,4 MPa) specimens were similar to that of the OPC (55,8 MPa). Compressive strength of the fly ash specimens (40,9 MPa) were significantly lower and that of the silica fume specimens (64,9 MPa) significantly higher.

Slower hydration rate and lower cementing capacity of fly ash concrete compared to slag and OPC concrete is reflected in the lower compressive strength at 28 days. A 30 % fly ash concrete achieves a compressive strength 20 % less that of OPC concrete at 28 days and a 50 % slag concrete 5 % less (Mantel, 1991). Superior compressive strength of the silica fume concrete was attributed to the powerful pozzolanic properties of the binder compared to the OPC binder. A 10 % silica fume concrete achieves a compressive strength of at least 20 % more than OPC concrete at 28 days (Mantel, 1991). A lower water:cement ratio partly assists in the improvement of strength.

Strength development in the CAC concrete was negligible after the initial period of steam curing. Steam-curing increases the rate of hydration of the CAC significantly more than the other OPC binders (Lea, 1970).

Relative density: Variation in the relative density of the mixtures depends on the density of the additives compared to the OPC and the amounts of the OPC replaced (average of six determinations - Table 4.3). CAC (3,25 g/cm^3) is of a higher density and replaces 100 % of the OPC (3,14 g/cm^3) leading to the higher density of the CAC concrete. Slag (2,9 g/cm^3) and fly ash (2,3 g/cm^3) are of a significantly lower density than OPC and the replacements are sufficient to lower the density of the respective concretes. Lower density of meta-kaolin (2,5 g/cm^3) and silica fume (2,1 g/cm^3) were not reflected in the density of the respective concrete as the 10 % addition was insufficient to alter the density of the concrete.

Table 4.3 Properties of standard and modified Blackheath concrete specimens at 28 days

Concrete	**Density** (g/cm^3)	**Oxygen permeability index**	**Water sorptivity** (mm/√hr)	**Porosity** (%)	**Acid insolubility** (%)
OPC (0,36)	2,55	10,69	4,63	7,9	12,48
Slag (0,36)	2,50	10,35	3,89	7,3	17,64
Fly ash (0,36)	2,51	10,30	5,40	9,0	15,16
Silica fume (0,32)	2,57	11,15	2,34	6,5	14,29
Meta kaolin (0,36)	2,54	10,89	2,54	4,6	14,26
CAC (0,36)	2,60	10,23	6,10	5,6	12,10

Durability indexes: Oxygen permeability indexes indicate that the concrete specimens were dense and impermeable (Table 4.3). Oxygen permeability of silica fume (11,15) and meta-kaolin (10,89) specimens were higher than that of the OPC specimens (10,69). Oxygen permeability indexes of the slag (10,35), fly ash (10,30) and calcium aluminate cement (10,23) specimens were lower.

Water sorptivity measurements indicate that the concrete specimens were of a low sorptivity (Table 4.3). Silica fume (2,34 mm/√hr), meta-kaolin (2,54 mm/√hr) and slag (3,89 mm/√hr) specimens were of a lower sorptivity than the OPC specimens (4,63 mm/√hr). Sorptivity of the fly-ash (5,40 mm/√hr) and CAC (6,10 mm/√hr) specimens were higher. Specimen porosities were low (Table 4.3).

Superior durability indexes of the silica fume and meta-kaolin specimens are due to the good reaction of the fine pozzolanic particles with calcium hydroxide, and also the fine filler effect. Calcium silicate hydrate effectively seals pores and reduces pore sizes producing a matrix less permeable to gas and with a lower absorption of liquids (Cheny-vi et al, 1985). Superplasticizers disperse the fine silica fume and meta-kaolin particles throughout the mixture allowing good interaction with the lime assisting in the pore refinement (Suramy, 1989). Slag and fly ash concrete were not as effective in refining the pore structure. Quantities of calcium hydroxide generated at such low w/b ratios were conceivably insufficient to completely activate the slag and fly ash particles (Jolicoeur et al, 1994).

Oxygen permeability and water sorptivity of the CAC specimens were inferior due to the conversion reaction that occurs on the ageing of CAC in moist warm conditions (Lea, 1970). Calcium aluminate cement hydrates to form alumina gel (AH_3) and calcium aluminate hydrates such as monocalcium aluminate (CAH_{10}) and dicalcium aluminate (C_2AH_8), which are metastable hexagonal products that gradually convert into the larger stable cubic tricalcium aluminate hydrates and alumina gel (i.e. aluminium hydroxide and water). A marked increase in porosity occurs especially with steam-curing which accelerates the conversion reaction (Lea, 1970).

Acid insolubility: Acid insolubilities of mineral additive modified specimens were higher than the OPC specimens due to the higher acid-insoluble silica contents imparted by the mineral additives (Table 4.3). Acid insolubilities of the fly ash (15,16 %) and slag (17,64 %) specimens were higher compared to those of the silica fume (14,29 %) and meta-kaolin (14,26 %) specimens due to the higher quantities added in the former mixtures. Acid insolubility of the CAC (12,10 %) and OPC (12,48 %) specimens were similar.

Hydrochloric acid solution testing of concrete specimens

Mass loss and hydrogen ion consumption of the specimens (average of four determinations) increased with time (Figure 4.3 and 4.4). Mass loss rates remained constant with time while hydrogen ion consumption rates increased with time. Consumption of the CAC and meta-kaolin specimens increased at faster rates than the consumption of the fly ash, slag and OPC specimens. Silica fume specimen consumptions increased at significantly slower rates. After 48 hours, mass loss and hydrogen ion consumption of the CAC (40,6 % and 34,28 mg/cm^2) and meta-kaolin (38,8 % and 34,45 mg/cm^2) specimens were significantly higher than those of the OPC specimens (33,4 % and 27,97 mg/cm^2). Specimen mass loss and consumption of the fly ash (36,9 % and 30,45 mg/cm^2) and slag (35,4 % and 28,72 mg/cm^2) specimens were slightly higher whereas that of the silica fume specimens (25,3 % and 21,00 mg/cm^2) were substantially lower.

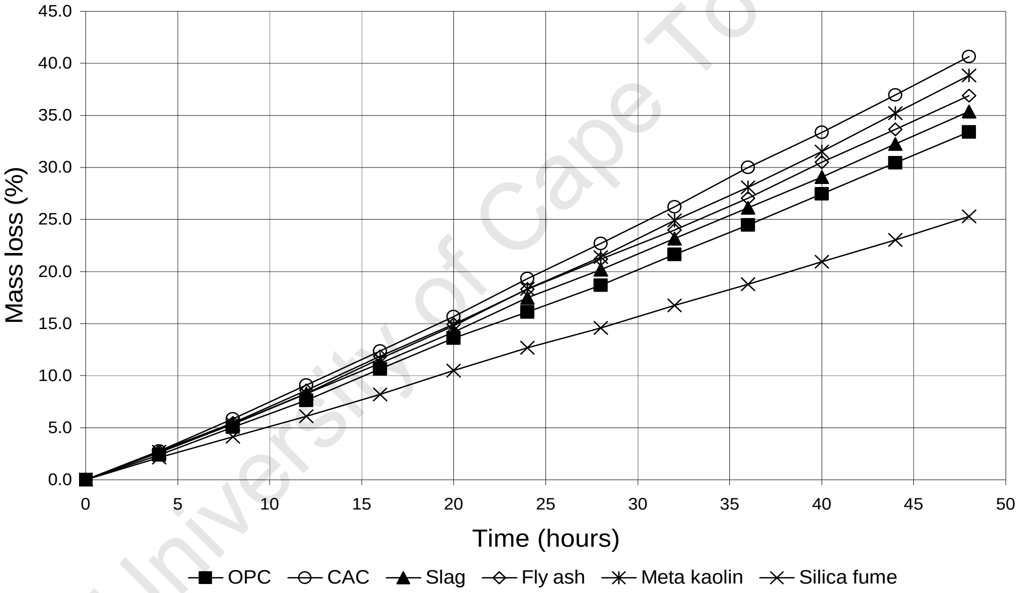


Figure 4.3 Mass loss with time of standard and modified Blackheath concrete specimens in hydrochloric acid solutions at a pH of 1.00

A direct correlation between mass loss and hydrogen ion consumption exists due to the acid-soluble nature of the concrete. An increase in hydrogen ion consumption rates with time relates to the exposure of the dolomite aggregates as the attack front progresses, which increases the area available for dissolution and the neutralisation capacity of the concrete. Consumption rates continue to increase after the exposure of the dolomite stone due to the soluble nature of the stone and the preferential dissolution of fractured stone particles.

Silica fume significantly improves the resistance of the mixture. Visual inspection revealed that the silica fume binder resists the acidic conditions better than the OPC binder (Figure 4.5). The silica fume binder, which was attacked at a significantly slower rate than the dolomite aggregate particles, stands proud of the attacked surface. As a result, significantly more cavities result from the preferential dissolution of the dolomite aggregate particles on the silica fume than on the OPC specimens.

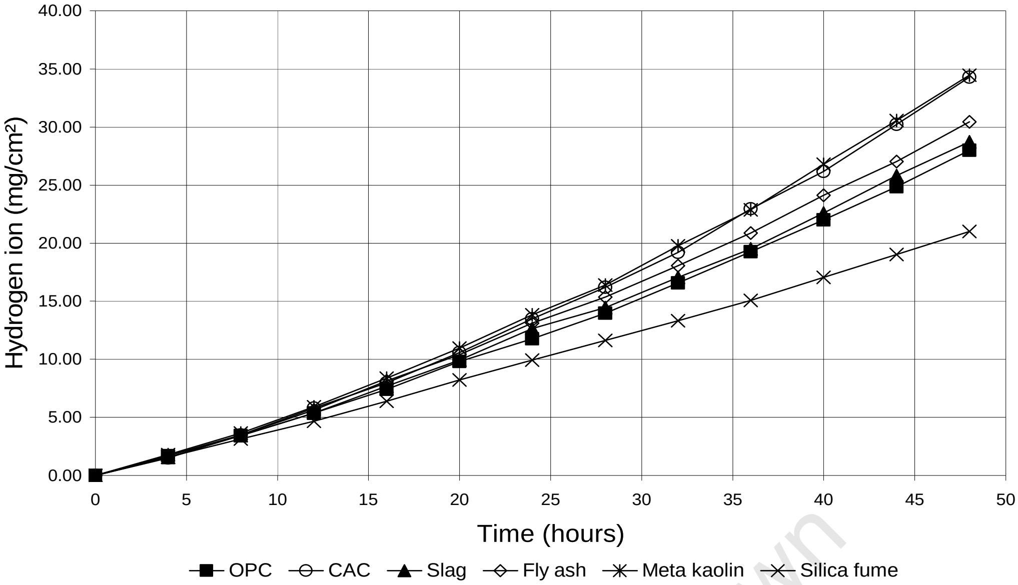


Figure 4.4 Hydrogen ion consumption with time of standard and modified Blackheath concrete specimens in hydrochloric acid solutions at a pH of 1,00

Figure 4.5 Attacked surfaces of OPC (left) and silica fume (right) specimens showing the rougher surface of the silica fume specimen resulting from the slower dissolution of the binder, which reflects the preferential dissolution of the dolomite aggregate particles more

Silica fume increases the density of the binder, and also densifies the interfacial zone between aggregate particles and binder where calcium hydroxide tends to precipitate more freely (Larbi et al, 1991). The fine silica fume particles react with the calcium hydroxide and generate additional calcium silicate, which fills small pores and seals-off large pore spaces. Acid solubility of the concrete decreases due to the depletion of calcium hydroxide, generation of a more acid-insoluble calcium silicate, improvement of particle packing and densification of the interfacial zone, which slows the fall-out of the insoluble siliceous sand particles.

The slower dissolution of the silica fume binder accounts for the roughly constant hydrogen ion consumption rates with time. Stone and crusher sand particles were exposed at significantly slower rates in comparison to the other concrete specimens and any increase in neutralisation capacity that occurs due to the exposure is counteracted by the decrease in the reactivity of the silica fume binder.

Slag and fly ash concrete are of lower acid resistance as the particles react with calcium hydroxide at a slower rate and less effectively fill pore spaces and generate similar calcium silicate and aluminate hydrates to the OPC (Larbi et al, 1991). Slower reaction rate of the fly ash particles explains the poorer acid resistance compared to that of the OPC concrete.

Aggressive attack on the CAC concrete directly relates to the faster dissolution of the binder. The CAC binder dissolves at a significantly faster rate than the OPC binder and the dolomite aggregate particles, which increases the dissolution rates of the CAC specimens in the hydrochloric acid solution (Figure 4.6).

Figure 4.6 Attacked surfaces of OPC (left) and CAC (right) Blackheath concrete specimens showing the rougher surface due to the preferential dissolution of the CAC binder leaving the dolomite aggregate particles standing proud

Additional calcium silicate, calcium aluminate and calcium alumino-silicate hydrates formed in the meta-kaolin concrete on reaction with the calcium hydroxide does not improve resistance of the concrete in the hydrochloric acid solution but modifications in the binder arising from the addition of meta-kaolin allows the concrete to deteriorate faster than the other OPC binder concretes.

Superior acid resistance of the silica fume concrete was not due to the impermeable nature as the meta-kaolin concrete possesses similar properties. Scanning electron microscopic (SEM) analysis of polished surfaces revealed that the attack is a surface phenomenon (Figure 4.7). Signs of penetration of attack into the concrete were not evident indicating the attack depends on dissolution of the concrete, which at a pH of 1,00 occurs at a faster rate than acid can be absorbed or penetrate into the concrete.

4.2.4 General discussion

Acid resistance of the sewer pipe concrete from the Western Cape fundamentally depends on the acid solubility and physical quality of the dolomite aggregates, which varied substantially. Acid insolubility of the dolomite stone in this investigation (4,90 %) was approximately half that of the stone used in the previous investigations (7,01 % and 9,00 % - Section 3.5.3 and 3.9.3 respectively), which accounts for the substantially higher dissolution rate of the specimens in this investigation. After 48 hours, the mass loss and hydrogen ion consumption of the OPC specimens in this investigation (33,4 % and 27,97 mg/cm^2) were twice those of the Blackheath specimens in the previous investigations (19,5 % and 13,08 mg/cm^2 – Section 3.8.2) (17,9 % and 11,44 mg/cm^2 - Section 3.9.3). Such variations in chemical and physical properties are of concern to sewer pipe manufacturers. An additive such as silica fume provides a good alternative to improve acid resistance of a concrete mixture in areas containing a poor quality dolomite aggregate.

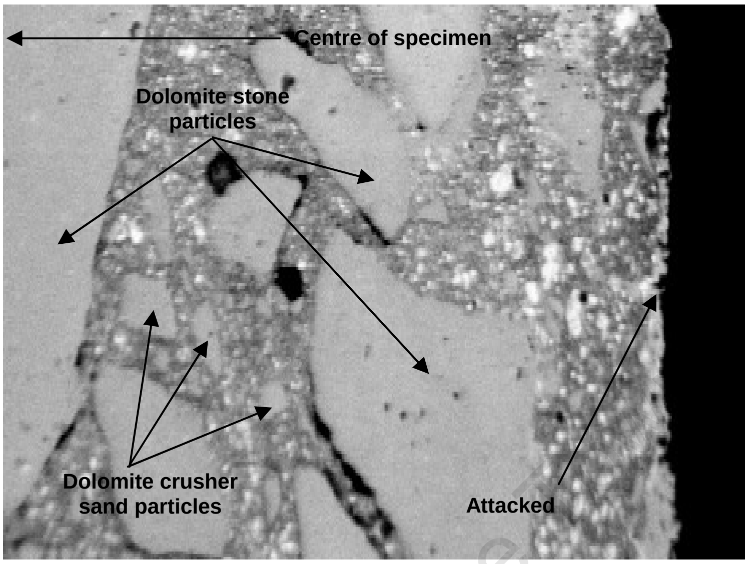


Figure 4.7 A SEM micrograph of a polished surface cut into an OPC/dolomite concrete specimen at right angles from the attacked surface, which illustrates attack depends on the dissolution of the concrete in contact with the hydrochloric acid solution at a pH of 1,00

Assessing the acid resistances in the hydrochloric acid solution method clearly illustrates the influences of the dolomite stone and silica fume, which is crucial for the design of concrete mixtures exposed to acidic environments. Acid insolubility measurements determine the soluble nature of the dolomite stone but fail to show the impact of the stone on the solubility of the concrete and the influence of the silica fume on the acid resistance of the concrete.

4.2.5 Conclusion

Silica fume significantly improves the resistance of sewer pipe concrete containing a poor quality dolomite aggregate to a hydrochloric acid solution at a pH of 1,00. Slag, fly ash, meta-kaolin and CAC fail to improve the direct acid resistance of the concrete.

4.3 Acid resistance of silica fume modified Western Cape sewer pipe concrete

The aim of this investigation was to determine the advantages of using silica fume to improve the acid resistances of concrete containing poor quality dolomite aggregates, including the feasibility of reducing the silica fume and cement contents to make the mixture more cost effective.

4.3.1 Concrete mixture proportions, specimen preparation and testing

Concrete mixtures were designed to assess the effects of the water, silica fume and binder contents on the acid resistances of the sewer pipe concrete from the Blackheath factory (Table 4.4):-

- 10 % silica fume mixture with a w/b ratio of 0,36 and total binder content of 16 %
- 10 % silica fume mixture with a w/b ratio of 0,36 and total binder content of 14 %
- 7,5 % silica fume mixture with a w/b ratio of 0,36 and total binder content of 14 %

- 5 % silica fume mixture with a w/b ratio of 0,36 and total binder content of 14 %

Table 4.4 Concrete mixture proportions based on ratio to total binder content

Mixture	Dolomite stone	Dolomite sand	Siliceous sand	Cement	Mineral Additives	w/b
10 % SF	3,45	1,32	0,53	0,90	0,10	0,36
10 % SF (LB)	4,01	1,53	0,62	0,90	0,10	0,36
7,5 % SF (LB)	4,01	1,53	0,62	0,93	0,07	0,36
5,0 % SF (LB)	4,01	1,53	0,62	0,95	0,05	0,36

Concrete specimens were prepared from the materials sourced for the previous investigation (Section 4.2). Water containing a superplasticizer (1 % of binder content) was added to give a w/b of 0,36. Specimens were compacted using the method developed.

Splitting tensile and compressive strengths were measured directly after steam curing to assess suitability of the silica fume mixtures for the manufacture of sewer pipes. Compressive strengths were done on further water-cured specimens at 28 days, and density, acid insolubility and durability index tests were done on further air-cured specimens at 28 days to assess compaction and quality of the silica fume concrete. Mass loss and hydrogen ion consumption of the specimens (four from each mixture air-cured for 28 days) were measured using the hydrochloric acid method over a 48 hour period.

4.3.2 Results and discussion

Specimen preparation and standard tests

Compaction of the mixture with the standard binder content was difficult due to the additional water added to give a w/b of 0,36. Concrete mixtures with the lower binder contents compacted well.

Splitting tensile strengths at 8 hours of silica fume specimens with a w/b ratio of 0,36 (Table 4.5 - average of six determinations) were similar to that of the standard OPC specimens but lower than that of the 10 % silica fume specimens with the w/b of 0,32. Compressive strengths at 8 hours and 28 days (Table 4.5 - average of six determinations) of the 10 % silica fume specimens with w/b ratio of 0,36 were higher than that of the OPC specimens with a w/b ratio of 0,36 and lower than that of the 10 % silica fume with w/b ratio of 0,32. Compressive strengths at 8 hours of the silica fume specimens with lower binder contents were lower and significantly lower at 28 days in comparison to the specimens with the standard binder contents.

Table 4.5 Splitting tensile strengths at 8 hours and compressive strengths at 8 hours and 28 days of the silica fume specimens with w/b ratios of 0,36

Concrete	Splitting tensile strength (MPa)	Compressive strength (MPa)	
	(8 hours)	(8 hours)	(28 days)
OPC (0,36)	2,4	30,5	55,8
10 % SF (0,32)	3,0	36,9	64,9
10 % SF (0,36)	2,5	32,5	60,6
10 % SF LB (0,36)	2,4	27,6	48,8
7,5 % SF LB (0,36)	2,4	29,2	48,5
5,0 % SF LB (0,36)	2,4	27,0	48,0

A concern is the significantly lower 28 day strengths of the lower binder materials. The premature failure during compression, which results from the cracks in the dolomite stone particles, is more apparent at the lower binder contents, and the higher water contents are partly responsible for the lower strengths.

Acid insolubility, relative density and durability index measurements of the silica fume specimens with w/b ratio of 0,36 (Table 4.6) were similar to that of the OPC specimens with the w/b of 0,36 (Table 4.3) and silica fume specimens with the w/b of 0,32 (Table 4.3). Oxygen permeability and water sorptivity measurements indicate that the silica fume specimens were dense and impermeable to gas and liquid. Acid insolubility indicates the concrete is suitable for sewer pipes exposed to sulphuric acid environments.

Table 4.6 Properties of silica fume specimens with w/b ratios of 0,36

Concrete	**Density** (g/cm^3)	**Oxygen Perm. Index**	**Water Sorp.** (mm/√hr)	**Porosity** (%)	**Acid Insol.** (%)
OPC (0,36)	2,55	10,69	4,63	7,9	12,48
10 % SF (0,32)	2,57	11,15	2,34	6,5	14,29
10 % SF (0,36)	2,49	10,66	3,21	6,9	14,26
10 % SF LB (0,36)	2,53	10,84	2,68	6,4	13,83
7,5 % SF LB (0,36)	2,57	10,61	2,97	8,2	13,65
5,0 % SF LB (0,36)	2,58	10,54	3,81	8,2	13,60

Hydrochloric acid solution testing of concrete specimens

Mass loss and hydrogen ion consumption rates of the silica fume specimens (average of four determinations) were constant with time (Figure 4.8 and 4.9). After 48 hours, mass loss of the 10 % silica fume specimens with the standard binder content and w/b of 0,36 (24,2 %) and that of the 10 % silica fume specimens with the lower binder content and w/b ratio of 0,36 (24,0 %) were similar to that of the 10 % silica fume specimens with the standard binder content and w/b ratio of 0,32 (25,3 %) and significantly lower than that of the standard OPC specimens (33,4 %). Mass loss of the 5,0 % and 7,5 % silica fume (28,8 % and 27,1 % respectively) was higher than that of the 10 % silica fume specimens but lower than that of the standard OPC specimens. Hydrogen ion consumption of the silica fume specimens (20,19 mg/cm^2 – 20,63 mg/cm^2) with the exception of the 5,0 % silica fume specimens (18,52 mg/cm^2) were similar to that of the 10 % silica fume specimens with the standard binder content and w/b ratio of 0,32 (21,00 mg/cm^2), which was significantly lower than that of the standard OPC specimens (27,97 mg/cm^2).

A decrease in the silica fume content results in a decrease in the amount of calcium hydroxide consumed, pore refinement and densification of the interfacial zone. As a result, mass loss of the lower silica fume specimens was higher compared to that of the 10 % silica fume specimens. A corresponding increase in hydrogen ion consumption was not evident as the binder content is negligible in comparison to the dolomite aggregate content, which dictates the neutralisation capacity of the concrete.

4.3.3 Conclusion

Acid resistance of sewer pipe concrete containing a poor quality dolomite aggregate, modified by addition of silica fume, was noticeably improved in a hydrochloric acid solution at pH of 1,00. A 10 % silica fume addition was more effective in improving the direct acid resistance of the concrete mixture. A silica fume concrete with lower binder content can be economically more viable from a manufacturing point of view.

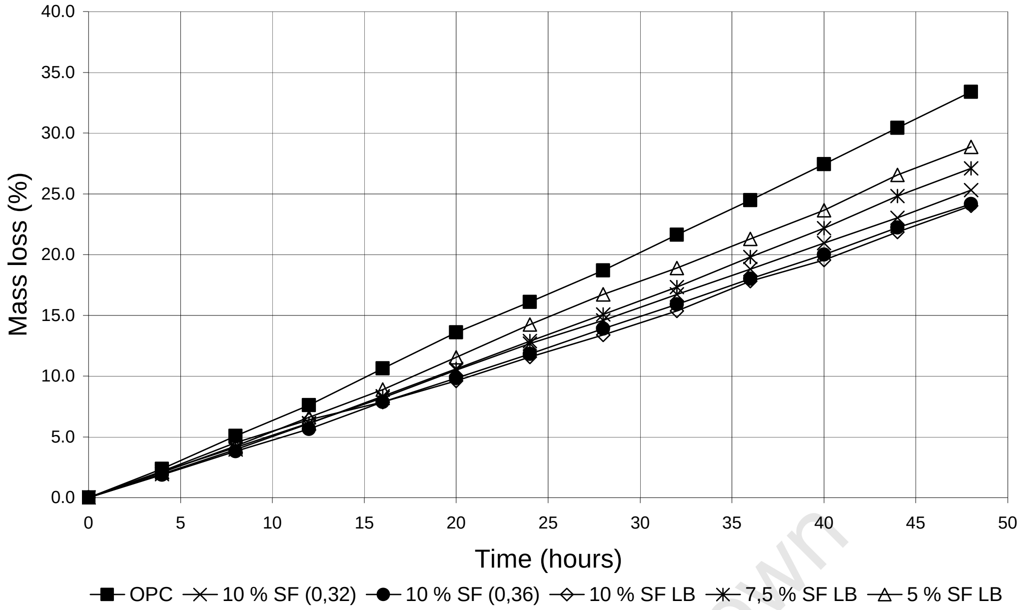


Figure 4.8 Mass loss with time of the OPC and silica fume modified Blackheath concrete specimens in a hydrochloric acid solution at a pH of 1,00

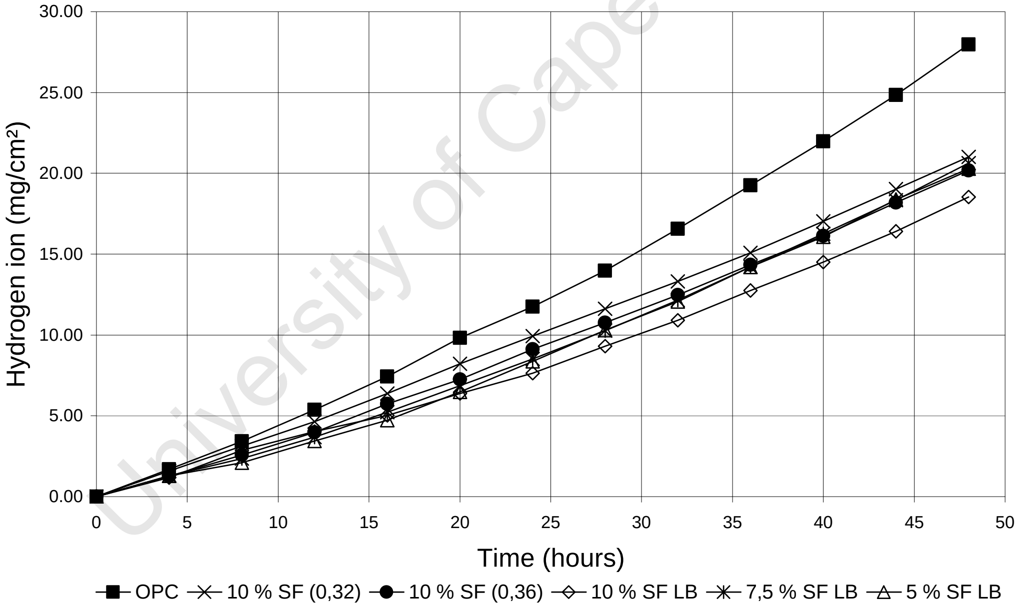


Figure 4.9 Hydrogen ion consumption with time of the OPC and silica fume modified Blackheath concrete specimens in a hydrochloric acid solution at a pH of 1,00

4.4 Acid resistance of additive-modified Gauteng mixtures

The aim of this investigation was to assess the effect of mineral additives and CAC on the acid resistance of a sewer pipe concrete containing a good quality dolomite aggregate such as that used at the Olifantsfontein factory, which dissolves at a slow rate in a hydrochloric acid solution and fractures substantially less than dolomite from the Western Cape during specimen and pipe compaction.

4.4.1 Specimen preparation and testing

Six concrete mixtures were prepared using the Olifantsfontein mixture proportions (Table 4.7). Additives were used in quantities similar to those used in industry. A superplasticiser (1 % of the binder content) was added to the silica fume and meta-kaolin mixtures to assist with dispersion.

Table 4.7 Mixture proportions based on ratio to total binder content

Mixture	Dolomite stone	Dolomite sand	Cement	Mineral Additives	w/b
OPC	2,28	2,28	1,0	-	0,30
Slag	2,28	2,28	0,5	0,5	0,30
Fly ash	2,28	2,28	0,7	0,3	0,30
Silica fume	2,28	2,28	0,9	0,1	0,28
Meta-kaolin	2,28	2,28	0,9	0,1	0,30
CAC	2,28	2,28	1,0	-	0,30

Standard raw materials (dolomite stone, dolomite crusher sand and OPC) were sourced from the factory. Additives and CAC cement were obtained in bags from the relevant suppliers. Particle size analysis and acid insolubility measurements were done on dolomite stone and dolomite crusher sand to assess quality.

Specimens were prepared from each mixture using the standard method. Aggregates were air-dried. A water : binder ratio (w/b) of 0,30 was used to achieve the desired consistency for compaction in all the mixtures except the mixture containing the silica fume, which required less water (due to the use of a superplasticiser) giving a w/b ratio of 0,28.

Splitting tensile and compressive strengths of each concrete were measured directly after steam curing. Acid insolubility, density, oxygen permeability, water sorptivity and porosity measurements were done on specimens air-cured for 28 days in a conditioning room maintained at 25 °C and 60 % relative humidity. Compressive strengths were measured on specimens cured in water at 23 °C for 28 days. Mass loss and hydrogen ion consumption of the specimens (four from each mixture air-cured for 28 days) were recorded with time using the hydrochloric acid method. A test period of 96 hours was used to achieve a better distinction between mass loss and hydrogen ion consumption of the specimens.

4.4.2 Results and discussion

Material analyses

Particle size analysis: Stone particles were all less than 19,0 mm (Figure 4.10). Crusher sand particles were all less than 6,70 mm (Figure 4.11) with a fineness modulus of 3,63. Aggregate particle sizes were similar to those used in the previous investigations (Section 3.5.3 and 3.9.3).

Acid insolubilities: Acid insolubilities of the dolomite aggregates were low and typical that of a good quality dolomite used for the manufacture of sewer pipes to neutralise an acidic environment. Acid insolubility of the dolomite stone (3,84 %) was lower than that sourced from the Olifantsfontein factory for the previous investigations (4,18 % and 5,89 % - Section 3.5.3 and 3.9.3 respectively). Acid insolubility of the dolomite crusher sand (5,20 %) was similar to that sourced for the previous investigations (6,28 % and 5,23 % - Section 3.5.3 and 3.9.3 respectively).

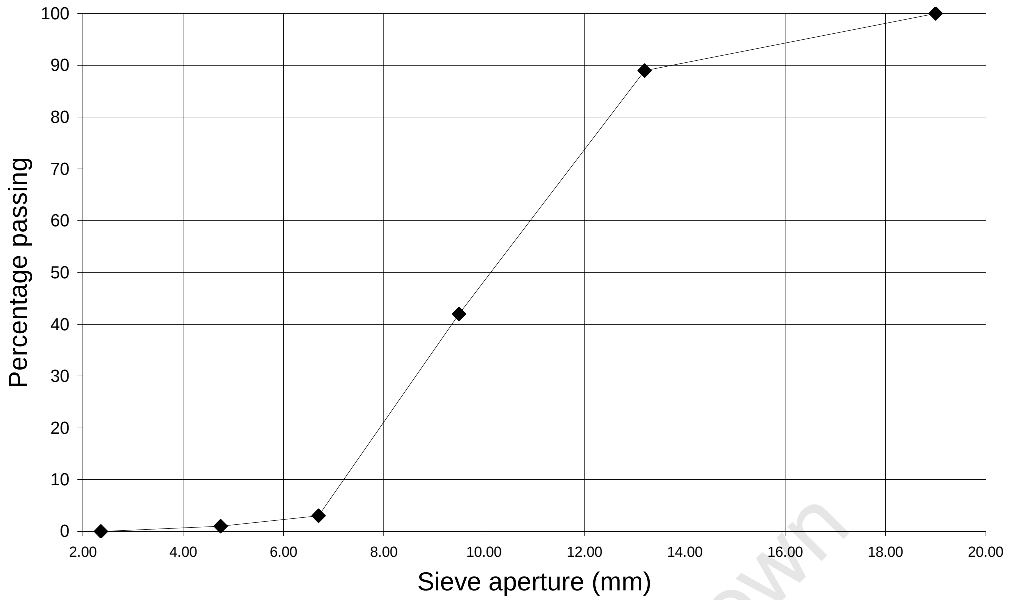


Figure 4.10 Particle size analysis of dolomite stone from Olifantsfontein (standard sieve sizes 19 mm, 13,2 mm, 9,5 mm, 6,7 mm, 4,75 mm and 2,36 mm)

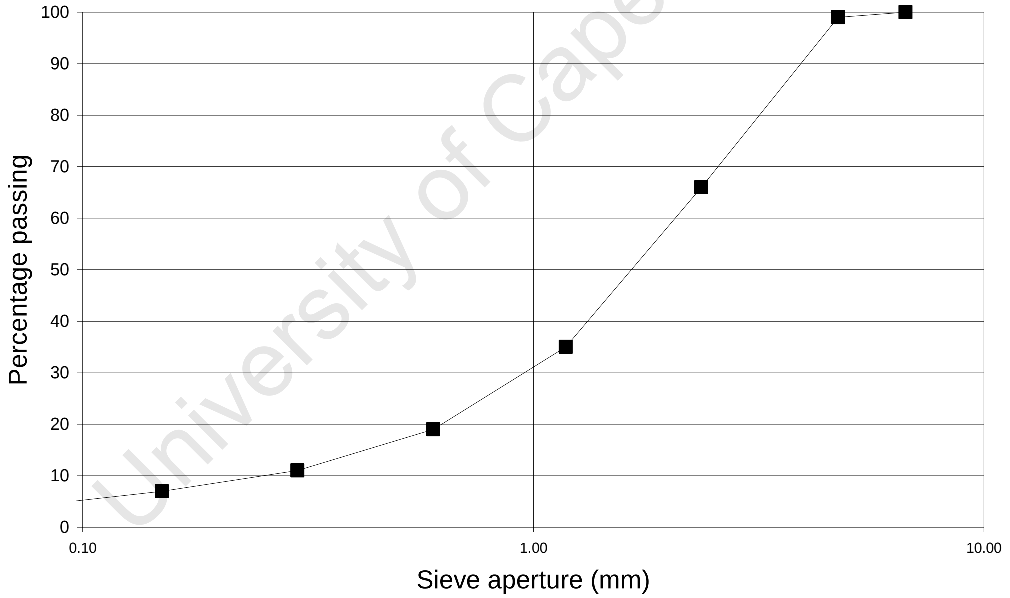


Figure 4.11 Particle size analysis of dolomite crusher sand from Olifantsfontein (standard sieve sizes 6,7 mm, 4,75 mm, 2,36 mm, 1,18 mm, 0,6 mm, 0,3 mm, 0,15 mm and 0,075 mm)

Standard testing of concrete specimens

Strengths: Splitting tensile and compressive strengths at 8 hours (Table 4.8 – average of six determinations) of the silica fume (6,1 MPa and 53,6 MPa) and CAC (4,5 MPa and 79,3 MPa) specimens were significantly higher than those of the OPC (3,6 MPa and 40,8 MPa) and meta-kaolin (3,8 and 38,1 MPa) specimens and those of the fly ash (2,1 MPa and 29,5 MPa) and slag (1,9 MPa and 25,2 MPa) specimens were significantly lower. Compressive strengths at 28 days (Table 4.8 – average of six determinations) of the fly ash (53,1 MPa) and CAC (63,9 MPa) specimens were significantly lower than those of the OPC (74,3 MPa) specimens to which that of the silica fume (70,7 MPa), meta-kaolin (70,5 MPa) and slag (67,3 MPa) specimens compared favourably.

Table 4.8 Splitting tensile strengths at 8 hours and compressive strengths at 8 hours and at 28 days of standard and modified Olifantsfontein concrete specimens

Concrete	**Strengths** (MPa)		
	Splitting tensile	Compressive	
	(8 hours)	(8 hours)	(28 days)
OPC (0,30)	3,6	40,8	74,3
Slag (0,30)	1,9	25,2	67,5
Fly ash (0,30)	2,1	29,5	53,1
Silica fume (0,28)	6,1	53,6	70,7
Meta-kaolin (0,30)	3,8	38,1	70,5
CAC (0,30)	4,5	79,3	63,9

The slow early-strength development of slag and fly-ash concrete makes de-moulding of sewer pipes directly after manufacture difficult. The superior early-strength of the silica fume specimens is due to the better compaction and improvement in the cohesion resulting from the decrease in water content and addition of the superplasticizer. The superior early-strength of the CAC specimens is due to the rapid rate of hydration of the cement in comparison to OPC. The significant decrease in strength of the CAC specimens at 28 days relates to the conversion of the calcium aluminate hydrates from the hexagonal to cubic form, which increases porosity causing a decrease in the strength of the concrete at later ages. Such a significant reduction in strength was not noticed with the CAC Blackheath specimens as the cracks in the dolomite stone particles cause premature failure and resulted in the significantly lower early-age strength of the CAC Blackheath specimens compared to that of the CAC Olifantsfontein specimens. The high early-age strength development and reduction in strength at later-ages was therefore not noticeable in the CAC Blackheath specimens.

Specimen properties: Density values of the modified specimens (Table 4.9 - average of six determinations) were comparable to those of the OPC specimens (2,59 g/cm^3). Oxygen permeability indexes of the mineral additive specimens (Table 4.9 - average of six determinations) were similar to those of the OPC specimens (10,59) representative of a dense concrete impermeable to gases. Water sorptivity values of the meta-kaolin (2,69 mm/√hr), slag (2,82 mm/√hr) and silica fume (3,55 mm/√hr) specimens were lower compared to those of the OPC (4,83 mm/√hr) and fly-ash (4,48 mm/√hr) specimens indicating a dense concrete of low fluid absorption. Oxygen permeability indexes and water sorptivity values of CAC specimens (9,83 and 7,97 mm/√hr) were poor in comparison to those of the OPC specimens reflecting the increase in porosity due to the expansive conversion reaction.

Table 4.9 Properties of standard and modified Olifantsfontein specimens at 28 days

Concrete	**Density** (g/cm^3)	**Oxygen permeability Index**	**Water sorptivity** (mm/√hr)	**Porosity** (%)	**Acid insolubility** (%)
OPC (0,30)	2,59	10,59	4,83	7,2	4,80
Slag (0,30)	2,55	10,74	2,82	7,7	5,75
Fly ash (0,30)	2,54	10,62	4,48	7,8	5,45
Silica fume (0,28)	2,59	10,88	3,55	3,9	5,11
Meta kaolin (0,30)	2,56	11,04	2,69	4,5	5,09
CAC (0,30)	2,63	9,83	7,97	8,5	4,62

Specimen porosities were low (less than 10 %) typical of a dense and compact concrete (Table 4.9 – average of six determinations). Acid insolubility values (Table 4.9 - average of six determinations) of the modified specimens were similar to those of the OPC specimens (4,80 %) representative of a concrete with a good neutralisation capacity typical of that for use in sewer pipe manufacture.

Hydrochloric acid solution testing of specimens

Mass loss rates (average of four determinations) were constant with time (Figure 4.12). Hydrogen ion consumption rates increased with time with the exception of the silica fume specimens, which reflected a reasonably constant consumption rate with time (Figure 4.13). Consumption of the CAC and meta-kaolin specimens increased at significantly faster rates with time. After 96 hours, mass loss and hydrogen ion consumption of the CAC (51,3 % and 47,53 mg/cm^2) and meta-kaolin (46,7 % and 48,03 mg/cm^2) specimens were substantially higher than those of the OPC specimens (39,3 % and 37,53 mg/cm^2). Mass loss and hydrogen ion consumption of the slag specimens (43,0 % and 40,88 mg/cm^2) and mass loss of the fly ash specimens (42,6 %) were significantly higher than those of the OPC specimens whereas the hydrogen ion consumption of the fly ash specimens (37,50 mg/cm^2) was similar to that of the OPC specimens. Mass loss and hydrogen ion consumption of the silica fume specimens (35,9 % and 32,24 mg/cm^2) were significantly lower than those of the OPC specimens.

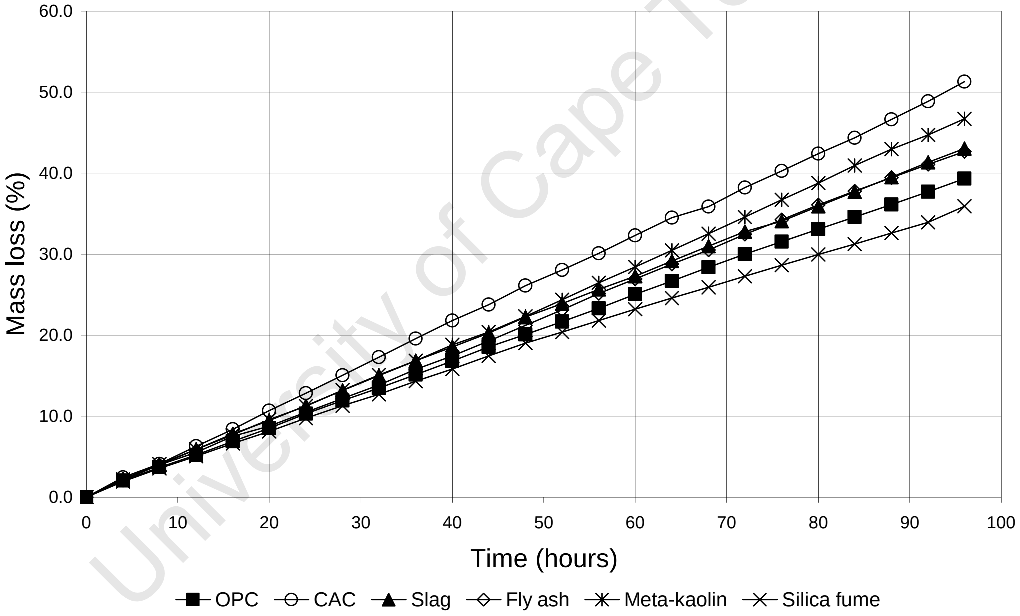


Figure 4.12 Mass loss with time of standard and modified Olifantsfontein concrete specimens measured in a hydrochloric acid solution at a pH of 1,00

Cement additives and CAC influence resistance of the Olifantsfontein concrete to the hydrochloric acid solution in a similar manner to that of the Blackheath concrete. CAC, meta-kaolin, slag and fly ash decrease and silica fume increases resistance of the concrete. Resistance of the Olifantsfontein concrete is decreased to a larger extent with the addition of CAC than that of the Blackheath concrete. Attack on the CAC binder appears more aggressive as the dolomite from Olifantsfontein dissolves at a significantly slower rate than that from Blackheath and reflects the faster dissolution of the CAC binder in comparison to the OPC binder to a larger extent. Stone and crusher sand particles are clearly seen standing proud of the attacked surfaces of the Olifantsfontein specimens (Figure 4.14).

Silica fume on the other hand improves resistance of the Olifantsfontein concrete to a lesser extent than that of the Blackheath concrete. Slower dissolution of the silica fume binder in comparison to the OPC binder in this instance is less evident as the slower dissolution of the Olifantsfontein dolomite masks the improvement in resistance of the binder.

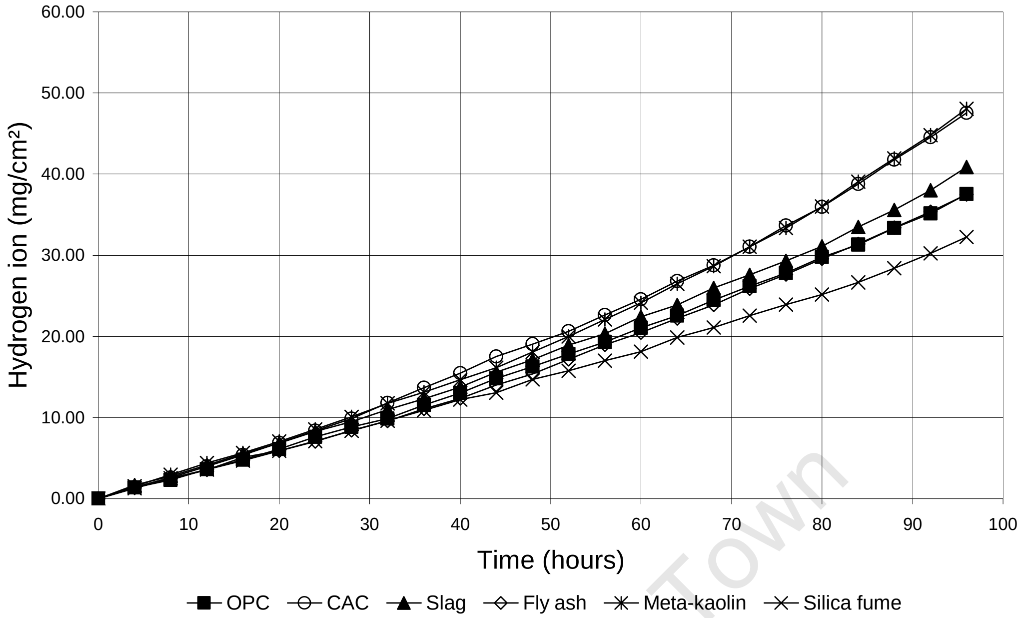


Figure 4.13 Hydrogen ion consumption with time of standard and modified Olifantsfontein concrete specimens in hydrochloric acid solution at a pH of 1,00

Figure 4.14 Attacked surfaces of OPC (left) and CAC (right) Olifantsfontein concrete specimens showing the rougher surface due to the preferential dissolution of the CAC binder leaving the dolomite aggregate particles standing proud

4.4.3 Conclusion

Silica fume improves the resistance of sewer pipe concrete in a hydrochloric acid solution at a pH of 1,00. The extent depends on the quality of the dolomite aggregate. A good quality dolomite dissolves at a slow rate and reflects improvements in the cement binder to a lesser extent than a poor quality dolomite, which dissolves at a faster rate than the cement binder. CAC and conventional mineral additives namely slag, fly ash and meta-kaolin reduce the resistance of sewer pipe concrete in a hydrochloric acid solution at a pH of 1,00 compared with OPC concrete. A concrete containing a good quality aggregate reflects the reduction in acid resistance more as the dissolution of the binder increases to a rate faster than that of the dolomite aggregate particles.

Acid resistance of sewer pipe concrete fundamentally depends on the quality of the dolomite aggregate. A dolomite aggregate needs to dissolve at a rate similar to that of the cement binder or slower to ensure the concrete withstands and neutralises an acidic environment. A dolomite aggregate dissolving at a faster rate allows for the quicker disintegration of the binder portion and produces cavities due to the preferential dissolution of the stone. A binder giving good acid resistance is essential in such cases as exposure of the soluble dolomite aggregate particles to the aggressive environment reduces improving the performance of the concrete.

Any improvement in the acid resistance of the binder is beneficial, but this also depends on the quality of the dolomite or aggregate type. A slowly soluble dolomite with a binder giving good resistance further slows dissolution and improves on the performance of the concrete in acidic environments. Such a binder also slows fall-out of insoluble siliceous aggregate particles to improve performance of the concrete.

4.5 Acid resistances of concrete containing siliceous aggregates

The aim of this investigation was to determine the effect of silica fume and the size and shape of acid-insoluble sand particles on the acid resistance of concrete containing siliceous aggregates. Absence of acid-soluble aggregates in certain areas presents a serious problem for sewer pipe manufacturers. An alternative means of extending the service life of sewer pipes in such areas is to modify the cement binder of a siliceous aggregate mixture to resist attack from acids and to vary the shape and size of the siliceous crusher and filler sands to minimise fine particle fall-out and slow attack on the cement binder portion of the concrete. A completely insoluble hydraulic cement binder is improbable due to the acid-soluble components occurring in hydrated cements.

4.5.1 Specimen preparation and standard testing

A total of eight siliceous aggregate mixtures were designed each containing the same granite stone but differing with respect to the type of binder or siliceous fine aggregate (Table 4.10). Binders were either OPC, or 10 % silica fume and OPC, the latter mixtures containing a superplasticiser (approximately 1 % by mass of binder). Siliceous fine aggregates were either filler or crusher sands or versions of the filler or crusher sands modified to give coarser gradings. Sands modified were both of similar particle sizes differing only in shape and were designed to assess the impact of siliceous fine aggregate particle size and shape on acid resistance. Coarser particles are exposed at a slower rate and take longer to fall out. Angular particles interlock and as a result are less likely to fall out than the rounder particles. Slower exposure and fall-out of the fine aggregate particles results in a slower attack on the binder and entraps corrosion debris more effectively further slowing the attack on the binder.

Table 4.10 Mixture proportions based on ratio to total binder content

Mixture	Stone	Sand	Cement	Additive	w/b
OPC standard filler	2,28	2,28	1,00	-	0,36
SF standard filler	2,28	2,28	0,90	0,10	0,32
OPC standard crusher	2,28	2,28	1,00	-	0,36
SF standard crusher	2,28	2,28	0,90	0,10	0,32
OPC modified filler	2,28	2,28	1,00	-	0,36
SF modified filler	2,28	2,28	0,90	0,10	0,32
OPC modified crusher	2,28	2,28	1,00	-	0,36
SF modified crusher	2,28	2,28	0,90	0,10	0,32

Particle size analyses and acid insolubility measurements were done on the granite stone, siliceous crusher and filler sands. A fines aggregate crushing test was done on the granite stone.

Specimens were compacted using the standard method. Aggregates were air-dried. Water was added to each mixture to obtain a consistency similar to that used in industry giving a w/c ratio of 0,36 for the OPC mixtures and a w/b ratio of 0,32 for the silica fume mixtures.

Splitting tensile and compressive strengths of the specimens were measured at 8 hours directly after steam curing. Acid insolubility, relative density and durability index tests were done on the specimens air-cured for 28 days. Compressive strengths were measured on specimens cured in water for 28 days.

Acid resistances of the specimens (four from each mixture air-cured for 28 days) were determined using the hydrochloric acid solution method. Specimen mass losses and hydrogen ion consumptions were determined using the standard procedure for the initial 48 hours of testing after which mass losses alone were determined using a modified test procedure. After 48 hours, hydrogen ion consumptions of the specimens were minimal and rates remained constant with time. Specimens required a more aggressive cleaning technique to remove the entrapped corrosion debris between the siliceous aggregate particles to accelerate the attack on the binder portion and fall-out of the stone particles.

Specimens (four from each mixture) were transferred into separate hydrochloric acid solutions maintained at a pH of 1,00. Specimens were removed once every 24 hours and sprayed with a high-pressure jet of water to remove the corrosion debris entrapped by the fine aggregate particles from between the stone particles. Sample mass losses were recorded to the point of stone particle fall-out. Solution renewals were done once every 48 hours.

4.5.2 Results and discussion

All the mixtures compacted well. Granite stone particles were not fractured during compaction. A 10 % FACT value of 360 kN was measured for the granite stone indicating that the stone was of a good strength capable of withstanding compaction during specimen preparation and sewer pipe manufacture.

Material analysis

Particle size analysis: Stone particles were all finer than 19,0 mm (Figure 4.15). Approximately 11 % of the particles were coarser than 13,2 mm whereas 85 % of the particles were finer than 13,2 mm and coarser than 6,7 mm of which 57 % were coarser than 9,5 mm. Approximately 4 % of the particles were finer than 6,7 mm.

Siliceous crusher sand particles were all finer than 6,70 mm (Figure 4.16) with a fineness modulus of 3,94. Approximately 4 % of the particles were coarser than 4,75 mm whereas 75 % of the particles were finer than 4,75 mm and coarser than 1,18 mm of which 64 % were coarser than 2,36 mm. Siliceous filler sand particles were all finer than 4,75 mm (Figure 4.16) with a fineness modulus of 1,90. Approximately 60 % of the sand particles were finer than 1,18 mm and coarser than 0,30 mm of which 27 % were coarser than 0,60 mm. Approximately 33 % of the particles were finer than 0,30 mm of which 15 % were finer than 0,15 mm.

Grading of the modified filler sand was identical to that of the modified crusher sand (Figure 4.16) both with a fineness modulus of 3,80. The modified sands were significantly coarser than that of the original filler sand but similar to that of the original crusher sand. All particles of the modified sands were smaller than 4,75 mm. A significant difference between the modified sands were the shapes of the particles larger than 1,18 mm. Siliceous filler sand particles were round and those of the siliceous crusher sand were flat and angular (Figure 4.17).

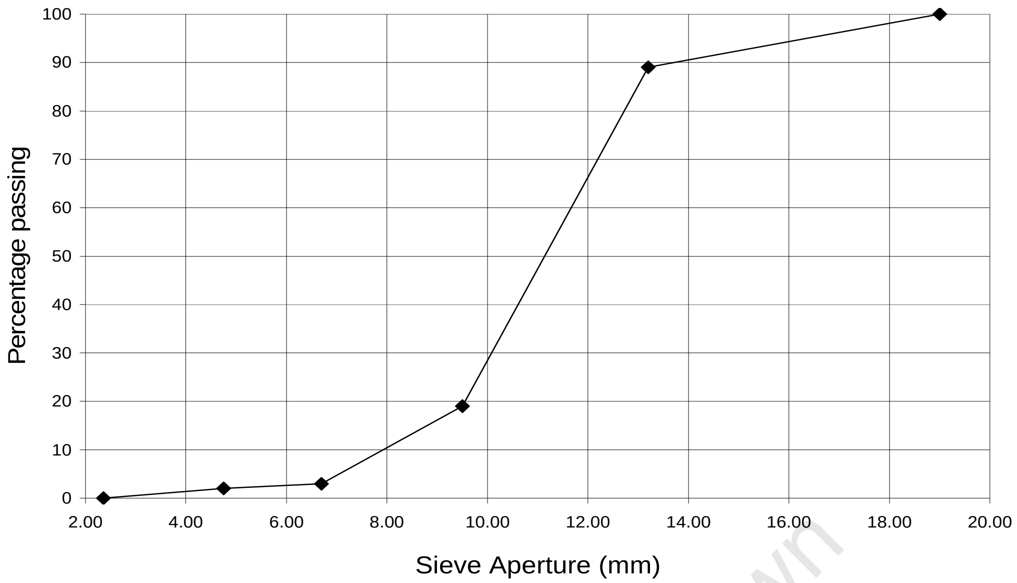


Figure 4.15 Particle size analyses of the granite stone (standard sieve sizes: 19,0 mm; 13,5 mm; 6,5 mm; 4,75 mm and 2,36 mm)

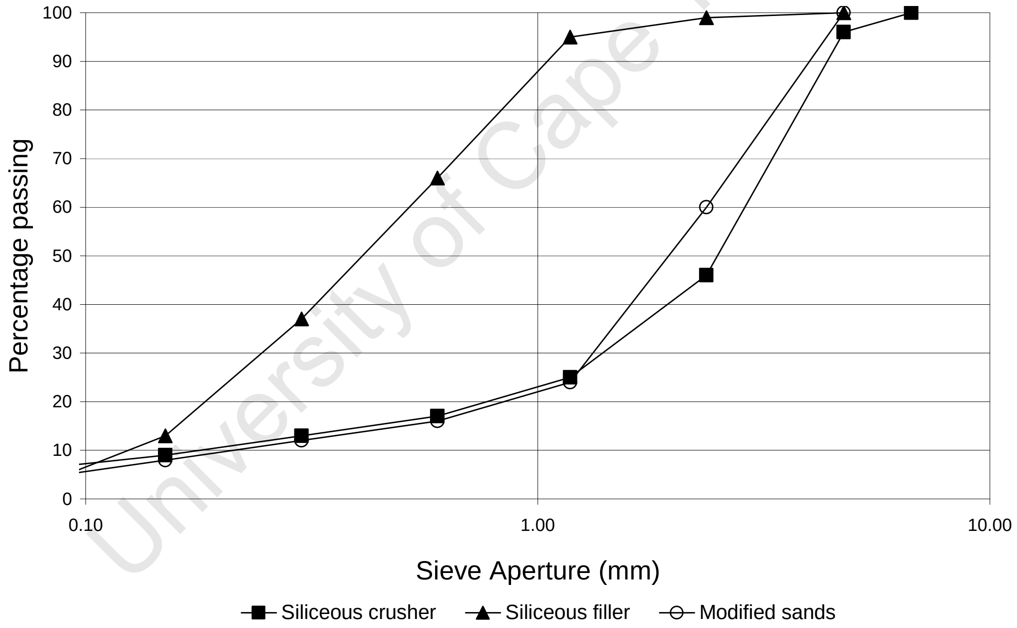


Figure 4.16 Sieve analyses of the siliceous crusher sand, siliceous filler sand and modified sands (standard sieve sizes: 6,7 mm; 4,75 mm; 2,36 mm; 1,18 mm; 0,6 mm; 0,3 mm; 0,15 mm and 0,075 mm)

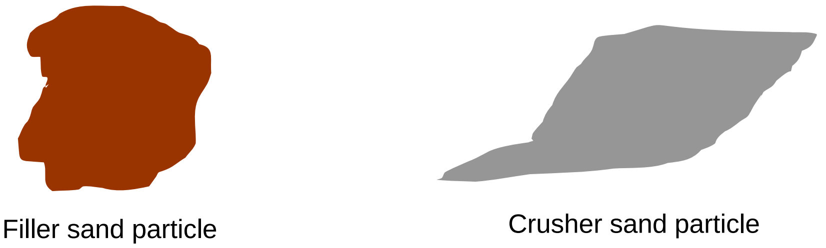


Figure 4.17 Schematic showing the different shapes of the filler and crusher sand particles

Acid insolubility: The siliceous aggregates were of a low acid solubility (Table 4.11 – average of six determinations) and cannot dissolve to neutralise an acidic environment such as the hydrochloric acid solution at a pH of 1,00.

Table 4.11 SABS acid insolubility of siliceous coarse and fine aggregates

Material	**Acid insolubility** (%)
Granite stone	90,0
Siliceous crusher sand	75,3
Siliceous filler sand	97,1

Standard testing of concrete specimens

Specimen strengths: Strengths (average of six determinations) of silica fume specimens were significantly higher than those of the OPC specimens (Table 4.12). Compressive strengths at 28 days of the specimens were substantially higher than the compressive strengths at 8 hours. Strengths at 8 hours and 28 days indicate the siliceous aggregate mixtures are suitable for the manufacture of sewer pipes.

Table 4.12 Splitting tensile strengths at 8 hours and compressive strengths at 8 hours and 28 days of siliceous aggregate concrete specimens

Concrete	**Strengths** (MPa)		
	Splitting	Compressive	
	(8 hours)	(8 hours)	(28 days)
OPC standard filler (0,36)	2,6	31,2	60,8
SF standard filler (0,32)	3,3	41,7	71,5
OPC standard crusher (0,36)	2,7	32,0	61,3
SF standard crusher (0,32)	3,1	42,1	71,5
OPC modified filler (0,36)	2,4	31,0	58,5
SF modified filler (0,32)	3,2	40,4	77,1
OPC modified crusher (0,36)	2,5	29,6	55,8
SF modified crusher (0,32)	3,3	42,6	82,9

Specimen properties: Specimens were of good density (Table 4.13 – average of six determinations). Oxygen permeability indexes of the specimens were similar indicative of dense and impermeable concrete. Water sorptivity and porosity values of the specimens were low, typical of dense and compact concrete showing exceptional resistance to ingress of fluid and gas. Acid insolubilities of the specimens were high (74 - 78 %).

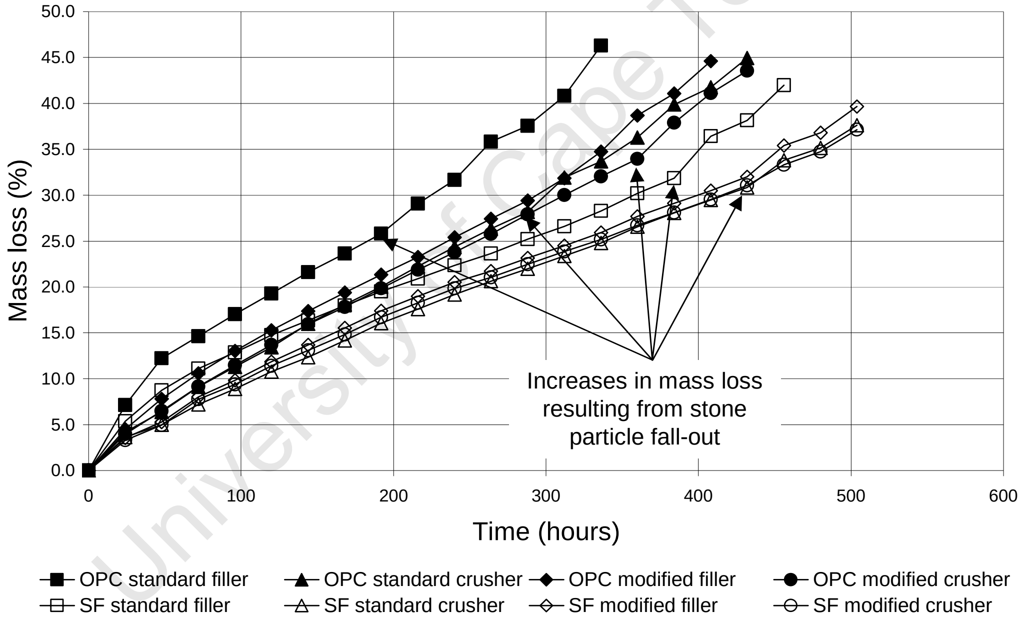
Hydrochloric acid solution testing of concrete specimens

Specimen mass loss rates (average of four determinations) decreased with time over the initial 72 hours of testing after which the rates remained constant with time, but sharply increased at the point of stone particle fall-out (Figure 4.18). OPC standard filler sand specimen mass losses were significantly higher than those of the remaining OPC and silica fume specimens.

OPC specimen mass losses and hydrogen ion consumptions were higher than those of the silica fume specimens. After 48 hours, mass losses of the OPC standard filler sand specimens (12,2 %) were substantially higher than those of the silica fume standard filler sand (8,7 %) and OPC modified filler sand (7,8 %) specimens (Table 4.14). OPC standard and modified crusher sand (6,5 %) and the silica fume modified filler, standard and modified crusher sand (5,0 %) specimen mass losses were slightly lower. Consumptions of the OPC standard filler sand (2,91 mg/cm^2), modified filler sand (2,54 mg/cm^2), modified crusher sand (2,48 mg/cm^2) and standard crusher sand (2,43 mg/cm^2) specimens were slightly higher than that of the silica fume modified filler sand (2,17 mg/cm^2), standard filler sand (2,05 mg/cm^2), standard crusher sand (1,70 mg/cm^2) and modified crusher sand (1,36 mg/cm^2) specimens.

Table 4.13 Siliceous aggregate concrete specimen properties at 28 days

Concrete	**Relative density** (g/cm^3**)**	**Oxygen perm.**	**Water sorp.** (mm/√hr)	**Porosity** (%)	**Acid insol.** (%)
OPC standard filler (0,36)	2,39	10,75	3,17	6,9	78,18
SF standard filler (0,32)	2,38	10,85	2,63	6,6	76,32
OPC standard crusher (0,36)	2,36	10,71	4,07	6,6	72,10
SF standard crusher (0,32)	2,37	10,79	3,07	7,2	73,90
OPC modified filler (0,36)	2,35	10,66	2,81	7,8	76,90
SF modified filler (0,32)	2,36	10,66	2,98	6,3	77,50
OPC modified crusher (0,36)	2,37	10,38	3,33	7,6	72,10
SF modified crusher (0,32)	2,38	10,72	2,89	6,6	71,90



Increases in mass loss resulting from stone particle fall-out

Figure 4.18 Mass losses with time of siliceous aggregate concrete specimens measured using a modified hydrochloric acid solution method

Specimen mass losses decreased significantly after the dissolution of the acid-soluble cement skin surfaces. Acid-insoluble siliceous stone and sand particles exposed decrease the solubility of the surface in contact with the hydrochloric acid solution. As attack progresses the acid-soluble binder portions between the stone particles decrease resulting in the continual decrease in mass loss rates with time. After approximately 72 hours, the acid-soluble binder portion in contact with the hydrochloric acid solution becomes constant resulting in the uniform mass loss rates with time. Specimen mass losses are dependant on the dissolution of the cement and fall-out of the siliceous sand particles until siliceous stone particle fall-out occurs, which leads to an increase in the mass loss rate with time.

Increases in mass loss rates, which reflect the onset of stone particle fall-out, occurred substantially earlier for the OPC standard filler sand specimens (192 hours) compared to that for the OPC standard crusher sand and modified filler sand specimens (288 hours), which was earlier compared to that for the OPC modified crusher sand (360 hours) and silica fume standard filler sand (384 hours) specimens. Sharp increases in the silica fume standard and modified crusher sand and modified filler sand specimen mass loss rates occurred noticeably later (432 hours).

Table 4.14 Mass loss and hydrogen ion consumption of the siliceous aggregate specimens after 48 hours exposure to the hydrochloric acid solution at a pH of 1,00

Concrete	**Mass loss** (%)	**Hydrogen ion** (mg/cm^2)
OPC standard filler (0,36)	12,2	2,91
SF standard filler (0,36)2	8,7	2,05
OPC standard crusher (0,36)	6,4	2,43
SF standard crusher (0,32)	5,0	1,70
OPC modified filler (0,36)	7,8	2,54
SF modified filler (0,32)	5,3	2,17
OPC modified crusher (0,36)	6,5	2,48
SF modified crusher (0,32)	4,9	1,36

Silica fume and the size of the fine aggregate particles substantially influence the acid resistance of the siliceous aggregate concrete. A substantial decrease in mass loss occurs with the addition of silica fume to the mixtures in comparison to the decrease in hydrogen ion consumption. Small differences in hydrogen ion consumptions relate to the decrease in the calcium hydroxide lowering the neutralisation capacity of the cement binder. It is speculated that corresponding large decreases in mass loss, relate to the improved integrity of the material, particularly improvements in the interfacial zone between the cement binder and siliceous aggregate particles and pore refinement (Larbi and Bijen, 1991).

Substantial increase in the time to stone particle fall-out (approximately 100 hours) supports the speculation that silica fume improves binding of the aggregate particles better than OPC alone. Specimens for a microscopic investigation were difficult to prepare, since slicing through the attacked concrete surfaces dislodged the siliceous aggregate particles standing proud (Figure 4.19). Cleaning the surfaces of the specimens revealed that the siliceous aggregate particles standing proud were easier to dislodge from the standard OPC binders than the silica fume binders.

Coarser siliceous sand particles reduce the attack on the cement binder portion substantially prolonging the stone particle fall-out. Coarse standard crusher and modified crusher and filler sands more than halved the mass loss of the OPC concrete after 48 hours and substantially increased stone fall-out time of the OPC concrete (standard crusher sand from 216 to 312 hours, modified filler sand to 336 hours and the modified crusher sand to 384 hours). Coarser sand particles decreased the mass loss of the silica fume concrete to a lesser extent. After 48 hours, mass losses of the specimens containing the coarser sands decreased approximately by a third and stone particle fall-out time increased from 384 to 432 hours.

Shape of the sand particles influenced mass loss and stone particle fall-out time less than size. Specimens containing the rounded modified filler sand particles lost similar amounts of mass and reflected similar stone particle fall-out times as the specimens containing the angular standard and modified crusher sand particles, which was due to the coarseness of the particles in comparison to that of the standard filler sand particles.

4.5.3 General discussion

Acid resistances of siliceous aggregate concrete and dolomite aggregate concrete are difficult to compare. Specimen mass loss and depth of attack measurements (Appendix D) indicate that the acid resistance of the siliceous aggregate concrete is significantly better, which is not the case in sulphuric acid environments encountered in sewers (Kelly and Krüger, 1996). Concrete containing dolomite aggregate is capable of neutralising the sulphuric acid generated in sewers slowing the development, growth and activity of the acid-loving thiobacillus bacterial colony more than concrete containing siliceous aggregate, which results in a slower rate of attack on dolomite aggregate concrete in sewer environments (Section 5.2.2). After 96 hours, mass losses of the siliceous aggregate specimens (7 to 17 %) were substantially lower than those of the dolomite aggregate specimens (35 to 60 %) implying the siliceous aggregate concrete gives better performance. Similarly, depth of attack measurements after 96 hours on the siliceous aggregate specimens (0,29 compared to 0,60 cm) were substantially lower implying the siliceous aggregate concrete provides better cover to steel-reinforcing.

Figure 4.19 An OPC standard filler sand concrete specimen subjected to a hydrochloric acid solution at a pH of 1,00 for 300 hours showing granite stone particles standing proud of the attacked surface

Attack on the siliceous aggregate concrete specimens is extremely slow in the hydrochloric acid solution due to the entrapment of corrosion debris between the closely-packed sand particles. Stagnant conditions generated as a result allows the build-up of a barrier consisting of insoluble cement residue, precipitated corrosion products such as aluminium and iron hydroxides and sand particles, which isolates the cement binder from the hydrochloric acid solution (Figure 4.20). Sustaining attack requires regular removal of the corrosion debris to prevent the development of a layer capable of stifling the attack. After exposure of the granite stone particles (approximately 48 hours), the brushing techniques are ineffective necessitating cleaning of the specimens with a high-pressure jet of water.

Accelerating the attack on the siliceous aggregate specimens with the removal of the corrosion debris once every 24 hours allows measurement of acid resistance in terms of mass loss and stone particle fall-out, within a relatively short period (300 to 500 hours) but fails to eradicate the influence of the corrosion debris on the attack mechanism and simulate that on the dolomite aggregate specimens. The acid-soluble nature of the dolomite aggregate concrete prevents entrapment of corrosion debris and continuous brushing is effective in removing any insoluble residue or filler sand particles collecting on the specimen surface. Accurately correlating acid resistances of the siliceous materials to that of the dolomite materials requires continuous removal of the corrosion debris entrapped between the siliceous aggregate particles, which is impractical.

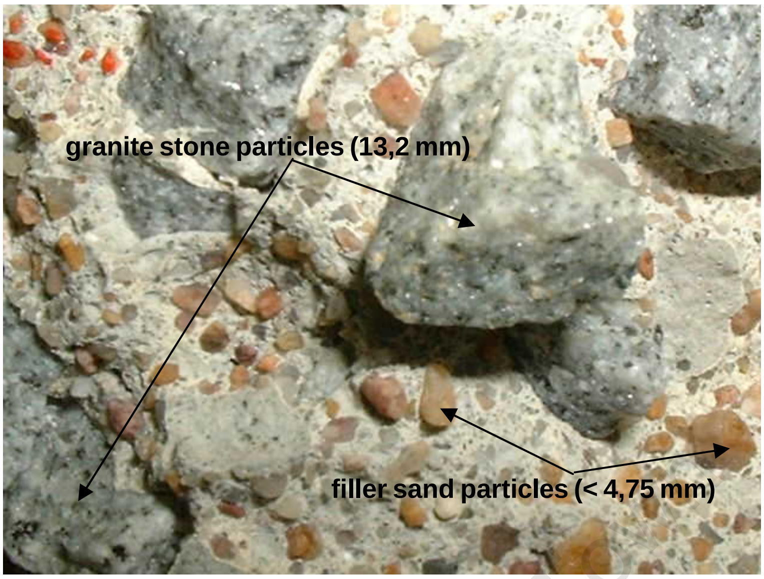


Figure 4.20 Attacked surface of an OPC standard filler sand concrete specimen showing the barrier between the exposed stone particles that builds-up due to the entrapment of corrosion debris between the filler sand particles

4.5.4 Conclusion

Silica fume substantially improves acid resistance of the cement binder. Silica fume decreases the calcium hydroxide reducing the solubility of the cement binder in acidic environments and the additional calcium silicate formed physically enhances the acid resistance of the siliceous aggregate concrete. Siliceous stone and sand particles are more effectively bound into the concrete matrix due to the densification and improvement in the interfacial zone between the particles and cement binder. Similar observations are not evident with the dolomite aggregate concrete due to the simultaneous dissolution of the dolomite aggregate particles and cement binders.

Siliceous sand particles significantly influence acid resistance of the siliceous aggregate concrete. Coarser sand particles (> 1,18 mm) interlock and entrap corrosion debris and lock in the siliceous stone particles more so than fine particles (< 1,18 mm) slowing stone particle fall-out and attack on the cement binder to a larger extent.

4.6 Acid resistance of concrete linings for sewer pipes

The aim of this investigation was to assess acid resistance of sewer pipe concrete linings designed to withstand sulphuric acid environments. A lining is different from a sacrificial layer. A sacrificial layer is the additional calcareous aggregate concrete cast into a sewer pipe to provide extra cover to the steel-reinforcing and extend service life in sulphuric acid environments. Sacrificial layers dissolve, without affecting the structural integrity of the sewer pipe, to neutralise and render a less corrosive environment (Stutterheim, 1954). A concrete lining, which is cast into a sewer pipe immediately after compaction, contains materials different to that of the substrate. For example, a lining may contain calcium aluminate materials, which are of a higher neutralisation capacity and toxicity towards the thiobacillus bacteria (Ehrich et al, 1999).

A lining resists a sulphuric acid environment and acts as a barrier protecting the concrete sewer pipe structural substrate. Concrete linings are designed to offer greater resistance to corrosive environments and are suitable for use in severely corrosive environments.

Assessing the resistance of concrete linings to the hydrochloric acid solution at a pH of 1,00 gives a good indication of the ability of the lining to withstand such severe corrosive sulphuric acid environments.

4.6.1 Lining concrete specimen preparation and testing

A total of five concrete mixtures were prepared (Table 4.15):-

- 23 % CAC dolomite aggregate mixture commonly used to line dolomite aggregate concrete sewer pipes in South Africa in areas were corrosive conditions occur
- 23 % OPC dolomite aggregate mixture to gauge the acid resistance of an OPC lining mixture
- 23 % and 18 % CAC synthetic alag™ aggregate (an aggregate manufactured from CAC clinker therefore of a similar chemical composition to CAC containing approximately 38 % CaO, 37 % Al_2O_3, 20 % Fe_2O_3 an 5 % SiO_2) mixtures of interest to cement and concrete pipe manufactures for use in areas where severely corrosive conditions occur
- 23 % silica fume mixture to ascertain the effect of silica fume on the acid resistance of concrete containing CAC and alag™ aggregates

Table 4.15 Mixture proportions based on ratio to total binder content

Mixture	Aggregate:cement ratio				
	Stone	Sand	Cement	Additive	w/b
23 % OPC dolomite	1,67	1,67	1,0	-	0,28
23 % CAC dolomite	1,67	1,67	1,0	-	0,28
18 % CAC alag™	2,28	2,28	1,0	-	0,33
23 % CAC alag™	1,67	1,67	1,0	-	0,28
23 % SF/CAC alag™	1,67	1,67	0,9	0,1	0,24

OPC, CAC and silica fume were obtained in bags from the relevant manufacturers. Stone and crusher sand was that sourced from Olifantsfontein factory for the previous investigation into the modification of sewer pipe concrete (Section 4.4.1). Synthetic coarse and fine alag™ aggregates were obtained in bags from the supplier. Sieve analyses and acid insolubility tests were done on the coarse and fine alag™ aggregates.

Specimens were prepared from each mixture using the standard method. Water was added to each mixture to obtain a consistency similar to that used in industry giving a w/b ratio of 0,24 for the silica fume/CAC mixture, 0,28 for the 23 % CAC and OPC cement mixtures and 0,33 for the 18 % CAC mixture. A superplasticizer (0,6 % of the binder content) was added to the silica fume mixture.

Acid insolubility, relative density, oxygen permeability, water sorptivity and porosity tests were done on steam-cured specimens air-cured for a further 28 days (25°C and RH of 60 %) and compressive strength tests on those water-cured at 23°C for a further 28 days to compare compaction and quality. Acid resistance of specimens air-cured for 28-days was determined using the hydrochloric acid solution test. Solutions were renewed every 12 hours to eliminate the effect of the aluminium ion build-up on the titration end-point (Appendix A – Section A.3.3).

4.6.2 Results and discussion

Material analyses

Coarse alag™ aggregate particles were all finer than 13,2 mm (Figure 4.21) and of a substantially finer grading than the dolomite stone particles from the Olifantsfontein factory

(Figure 4.10). Approximately 94 % of the coarse alag particles were finer than 9,5 mm, 67 % finer than 6,70 mm, and 22 % finer than 4,75 mm.

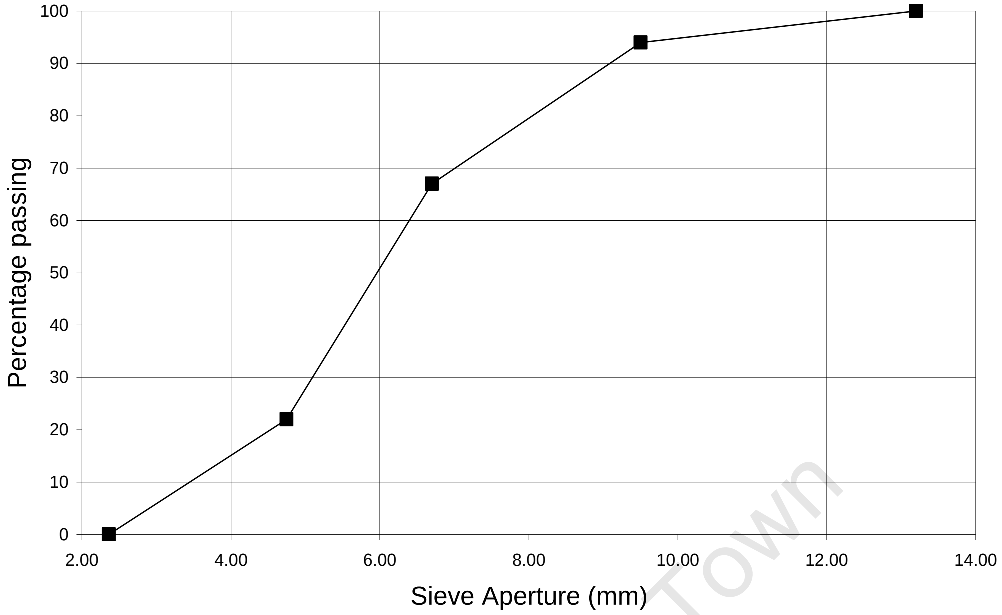


Figure 4.21 Particle size analysis of coarse alag™ aggregate (standard sieve sizes 19 mm; 13,2 mm; 9,5 mm; 6,7 mm; 4,75 mm and 2,36 mm)

Fine alag™ aggregate particles were all finer than 6,70 mm (Figure 4.22) with a fineness modulus of 3,66. Grading was similar to that of the dolomite crusher sand particles from the Olifantsfontein factory (Figure 4.11). Effectively, the fine aggregate was finer than 4,75 mm.

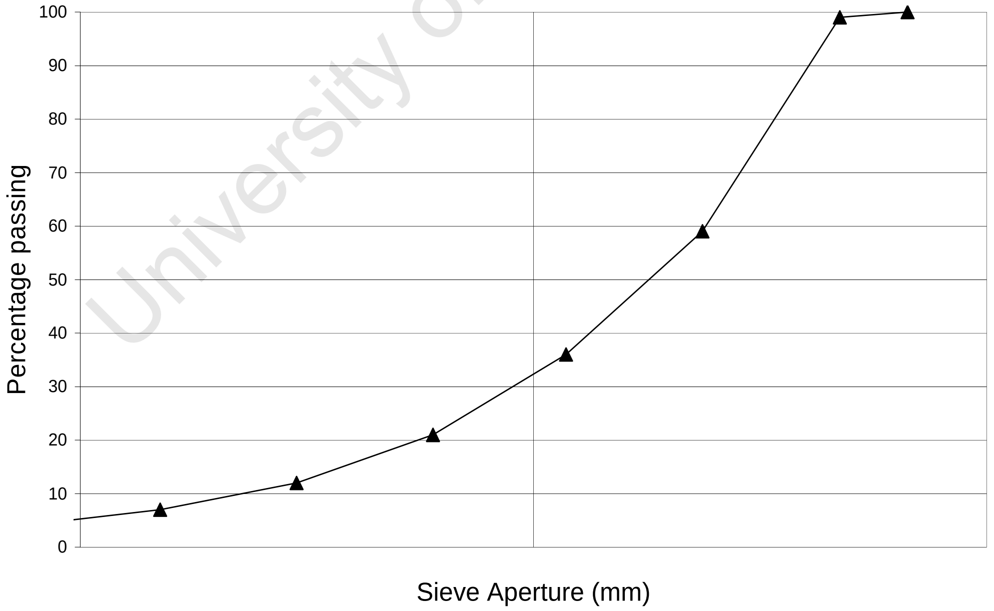


Figure 4.22 Sieve analysis of the fine alag™ aggregate (standard sieve sizes: 6,7 mm; 4,75 mm; 2,36 mm; 1,18 mm; 0,6 mm; 0,3 mm; 0,15 mm and 0,075 mm)

Acid insolubilities of the alag™ aggregates were typical of a good quality dolomite aggregate capable of neutralising a sulphuric acid environment. Acid insolubility of the coarse alag™ aggregate (3,32 %) was similar to that of the Olifantsfontein dolomite stone (3,84 %). Acid insolubility of fine alag™ aggregate (3,18 %) was lower than that of the Olifantsfontein dolomite crusher sand (5,20 %).

Standard testing of concrete specimens

Density: Specimens containing the alag™ aggregates were of a significantly higher density than the specimens containing the dolomite aggregates (Table 4.16) due to the higher density of the alag™ aggregate (ca. 3,25 g/cm^2) compared to that of the dolomite aggregate (ca. 2,80 g/cm^2) and accounts for the higher density of the 18 % CAC specimens, which contains a higher percentage of the alag™ aggregates. Specimens containing the 23 % OPC and CAC and the dolomite aggregate were of a similar density to the standard 18 % OPC and CAC dolomite aggregate specimens (2,59 and 2,63 g/cm^2 respectively).

Table 4.16 Concrete lining specimen properties at 28 days

Concrete	**Density** (g/cm^3)	**Acid insol.** (%)	**Comp. strength** (MPa)	**Oxygen perm.**	**Water sorp.** (mm/√hr)	**Porosity** (%)
23 % OPC dolomite	2,60	4,35	74,8	10,60	4,49	8,0
23 % CAC dolomite	2,62	4,00	68,8	10,35	10,64	7,6
18 % CAC alag™	2,87	7,83	81,3	10,27	9,01	6,5
23 % CAC alag™	2,80	6,41	84,7	10,23	11,48	8,4
23 % SF/CAC alag™	2,81	6,02	82,7	10,30	7,09	6,8

Acid insolubility: Specimens were of low acid insolubility capable of neutralising an acidic environment (Table 4.16). Acid insolubility values of the alag™ aggregate specimens were higher than those of the dolomite aggregate specimens. Acid insolubility of the 23 % OPC and CAC dolomite aggregate specimens were similar to that of the 18 % OPC and CAC dolomite aggregate specimens (4,80 and 4,62 % respectively).

Compressive strengths: Specimens containing the alag™ aggregates were of a significantly higher strength than the specimens containing the dolomite aggregates due to the absence of the interfacial zone resulting from the good bonding between the alag™ aggregate particles and CAC binder (Table 4.16).

Durability indexes: Oxygen permeability indexes indicate the specimens were dense and impermeable (Table 4.16). Water sorptivity of the CAC specimens were significantly higher than that of the OPC specimens (Table 4.16). Silica fume improved the sorptivity of the CAC/alag™ concrete. Porosities of the specimens were low typical that of a well-compacted dense concrete (Table 4.16).

Hydrochloric acid testing of concrete specimens

Mass loss and hydrogen ion consumption of the specimens (average of four determinations) were compared with those of the 18 % OPC and 18 % CAC dolomite aggregate specimens previously investigated (Section 4.4.2). Specimen mass loss rates remained constant with time (Figure 4.23). Specimens containing the alag™ aggregates reflected substantially lower mass loss rates with time than the specimens containing the dolomite aggregates. After 96 hours, the mass loss of the 23 % CAC/dolomite specimens (50,9 %) was significantly higher than that of the 23 % OPC/dolomite specimens (43,2 %). Mass losses of the 23 % CAC/alag™ (15,2 %), 18 % CAC/alag™ (11,8 %) and 23 % silica fume/CAC alag™ (10,9 %) specimens were substantially lower. Mass loss of the 23 % OPC/dolomite specimens (43,2 %) was higher than that of the standard 18 % OPC/dolomite specimens (39,3 %) whereas mass loss of the 23 % CAC/dolomite specimens (50,9 %) was similar to that of the standard 18 % CAC/dolomite (51,3 %) specimens.

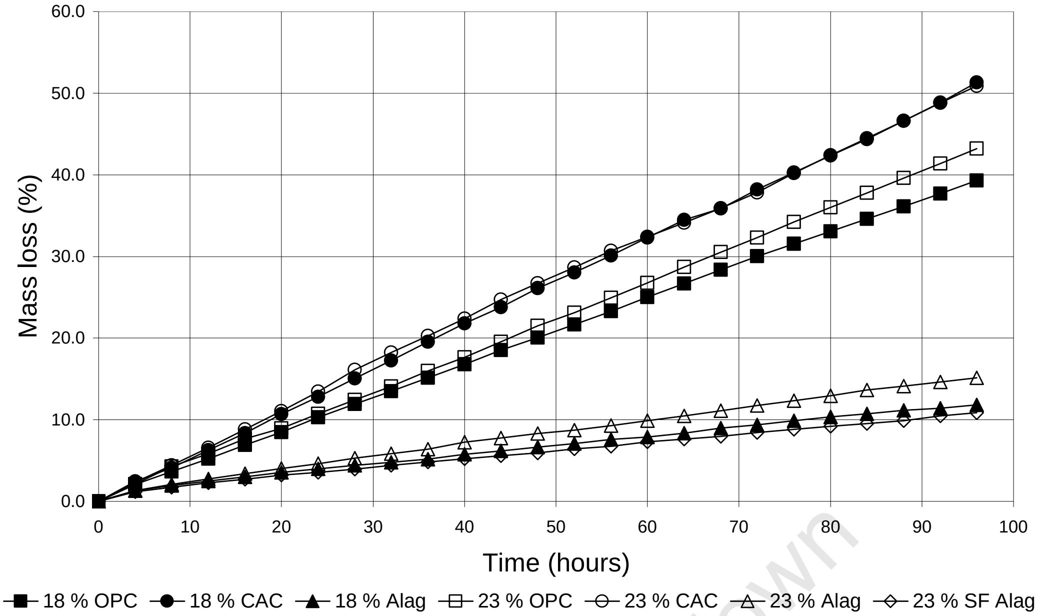


Figure 4.23 Mass loss with time of 18% standard and 23 % lining dolomite aggregate and alag™ aggregate specimens in a hydrochloric acid solution maintained at a pH of 1,00

Hydrogen ion consumption rates of the specimens containing the alag™ aggregates remained constant with time and were substantially lower than those of the specimens containing the dolomite aggregates, which increased with time (Figure 4.24). The constant consumption rate of the CAC/alag™ specimens was due to the similar acid-solubility of the CAC binder and alag™ aggregate. After exposure of the alag™ aggregate particles, hydrogen ion consumption remains the same, and does not increase with time as with the exposure of the dolomite aggregate particles, which consume more hydrogen ions than the cement binders.

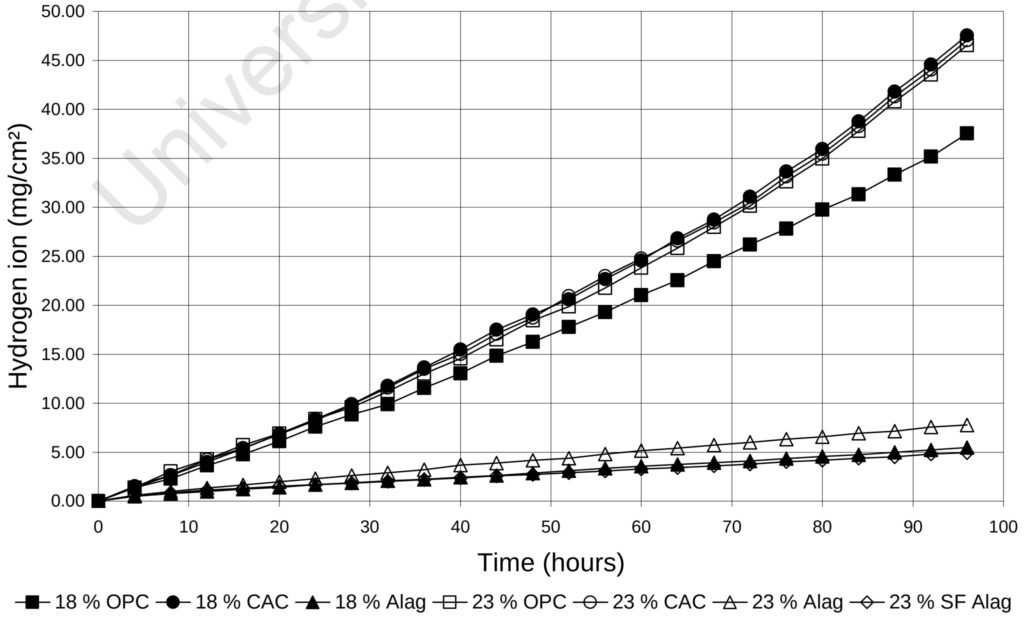


Figure 4.24 Hydrogen ion consumption with time of 18 % standard and 23 % lining dolomite aggregate and alag™ aggregate specimens in a hydrochloric acid solution maintained at a pH of 1,00

Consumption rates of the 23 % CAC/dolomite and 23 % OPC/dolomite specimens increased at a similar rate to those of the 18 % CAC/dolomite specimens, but at a faster rate than the 18 % OPC/dolomite specimens. After 96 hours, hydrogen ion consumptions of the 23 % SF/alag™ (4,96 mg/cm^2), 18 % CAC/alag™ (5,48 mg/cm^2) and 23 % CAC/alag™ (7,79 mg/cm^2) specimens were substantially lower than those of the 23 % OPC/dolomite (46,53 mg/cm^2) and 23 % CAC/dolomite (47,03 mg/cm^2) specimens. Consumption of the standard 18 % CAC/dolomite specimens (47,53 mg/cm^2) was similar to that of the 23 % CAC/dolomite specimens (47,03 mg/cm^2) whereas consumption of the standard 18 % OPC/dolomite specimens (37,53 mg/cm^2) were significantly lower than that of the 23 % OPC/dolomite specimens (46,53 mg/cm^2).

The substantially lower mass losses and hydrogen ion consumptions of the alag™ aggregate concrete specimens compared to the dolomite aggregate concrete specimens are considered to be due to a combination of the following factors:-

- absence of an interfacial zone between the CAC binder and alag™ aggregate particles
- slower dissolution of the alag™ aggregate particles than the dolomite aggregate particles
- finer size of the alag™ aggregate particles compared to the dolomite aggregate particles
- entrapment of corrosion debris between the slower dissolving alag™ aggregate particles

A strong bond forms on reaction between the CAC paste and alag™ aggregate particles due to their similar compositions and the reactivity of the alag™ aggregate particles in the concrete mixture. A weaker bond of a lower density (an interfacial zone) forms between the cement pastes (CAC and OPC) and the dolomite aggregate particles due to their different compositions and the inert nature of the dolomite aggregate particles in the concrete mixture. Such a weak bond degrades at a faster rate in the hydrochloric acid solution and increases the dissolution rates of both the binder and dolomite aggregate particles thereby contributing to the faster dissolution of the dolomite aggregate specimens.

An investigation into the solubility of the different types of aggregate particles in a hydrochloric acid solution revealed that the alag™ aggregate particles dissolved at a significantly slower rate than the dolomite aggregate particles. Approximately 300 g of alag™ coarse aggregate particles retained on a 6,70 mm sieve and a similar amount and size of dolomite stone particles were exposed to separate hydrochloric acid solutions maintained at a pH of 1,00. After 96 hours, the mass loss of the alag™ coarse aggregate particles was approximately half that of the dolomite stone particles. After dissolution of the cement skin and the exposure of the aggregate particles the less acid-soluble alag™ particles consume significantly less hydrogen ions than the dolomite aggregate particles resulting in the lower mass losses of the CAC/alag™ specimens compared to the CAC/dolomite and OPC/dolomite specimens.

Alag™ aggregate particle are also finer in comparison to the dolomite aggregate particles (Figure 4.21 and 4.10 respectively) and occupy more of the separate but related surfaces exposed to the hydrochloric acid solutions. As a result, the surfaces of the alag™ aggregate specimens are rendered less soluble and resist the hydrochloric acid solution better than the dolomite aggregate specimens.

Attack on the binder in the CAC/alag™ specimens is reduced due to the entrapment of corrosion debris between the tightly packed network of alag™ particles standing proud of the attacked surfaces of the specimens (Figure 4.25), which results due to the slow dissolution and fineness of the alag™ aggregate particles. Attack on the CAC binder is masked in a manner similar to that on the OPC binder in the siliceous aggregate specimens (Section 4.5.4). The entrapped corrosion debris creates static conditions that result in a localised drop in the pH between the exposed aggregate particles allowing the precipitation of salts mainly alumina, which isolates the binder from the hydrochloric acid solution. The masking effect is not as effective in the alag™ aggregate specimens as in the siliceous aggregate specimens. Alag™ particles dissolve to re-expose the CAC binders.

Figure 4.25 Surfaces of a 23 % CAC/dolomite (left) and 23 % CAC/alag™ (right) specimens subjected to a hydrochloric acid solution at a pH of 1,00 for 96 hours showing the preferential dissolution of the CAC binders and the denser network of alag™ aggregate particles than dolomite aggregate particles

The slower dissolution of the alag™ aggregate particles and binder in the CAC/alag™ aggregate specimens compared to the dolomite aggregate particles and binder in the OPC/dolomite and CAC/dolomite aggregate specimens was noticeable after the dissolution of the cement skin surrounding the respective specimens (Figure 4.26). After exposure of the aggregate particles, mass losses of the alag™ aggregate specimens were approximately three times less than the those of the dolomite aggregate specimens, and hydrogen ion consumptions of the alag™ aggregate specimens were seven times less than those of the dolomite aggregate specimens.

Figure 4.26 Attacked surfaces of the 23 % OPC (left) and 23 % CAC (right) dolomite aggregate concrete specimens subjected to a hydrochloric acid solution at a pH of 1,00 for 96 hours showing the smooth surface of the OPC specimen compared to the rougher surface of the CAC specimen resulting from the faster dissolution of the CAC binder

Ratios of mass loss to hydrogen ion consumption of the alag™ aggregate specimens (100 – 110) were significantly higher than those of the dolomite aggregate specimens (55 – 70). The substantially lower hydrogen ion consumption of the alag™ aggregate specimens compared to that of the dolomite aggregate specimens in relation to the differences in mass loss is due to a combination of factors:-

- entrapment of corrosion debris between alag™ aggregate particles
- low acid-solubility of the alag™ aggregate particles
- fall-out of the fine alag™ aggregate particles

As discussed above, the build-up of corrosion debris and lower acid-solubility of the alag™ aggregate particles in the hydrochloric acid solution significantly lowers the hydrogen ion consumption potential of the alag™ aggregate specimens. Alag™ fine aggregate particles fall-out with time due to their slow dissolution rate in comparison to the CAC binder. The acid- soluble nature of the dolomite crusher sand limits particle fall-out and results in lower mass loss to hydrogen ion consumption ratios.

Adding silica fume to the CAC/alag™ concrete slightly improves the resistance of the CAC binder in the hydrochloric acid solution. A more cost effective option is to lower the CAC binder content, which improves the resistance of the concrete in the hydrochloric acid solution to a similar extent. Attack on the 18 % CAC binder decreases as the closer packed network of alag™ particles more effectively masks the binder from the hydrochloric acid solution.

A higher CAC binder content (23 % compared to 18 %) does not affect the mass loss and hydrogen ion consumption of the dolomite aggregate concrete whereas a higher OPC binder content (23 % compared to 18 %) increases the mass loss and hydrogen ion consumption of the dolomite aggregate concrete. Hydrogen ion consumptions of the 23 % OPC/dolomite aggregate specimens increase due to the larger amount of calcium oxide available in the 23 % OPC binder, which results in the corresponding increase in mass loss of the specimens. Mass losses and hydrogen ion consumptions of the 23 % CAC/dolomite aggregate specimens were significantly higher than those of the 23 % OPC/dolomite aggregate specimens due to the faster dissolution of the CAC binder compared with that of the OPC binder (Figure 4.26), which was also evident with the 18 % OPC/dolomite and 18 % CAC/dolomite aggregate specimens (Section 4.4.2 - Figure 4.14). Although the dissolution rate of the CAC binder in the CAC/alag™ aggregate specimens was faster than that of the alag™ aggregate particles it was substantially slower than that of the CAC binder in the CAC/dolomite aggregate specimens (Figure 4.25).

An electron microscope examination of a CAC/alag™ aggregate specimen surface reveals that the attack is a surface phenomenon (Figure 4.27), which is similar to the attack on the OPC/dolomite aggregate specimens (Figure 4.7).

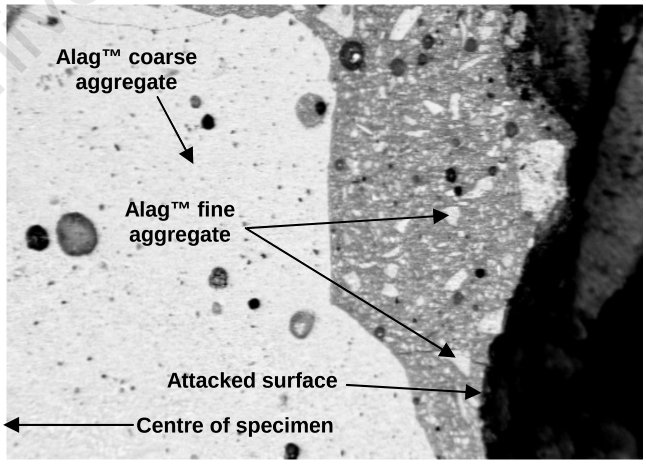


Figure 4.27 A SEM analysis of a polished surface cut into an CAC/alag™ aggregate concrete specimen at right angles from the attacked surface, which illustrates the attack depends on the dissolution of the concrete in contact with the hydrochloric acid solution at a pH of 1,00

4.6.3 Conclusion

Alag™ aggregate significantly improves the acid resistance of a CAC concrete. Alag™ improves the structural integrity of a CAC concrete in an acidic environment allowing the concrete to dissolve at a significantly slower rate than dolomite aggregate concrete. Slower dissolution of the CAC/alag™ aggregate concrete results from the substantially lower solubility of the alag™ aggregate compared to the dolomite aggregate in the hydrochloric acid solution at pH of 1,00 (a chemical factor) and physical factors namely strong bonding between CAC and alag™ aggregate and the entrapment of corrosion debris between the alag™ aggregate particles.

Slow dissolution of the CAC/alag™ aggregate concrete in the hydrochloric acid solution implies that the concrete is suitable for use in severely corrosive conditions where the pH of a sulphuric acid environment in the sewer is 1,00 or lower. A dolomite aggregate concrete is more vulnerable to such a corrosive environment and readily dissolves to neutralise the acid generated giving the concrete poor structural integrity. In contrast, the CAC/alag™ aggregate concrete, which is of similar neutralisation capacity to the dolomite aggregate concretes (SABS acid insolubility measurements – Table 4.16) dissolves at a slow rate maintaining it's structural integrity. In addition, the stifling effect of the calcium aluminate materials (Ehrich et al, 1999) on the growth of the thiobacillus bacterial colony limits conditions favouring the growth of the thiobacillus thiooxidans and generation of a severely corrosive environment.

Acid resistance of the CAC/dolomite aggregate concrete is poor in the hydrochloric acid solution and not suitable for use in sulphuric acid sewer environments where a pH of 1,00 is imminent. The ability of the CAC to stifle the growth of the thiobacillus bacteria implies the concrete performs better in sulphuric acid environments encountered in sewers than a similar OPC/dolomite aggregate concrete. A concern is the vulnerability of the CAC binder towards the sulphuric acid generated particularly when severe corrosive conditions occur.

Assessing the acid resistances of the concrete linings in the hydrochloric acid solution clearly illustrates the nature of attack on the different types of concrete and the influence of the physical and chemical properties on the resistance of the concrete towards acidic solutions. Assessing the physical ability of the concrete linings to resist an acid solution is essential to allow modifications to the mixtures to improve on the resistance of components such as the binders and develop a concrete lining capable of protecting the inside of a sewer pipe in corrosive environments.

4.7 General discussion

A critical factor in assessing the acid resistance of sewer pipe concrete is aggregate type. Acid resistance measured as a function of mass loss and hydrogen ion consumption using the hydrochloric acid solution test is substantially better for concrete containing the acid-soluble alag™ aggregates than concrete containing acid-soluble dolomite aggregates, which are conventionally used in the manufacture of sewer pipes. Concrete containing a good quality dolomite aggregates are suitable for use in acidic environments as the acid-soluble aggregate dissolves to consume substantially more hydrogen ions in the hydrochloric acid solution than a similar concrete containing acid-insoluble siliceous aggregates, thereby rendering the acidic environment less aggressive with time. Structural integrity of siliceous aggregate concrete in the hydrochloric acid solution diminishes rapidly with the dissolution of the cement paste and fall-out of aggregate particles. Similarly does the structural integrity of concretes containing a poor quality dolomite, which dissolves at a substantially faster rate than the cement paste in the hydrochloric acid solution.

Acid resistances (at a low pH of 1) of dolomite aggregate concretes containing CAC binders are significantly poorer than the acid resistances of similar conventional dolomite aggregate concretes containing OPC binders that is, the ability for CAC binders to neutralise and resist acidic environments better than OPC binders as stated (Ehrich et al, 1999) is not evident from the mass loss and hydrogen ion consumption measurements in the hydrochloric acid solutions. According to literature (Ehrich et al, 1999), an improvement in neutralisation capacity results from the aluminium hydrates in the CAC binder, which are capable of neutralising more hydrogen ions than the calcium hydrates in the OPC binder (Equation 4.1 and 4.2), and an improvement in the acid resistance results from the lower amount of calcium hydroxide in the CAC binder compared to that in the OPC binder (De Belie et al, 1997) and the formation of an alumina gel, which isolates the CAC binder from an acid environment (Ehrich et al, 1999).

$$Al(OH)_3 + 3HCl \rightarrow Al^{3+} + 3Cl^- + 3H_2O \tag{4.1}$$
$$Ca(OH)_2 + 2HCl \rightarrow Cl^{2+} + 2Cl^- + 2H_2O \tag{4.2}$$

Arguably, CAC is more resistant than OPC in milder mineral acid solutions that is, at a pH of 3,00 and above (Lea, 1975). Such an improvement is mainly due to the insoluble nature of the aluminium hydroxide above a pH of 3,00 than the absence of calcium hydroxide in the CAC binder, which readily leaches out at a pH of 3,00 and above. Aluminium hydroxide precipitates forming an alumina gel (Ehrich et al, 1999), which is denser and insoluble in comparison to the calcium silicate gel and corrosion debris that forms on the OPC binder. At a pH of 1,00 to 3,00 aluminium hydroxide is soluble and offers no protection to the CAC binder, which results in the significantly lower acid resistances of the binder in the hydrochloric acid solution at a pH of 1,00.

4.8 Conclusions

Alag™ aggregate calcium aluminate cement concrete resists an acid solution and gives better performance than a similar concrete containing dolomite aggregate. Alag™ aggregate particles dissolves at a slower rate than dolomite aggregate particles to neutralise the acid solution and good bonding between the CAC and alag™ slows the attack rate on the cement binder. Acid resistance and the neutralisation capacity of the dolomite aggregate concrete depend on the quality of the aggregate. Aggregate of a good quality dissolves slowly and at a similar rate to the cement binder. A poor quality aggregate dissolves at a faster rate diminishing the structural integrity of the concrete. Concrete containing siliceous aggregate is not suitable for use in an acidic environment. Acid attacks the cement binder exposing the siliceous aggregate particles leading to particle fall-out. Structural integrity of the concrete diminishes rapidly and dissolution of the cement alone fails to neutralise the acid solution as effectively as the dolomite aggregate in concrete.

Acid resistance assessed in the hydrochloric acid solution test gives a good indication of the ability of sewer pipe concrete to resist and neutralise an acidic environment such as a biologically-induced sulphuric acid environment encountered in sewers. Studying the performance of the concrete in the hydrochloric acid solution clearly indicates how the constituents of the concrete influence the resistance and neutralisation capacity of the concrete. Concrete mixtures designed using the information is easily and quickly tested to allow development of a concrete aiming to give good acid resistance and/or acid neutralisation. Although the test measures the ability of the concrete to neutralise a biologically-induced sulphuric acid environment, which influences growth and development of the acid-loving thiobacillus bacterial colony, it fails to asses the influence different constituents have on the growth and activity of the thiobacillus bacteria. Constituents that are toxic towards the thiobacillus bacteria slow the bacterial activity and generation of sulphuric acid leading to a slower rate of attack and more importantly allows development of a concrete resistant to the biologically-induced sulphuric acid environment.

Assessing toxicity of concrete towards the thiobacillus bacterial colony requires a more complex test method simulating growth of the bacterial colony on a concrete substrate and ascertaining the effect of different constituents on the growth and activity of the bacterial colony. Such a test is essential for development of a sewer pipe concrete to resist and/or neutralise a biologically-induced sulphuric acid environment but does not fall within the scope of this research. An understanding of how the concretes tested above influence the growth and activity of the thiobacillus bacterial colony is important to illustrate the relevance of the hydrochloric acid test method and is the subject of the following chapter, which documents a study on the performance of sewer pipe concrete in a sulphuric acid environment encountered in an experimental sewer section at Virginia, South Africa (Kelly and Krüger, 1996).

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CHAPTER 5

CONCRETE RESISTANCE TO BIO-SULPHURIC ACID ENVIRONMENTS

5.1 Introduction

Acid resistance of sewer pipe concrete in a biologically generated sulphuric acid environment depends not only on the ability of the concrete to resist and neutralise the acidic conditions but also very importantly on the influence of the concrete on the growth and activity of the thiobacillus bacteria responsible for the sulphuric acid generation. The hydrochloric acid resistance test determines the ability of concrete to resist and neutralise an acidic environment but fails to simulate the impact of the concrete composition and neutralisation capacity on the growth and activity of the thiobacillus bacterial colony. Concrete containing calcium aluminate materials and/or biocides, which are toxic towards the thiobacillus bacteria, are liable to perform better in the bio-sulphuric acid environment than a similar non-biological mineral acid environment such as the hydrochloric acid solution.

An investigation into the resistance of concrete to a biologically generated sulphuric acid environment was done on specimens inserted into a manhole at the entrance to the experimental section located in the sewer line at Virginia to develop an understanding into the attack mechanism and the manner in which different concrete mixtures resist the sulphuric acid generated. Such a site is ideal as:-

- the hydrochloric acid solution test was formulated to give similar attack on concrete to that in the experimental section
- the manhole was easily accessible
- the severe conditions in the sewer line were of a concern to concrete pipe manufactures
- extensive data was available from research done in the sewer (Kelly and Krüger, 1996)
- additional research into the corrosion problem is ongoing and planned for the future

The Virginia sewer line was commissioned in March 1989. The experimental section was constructed approximately 600 m downstream from a rising main (Figure 5.1) to investigate the performance of various materials of interest to concrete pipe manufacturers (Krüger, 1989):-

- asbestos-cement pipe sections
- OPC siliceous aggregate concrete pipe sections
- OPC dolomite aggregate concrete pipe sections
- CAC siliceous aggregate concrete pipe sections
- epoxy-tar-coated asbestos-cement pipe sections
- epoxy-coated asbestos-cement pipe sections
- polyurethane-coated asbestos-cement pipe sections
- high-density polyethylene (HDPE) lined OPC siliceous aggregate concrete pipe sections
- HDPE lined OPC dolomite aggregate concrete pipe sections
- HDPE pipe sections

The Council for Scientific and Industrial Research of South Africa (CSIR) monitored the conditions in the sewer line and the corrosion rates on the different pipe sections in the experimental line over a period of 5 years (1989 – 1994). Conditions in the sewer line were aggressive (Kelly and Krüger, 1996). Average sulphide concentration in the sewage was 0,7 mg/l and average concentration of hydrogen sulphide gas in the sewer atmosphere was 50 ppm. Concrete and fibre-cement pipe sections in the experimental sewer were severely attacked after 5 years. Coated (epoxy, epoxy-tar and polyurethane) fibre-cement pipe sections were blistered and peeling off at the pipe joints, the underlying concrete showing severe signs of attack. Corrosion was not evident on the HDPE pipe sections and the concrete pipe sections lined with HDPE.

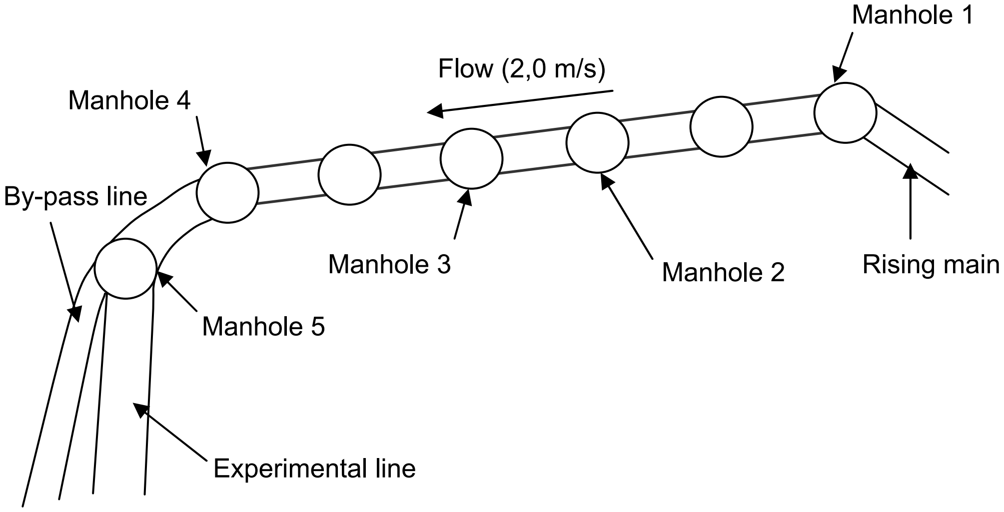

Figure 5.1 Diagram of sewer line at Virginia, Free State, South Africa showing rising main and gravity sewer flowing into the experimental test section located 600m downstream of the rising main

A second and ongoing investigation was started by the University of Cape Town (UCT) and the various pipe-manufacturers in October 2000 (after 12 years of operation). The investigation involved assessing the aggressiveness of the sulphuric acid environment (monitoring the hydrogen sulphide gas profiles in the manhole and pH on the sewer walls) and measuring the biological sulphuric acid resistance of concrete specimens inserted into the manhole, namely:-

- OPC specimens to compare attack mechanisms of concrete containing siliceous aggregates with those containing dolomite aggregates and to assess the attack on a good quality dolomite (Olifantsfontein) and poor quality dolomite (Blackheath) aggregates
- modified OPC specimens to assess the influence of mineral additives (fly ash, silica fume and slag) on acid resistance of sewer pipe concrete
- CAC/dolomite and CAC/alag™ specimens to assess the influence of calcium aluminate materials on the growth and activity of the thiobacillus bacterial colony
- specially modified OPC/dolomite aggregate specimens to assess the influence of antibacterial biocides containing metals toxic towards bacteria (nickel, silver, copper and/or zinc) on the growth of the thiobacillus bacterial colony

5.2 Experimental methodology

5.2.1 Assessing aggressiveness of the sewer environment

The amount of hydrogen sulphide was measured in the sewer atmosphere in the manhole at the entrance to the experimental section of the sewer line located approximately 600 m downstream from a rising main. Sewer gas was extracted through a thin silicone tube inserted through a hole in the closed manhole cover from directly above the sewage by an instrument (Appendix E) capable of measuring the hydrogen sulphide content directly. Amounts of hydrogen sulphide were recorded during the warmest months (December to February) of the years 2000, 2001 and 2002 and the coldest months (May to July) of the years 2001 and 2002 at various times of the day for a 3 to 5 day period. A measurement consisted of logging data for an entire flow cycle that is, for the period of flow (pumping of sewage from main), which corresponds to a high release of hydrogen sulphide and no flow (retention of sewage in main), which corresponds to a low release of hydrogen sulphide. Hydrogen sulphide profiles were generated from 06:00 to 20:00 hours.

The pH on the concrete wall in the manhole directly above the sewage level was measured during the summer and winter months. Sewage flow was stopped and the pH was measured by inserting a pH-probe into the slimy moisture layer along the concrete wall directly above the sewage level.

5.2.2 Assessing attack on concrete specimens

Acid resistance of concrete specimens prepared from twelve different mixtures were determined (Table 5.1). The nickel (Ni), silver-zinc (Ag-Zn) and silver-zinc-copper (Ag-Zn-Cu) based biocides in powder form were added as part-replacement of the OPC prior to adding water to the mixture, and the silver (Ag) based biocide in the form of a slurry was added to the mixture water. A steam-cured specimen (80 mm diameter × 150 mm) from each mixture (air-cured for 28 days at 60 % relative humidity) was sliced lengthwise to yield two half cylinders (40 mm radius × 150 mm length) one of which was inserted into a PVC holder mounted onto the manhole wall directly above the average daily sewage level region in an area where similar and turbulent flow conditions occurred (specimen from mixture 1 closest to the area of turbulent flow and that from mixture 12 furthest downstream, approximately 1,5 m apart) (Figure 5.2). The other half of the cylinder was kept to do further testing if necessary.

Table 5.1 Mixture proportions of raw materials of first series of specimens inserted into the manhole based on ratio to total binder content

Mixture	Stone	Crusher sand	Filler sand	Cement	Additive	w/c
1. OPC/siliceous (quartzite)	3,25	2,89	-	1,00	-	0,30
2. CAC/Olifantsfontein	1,67	1,67	-	1,00	-	0,26
3. CAC/alag™	1,67	1,67	-	1,00	-	0,26
4. OPC/Olifantsfontein	1,67	1,67	-	1,00	-	0,26
5. OPC/siliceous (granite)	1,64	0,82	0,82	1,00	-	0,32
6. OPC/SF Blackheath	3,45	1,32	0,53	0,90	0,10	0,32
7. OPC/Ni Blackheath	3,45	1,32	0,53	0,99	0,01	0,36
8.OPC/Blackheath	3,45	1.32	0,53	1,00	-	0,36
9. OPC/Olifantsfontein	2,28	2,28	-	1,00	-	0,30
10. OPC/Ag-Zn Olifantsfontein	2,28	2,28	-	0,99	0,01	0,30
11. OPC/Ag-Zn-Cu Olifantsfontein	2,28	2,28	-	0,99	0,01	0,30
12. OPC/Ag Olifantsfontein	2,28	2,28	-	0,95	0,05	0,30

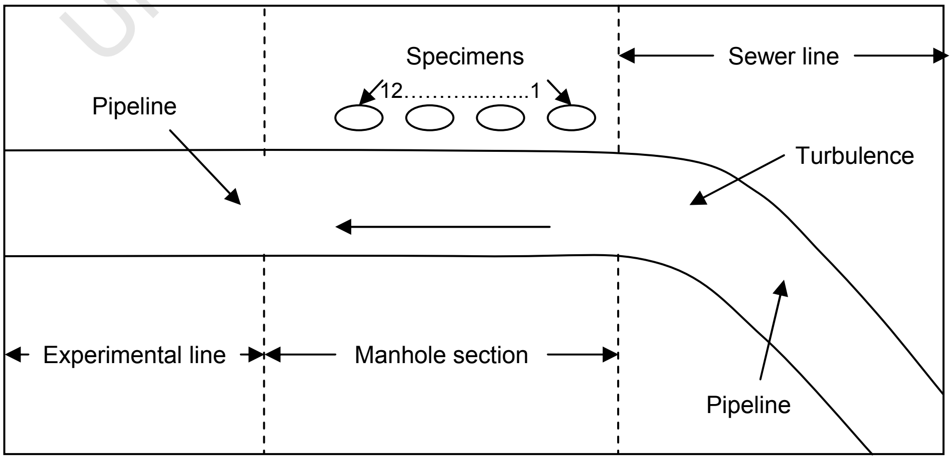

Figure 5.2 Plan showing pipeline and manhole positioned at entrance of the experimental section and location of specimens (1 furthest upstream and 12 furthest downstream)

Conditions of aggressiveness in the test area were similar as activity of a thiobacillus colony depends on a constant supply of hydrogen sulphide and the moist conditions, which were similar:-

- specimens were located directly in the path of the hydrogen sulphide released
- specimens were continuously moistened with splashing sewage
- run-off from concrete walls above specimens was similar

Specimens were installed during the summer month of December 2000. Specimen masses were recorded prior to insertion into the manhole. Specimens were visually inspected after 5 months (May 2001) and 17 months (May 2002) and surface pH of the specimens was measured. Specimens were removed after 17 months and cleaned (under running water using a stiff nylon bristle brush) to remove the loose corrosion debris. Specimen masses were recorded and mass losses were calculated.

5.3 Results and discussion

5.3.1 Aggressiveness of the sewer environment

A substantial amount of hydrogen sulphide was liberated from the sewage flowing through the manhole throughout the year (Figure 5.3). During the summer months, the hydrogen sulphide levels in the manhole were high throughout the day. Hydrogen sulphide levels steadily increased from 06:00 (26 ppm) to 14:00 (113 ppm) and remained constant until 19:00 after which the levels sharply decreased. During the winter months, the daytime hydrogen sulphide levels were substantially lower than those in the summer months. Average daily hydrogen sulphide concentration during the summer months was 55 ppm whereas that during the winter months was 27 ppm. Daytime hydrogen sulphide concentrations during the winter months were negligible in the mornings and evenings. Concentrations steadily increased from 06:00 (2 ppm) to 13:00 (60 ppm) remaining constant until 17:00 after which a sharp decrease occurred.

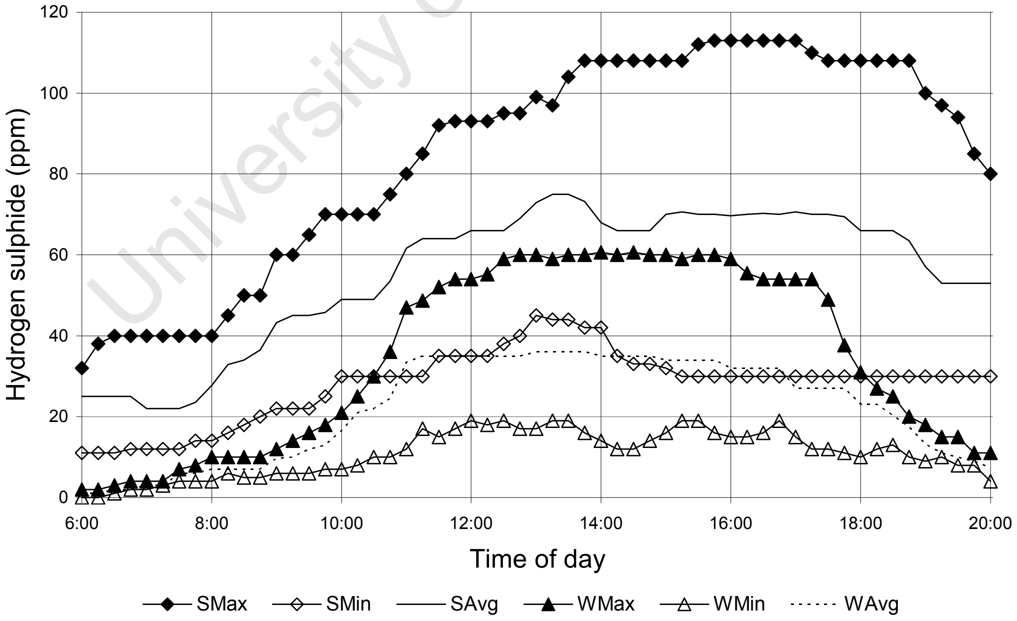

Figure 5.3 Typical maximum, minimum and average daytime hydrogen sulphide profiles for summer (S) and winter (W) months in the manhole atmosphere at the entrance to the experimental section in the sewer line located at Virginia

A significant concentration of hydrogen sulphide was maintained in the manhole throughout the flow cycle that is, during pumping and retention times (typically 7 minutes and 5 minutes respectively). Concentrations rapidly increased to maximum within 2 minutes after the sewage reached the manhole from the pumping main, which was sustained until the end of the pumping cycle. Concentrations decreased gradually reaching a minimum 3 to 4 minutes after the pumping cycle.

Amounts of hydrogen sulphide emitted into the sewer atmosphere are sufficient to sustain a corrosive sulphuric acid environment throughout the year. Concentrations were substantially higher than the concentration (10 ppm) to sustain a sulphuric acid environment capable of severely attacking concrete sewers (Thistlethwayte, 1972). A direct relationship exists between hydrogen sulphide concentration and the growth and activity of the thiobacillus bacteria (Parker, 1965). A constant supply of hydrogen sulphide establishes the conditions necessary for the growth of the thiobacillus colony within a few months (Parker, 1947) leading to the acidic conditions favouring the growth of the thiobacillus thiooxidans causing severe corrosion on sewer concrete within a year (Parker, 1945).

Such high concentrations of hydrogen sulphide in the manhole atmosphere were due to large amounts of sulphide (3,50 mg/ℓ) generated in the sewage throughout the year (Lu Y, 2001). Sulphide generation in the sewer system was high due to the flat topography (slow sewage flow, rising main and pumping station storage sumps) and high temperatures throughout the year, which sustains a high bacterial activity throughout the entire wastewater system. Summer temperatures seldom drop below 30 °C during the afternoons and to below 20 °C during the evenings. Winter temperatures of up to 30 °C toward mid-afternoon are common and low temperatures (0 to 5 °C) only occur prior to and directly after sunrise for a few months of the year. Winter mid-afternoon temperatures seldom drop below 20 °C.

Sulphide was readily emitted into the manhole atmosphere due to extensive turbulence in the flow, which results from the direction change of the line entering into the experimental section. Substantially higher concentrations of hydrogen sulphide in the manhole atmosphere during summer months relates directly to the higher sulphide content of the sewage and influence of temperature on the absorption of oxygen into the sewage. Oxygen absorption decreases with an increase in temperature oxidising less of the sulphide generated and allowing more to escape into the manhole atmosphere. Similarly, temperature accounts for the increase in the hydrogen sulphide content from morning to mid-afternoon. At times of monitoring, summer daily temperatures increased from 20 °C at sunrise (06:00) to 36 °C by midday remaining constant until sunset (20:00). Winter temperatures increased from 10 °C at sunrise (08:00) to 22 °C by midday remaining constant until sunset (18:00).

Surface pH on the manhole walls throughout the year directly relates to the continuous release of hydrogen sulphide and sustained growth of the thiobacillus colony. During the summer months the pH in the slimy moisture layer directly above the average daily sewage level was less than 1,00 and during the winter months between 1,00 and 2,00. Such low pHs throughout the year provides an ideal environment for growth of the thiooxidans and explains the severe attack on the concrete walls above the sewage level in the manhole.

5.3.2 Sulphuric acid attack on specimens

Signs of attack were evident on the specimens in the manhole five months after insertion. Specimen surfaces were acidic, that is pH of less than 7,00 (Table 5.2) and covered with a moist slimy layer of corrosion debris (Figure 5.4). OPC/siliceous specimens in positions 1 and 5 were similarly attacked. Surfaces appeared frothy in the areas of the binder showing severe signs of attack. A measurement of pH within the frothy areas of the OPC/siliceous specimens was difficult as the protruding particles prevented insertion of the probe into the severely attacked binder areas.

Attacked surfaces of the OPC/siliceous specimens were different to those of the CAC/Olifantsfontein, OPC/Olifantsfontein and CAC/alag™ lining specimens in positions 2, 3 and 4 respectively. Attack was negligible on the lining specimens. A slight dissolution of the cement skin was evident on the specimen surfaces. Surface pH of the lining specimens was between 6,00 and 6,50 significantly higher than that of the surrounding manhole walls (pH < 2,00) implying that substantially less sulphuric acid was generated on the specimens.

Table 5.2 Comparison of attack on the 12 specimens after 5 months and 17 months of exposure in the manhole

Position/Mixture	After 5 months		After 17 months		
	Attack[*]	pH	Attack[**]	pH	% Mass Loss
1) OPC/siliceous (quartzite)	aggressive	-	aggressive	6,70	4,14
2) CAC/Olifantsfontein	negligible	6,00	negligible	6,70	0,35
3) CAC/alag™	negligible	6,50	negligible	7,14	0,00
4) OPC/Olifantsfontein	negligible	6,00	moderate	6,70	2,46
5) OPC/siliceous (granite)	aggressive	-	aggressive	6,70	6,09
6) OPC/SF Blackheath	aggressive	1,20	aggressive	2,40	4,72
7) OPC/Ni Blackheath	aggressive	2,00	aggressive	2,40	4,69
8) OPC/Blackheath	aggressive	1,20	aggressive	2,40	4,71
9) OPC/Olifantsfontein	aggressive	0,5	aggressive	1,44	6,30
10) OPC/Ag/Zn Olifantsfontein	aggressive	0,4	aggressive	1,51	5,45
11) OPC/Ag/Zn/Cu Olifantsfontein	aggressive	0,4	aggressive	1,45	5,92
12) OPC/Ag Olifantsfontein	aggressive	0,4	aggressive	1,21	5,11

[*] aggressive – frothy surface due to dissolution of cement skin, negligible – slight dissolution of cement skin

[**] aggressive – aggregate standing proud of attacked surface, moderate – exposure of aggregate, negligible – dissolution of cement skin

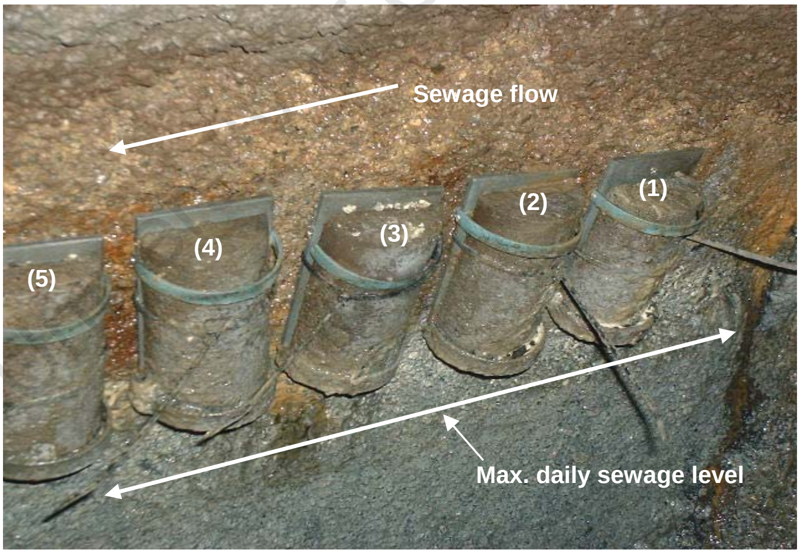

Figure 5.4 Specimens located in positions 1 to 5 on manhole wall directly above the maximum daily sewage level mark (position 1 upstream closest to region of turbulence to position 5 further downstream)

OPC/Blackheath specimens in positions 6 to 8 further downstream were severely attacked. A number of frothy blisters were apparent on the surfaces of the specimens. A milky liquid with a pH significantly lower (pH of 1,20 to 2,00) than that on the remaining surface area (pH of 6,00 to 6,50) was released on piercing with the pH probe (Figure 5.5). Attack in the frothy areas was severe and of similar appearance to the attack on the binder portions of the OPC/siliceous specimens positioned further upstream. A portion of the surfaces of the OPC/Olifantsfontein specimens in positions 9 to 12 were each covered with a large blister (pH of 0,40 to 0,50). Signs of attack were severe in the area of blistering and corrosion debris appeared white resembling calcium sulphate. Areas outside the blister were not as aggressively attacked (pH of 5,00 to 6,00).

Figure 5.5 Attacked surface of concrete specimen showing release of milky white liquid on piercing of the concentrated sulphuric acid blisters

After 17 months, surfaces of the specimens except that of the CAC lining specimens (positions 2 and 3) were entirely covered with a frothy layer similar in appearance to the blisters detected after 5 months (Figure 5.6).

Figure 5.6 Attacked surfaces of concrete specimens 17 months after insertion

Surface pH of the specimens in the manhole and the mass losses after 17 months differed significantly (Table 5.2 and Figure 5.7). CAC/alag™ specimen in position 3 experienced no mass loss, while the mass loss of the CAC/Olifantsfontein specimen in position 2 (0,35 %) was very slight. Mass loss of the OPC/Olifantsfontein specimen in position 4 (2,46 %) was significantly higher but substantially lower than the mass loss of the OPC/siliceous specimen in position 1 (4,14 %) and the mass losses of the OPC/Blackheath specimens in positions 6, 7 and 8 (4,72 %, 4,69 % and 4,71 % respectively). Mass losses of the biocide modified OPC/Olifantsfontein specimens in positions 10, 11 and 12 (5,45 %, 5,92 % and 5,11 % respectively), the OPC/siliceous specimen in position 5 (6,09 %) and the standard

OPC/Olifantsfontein specimen in position 9 (6,30 %) were higher. Surface pH of the OPC/Olifantsfontein dolomite specimens (1,21 to 1,51) in positions 9 to 12 were significantly lower than that of the OPC/Blackheath dolomite specimens (2,40) in positions 6, 7and 8. Surface pH of the OPC/siliceous specimens in positions 1 and 5 (6,70), the CAC and OPC/Olifantsfontein lining specimens in positions 2 and 4 respectively (6,70) and CAC/alag™ specimen in position 3 (7,14) were substantially higher.

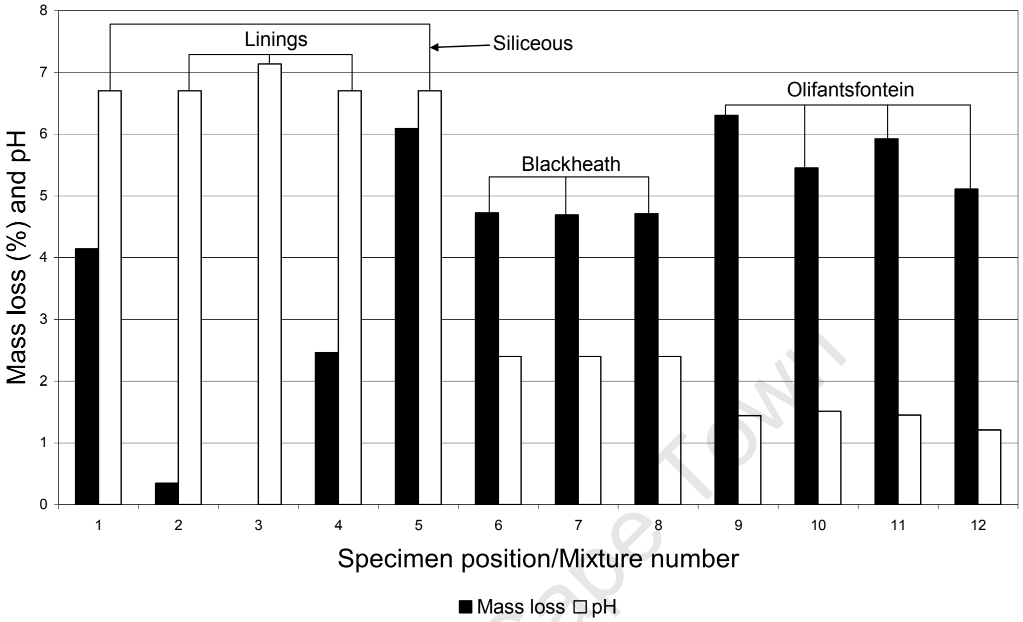

Figure 5.7 Mass loss and surface pH of the concrete specimens 17 months after insertion

Attack on the siliceous aggregate specimens in position 1 and 5 was noticeably higher than that on the dolomite and alag™ aggregate specimens in the other positions. Siliceous stone particles were fully exposed in areas and particle fall-out was evident (Figure 5.8). Attack occurred between the siliceous aggregate particles, which led to the preferential dissolution of the cement binders. As specimen mass losses were mainly due to the dissolution of the cement binder the similar/higher mass losses imply siliceous aggregate specimens were attacked to a significantly deeper extent than dolomite aggregate specimens, in which the aggregates were also attacked. Mass loss on the siliceous aggregate specimen in position 5 was significantly higher than that on the siliceous aggregate specimen in position 1 due to the preferential dissolution of the cement binder, that is, the higher cement content (23 %) of the specimen in position 5 led to the higher mass loss compared with the specimen in position 1 with the lower binder content (14 %).

Attack on the lining specimens in positions 2 and 3 was the lowest mainly due to the influence of the calcium aluminate materials and to a lesser extent the dolomite aggregate on the activity of the thiobacillus bacterial colony. Calcium aluminate materials stifle the growth of the bacteria lowering the generation of sulphuric acid and prolonging the growth of the acid-loving thiobacillus thiooxidans responsible for the severe corrosion evident on the other specimens. On visual inspection, the negligible signs of attack on the CAC/alag™ and CAC/dolomite lining specimens are clear (Figure 5.9). Only a small area of exposed dolomite aggregate was visible on the CAC/dolomite specimen due to dissolution of the surrounding cement layer.

Attack on the OPC/dolomite lining and standard specimens was substantially higher than that on the CAC/dolomite lining specimen (Figure 5.10). The cement skin was entirely removed and areas were noticeable in which severe attack was starting. Such areas coincided with blisters detected on the specimen after exposure in the manhole for five months.

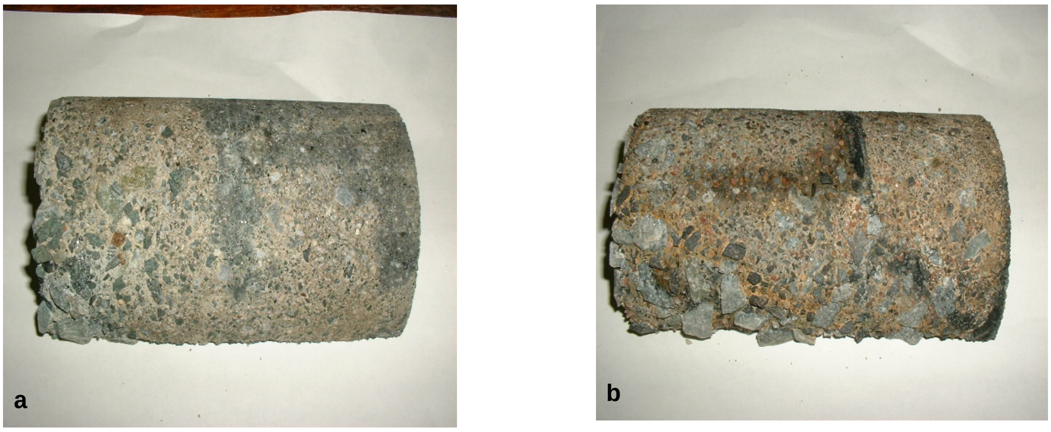

Figure 5.8 OPC/siliceous specimens a) in position 1 and b) in position 5 after 17 months exposure to the corrosive conditions in the manhole

Figure 5.9 a) CAC/alag™ and b) CAC/dolomite lining specimens showing negligible (a) to slight (b) signs of attack after 17 months exposure to the corrosive conditions in manhole

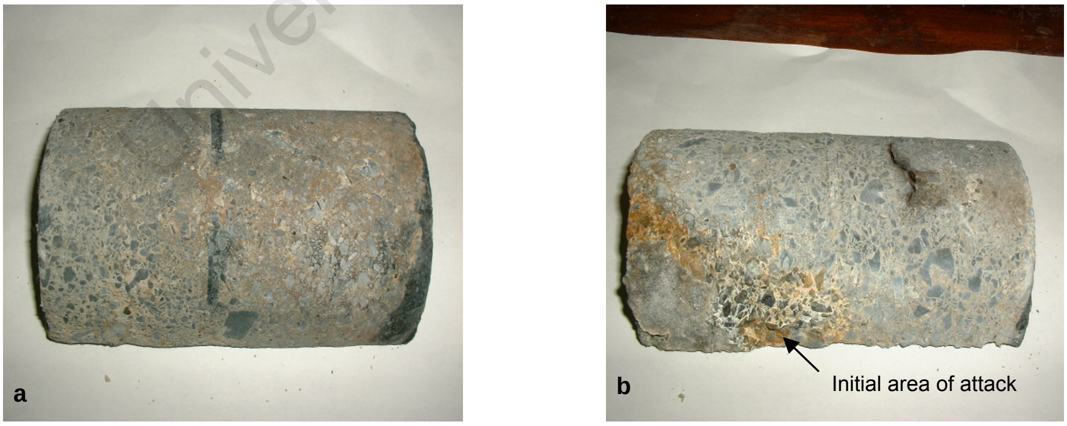

Figure 5.10 a) OPC/Olifantsfontein lining and b) OPC/Olifantsfontein standard specimens after 17 months exposure to corrosive conditions in manhole

Aggressive attack on the OPC/Olifantsfontein dolomite lining and standard specimens, which were of similar neutralisation capacities to the calcium aluminate lining specimens, indicates that the ability of the dolomite to neutralise the sulphuric acid environment was less effective than the toxic effect of the calcium aluminate materials on the thiobacillus bacterial colony. Neutralisation only lowers the activity of the thiobacillus bacterial colony slowing sulphuric acid generation but fails to stifle the growth of the thiobacillus bacteria. Sulphuric acid generated from the absorption and auto-oxidation of the hydrogen sulphide into the moisture on the surfaces of the specimens sufficiently attacks the concrete creating the conditions for the growth of the thiobacillus. This leads to further attack generating sites for the growth of the acid-loving thiobacillus thiooxidans, which result in the corrosive blisters and severely attacked areas on the dolomite aggregate specimens. However, on the surfaces of the calcium aluminate specimens, growth of the thiobacillus is stifled by the toxic nature of the binder.

Attack on OPC/Blackheath dolomite specimens was less aggressive than that on standard and biocide modified OPC/Olifantsfontein dolomite specimens due to the higher dissolution of the Western Cape dolomite stone in an acidic environment. Attacked surfaces of the OPC/Blackheath dolomite specimens were smoother (Figure 5.11) than those of the standard and modified OPC/Olifantsfontein dolomite specimens (Figure 5.10 and 5.12 respectively).

Figure 5.11 OPC/Blackheath specimens after 17 months exposure to the corrosive conditions in the manhole a) silica fume b) nickel-based biocide c) standard

Western Cape dolomite stone particles dissolved at a similar rate to the cement binder portion in the areas of blistering noticed after five months of exposure. Surfaces of the modified OPC/Olifantsfontein dolomite biocide specimens were attacked significantly more at the sites of blistering noticed after five months than the standard OPC/Olifantsfontein dolomite specimen (Figure 5.12). Areas show the dolomite aggregate particles standing proud of the surfaces due to preferential dissolution of the binder. Specimens containing the Western Cape dolomite were almost twice as soluble in the hydrochloric acid resistance test as specimens containing the Gauteng dolomite. Stone from the Western Cape dissolves at a faster rate neutralising the sulphuric acid generated and slowing thiobacillus activity more than the stone from Gauteng. Slower dissolution of the dolomite stone from Gauteng than that of the cement binder proves detrimental and was detected in investigations done previously on pipe sections in the experimental line, which contained a dolomite stone aggregate of a similar quality (Kelly and Krüger, 1996). Slow dissolution eventually led to exposure and fall-out of the dolomite stone particles.

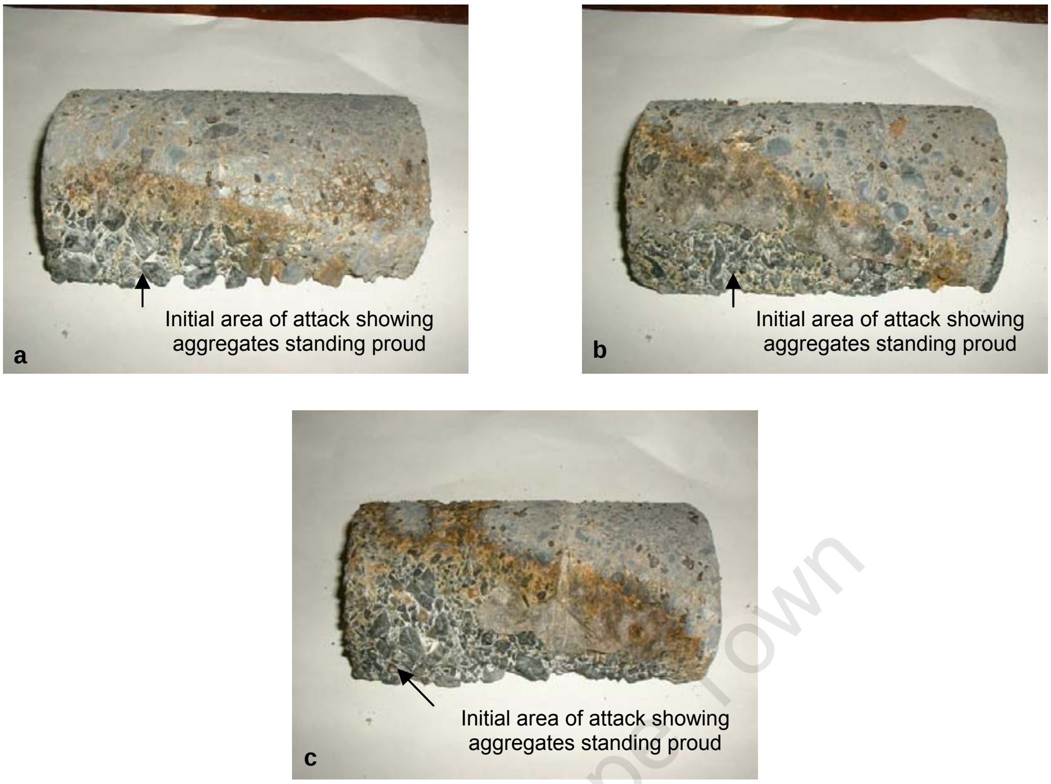

Figure 5.12 OPC/Olifantsfontein biocide specimens after 17 months exposure to corrosive conditions in manhole a) silver/zinc b) silver/zinc/copper c) silver-based

Anti-bacterial biocides failed to materially improve the resistance of the Olifantsfontein and Blackheath concrete mixtures to the biologically generated sulphuric acid environment. The amounts of biocide batched as recommended were not sufficient to stifle the growth of the thiobacillus bacteria. Continuous absorption of the large amounts of hydrogen sulphide available in the atmosphere into the moisture layer on the surface of the specimens sufficiently lowers the pH and attacks the concrete to create sites favouring growth of the thiobacillus bacteria. Such sites are evident from the severe areas of attack seen on the biocide modified specimens namely on the surfaces of the OPC/Olifantsfontein dolomite specimens (Figure 5.12). Conversely, in the CAC specimens, calcium aluminate contents were substantially higher than the biocide contents and prevented the development of the sites favouring growth of the thiobacillus. Signs of deterioration on the calcium aluminate specimens are of a concern as the corrosion debris accumulating eventually isolates the concrete substrate from the environment to create sites for unrestricted growth of the thiobacillus bacteria. An adequate amount of hydrogen sulphide was however absorbed into the alkaline moisture layer surrounding the calcium aluminate specimens to lower the pH to that required for growth of the lesser tolerant thiobacillus species (pH less than 8,00).

Silica fume reflects no improvement in the resistance of the OPC/Blackheath dolomite specimen to the sulphuric acid environment. Acid resistance in a sewer depends more on the capacity of a material to stifle the activity of the thiobacillus bacterial colony that is, not resisting but neutralising the sulphuric acid environment.

Surface pH and the amount of mass loss of the specimens are closely related. A low surface pH, which represents a more aggressive sulphuric acid environment, relates to a higher specimen mass loss except for the siliceous aggregate specimens where a high pH related to a high mass loss. Such a discrepancy relates to the method of pH measurement, which was misleading and not representative of the aggressive attack occurring on the binder portion in the specimens. The pH probe was too large to penetrate into the layer of corrosion debris between the siliceous aggregate particles to assess the aggressiveness of the environment on the binder portion where the acid attack was occurring.

Aggressiveness of attack on the specimens was not related to the position of the specimens in the manhole, but rather to specimen composition. Specimens were located in an area where the corrosive conditions were similar that is, conditions such as pH, moistness and hydrogen sulphide content in the area along manhole wall in which specimens were located were similar. A higher level of aggressiveness may be more likely to occur upstream in the region closest to the turbulent flow where the release of hydrogen sulphide and splashing is highest and not downstream, but this was not observed, for example the attack on the downstream specimens was generally higher.

5.4 General discussion

The sewer manhole test site at Virginia proved ideal for monitoring the biological sulphuric acid resistance of concrete specimens. Specimens were kept moist due to splashing and condensation of sewage from the turbulent flow conditions below. A constant supply of sewage ensures bacteria were continuously seeded onto the concrete specimens. A continuous high release of hydrogen sulphide gas throughout the year (maximum of 70 ppm in winter months to a maximum of 150 ppm in summer months) ensures that the surfaces of the concrete deteriorate creating conditions for growth of the thiobacillus colony and more importantly sites for growth of the thiobacillus thiooxidans responsible for the severe corrosion in concrete sewers within 5 months. Concentrations of hydrogen sulphide are high enough to ensure thiobacillus rapidly reproduce sustaining the attack on the concrete specimens.

Studying the attack on the concrete specimens in the acid environment encountered in the experimental sewer section illustrates the mechanism of the biological sulphuric acid attack. Attack is gradual at first and depends on the amount of hydrogen sulphide in the sewer atmosphere (Thistlethwayte, 1972), which on absorption into the moisture on the sewer walls reacts to form sulphuric acid gradually deteriorating the concrete surface (Parker, 1965). A film of debris with a pH substantially lower (pH of 8,00) than the concrete substrate (pH of 12,00) develops, which generates localised sites for the growth of thiobacillus bacteria (Parker, 1947).

At this stage the composition of the concrete is a critical factor and governs the rate of corrosion. Concrete containing materials toxic towards the thiobacillus bacteria (calcium aluminate materials) and materials of a high neutralisation capacity (dolomite aggregates) slows the development of the thiobacillus bacterial colony preventing the development of the acid-loving thiobacillus thiooxidans responsible for sewer corrosion (Parker, 1945). After growth of the thiobacillus bacteria pH of the localised sites decreases at a faster rate and eventually leads to the growth of the acid-loving thiobacillus thiooxidans, which decreases pH to less than 2,00 and results in the corrosion of the concrete substrate. A substantial amount of sulphuric acid is generated within these localised sites inducing growth of the thiobacillus thiooxidans and corrosion over the entire surface of the concrete structure above the average daily sewage level. Such sites can explain the reason why the cement binder portion of dolomite aggregate concrete is attacked at a faster rate (Kelly and Krüger, 1996). The cement binder portion readily absorbs the moisture in the sewer atmosphere allowing the absorption of hydrogen sulphide, which forms the sulphuric acid responsible for the deterioration required to develop the sites for the growth of the thiobacillus bacterial colony.

An important factor not investigated was the influence of the flowing sewage on the corrosion rate. Owing to the liquid nature of the corrosion product observed on the specimens above the average daily sewage level it is realistic to assume that flowing sewage is capable of easily removing the corrosion debris exposing the concrete to the corrosive acidic environment generated above the sewage level.

5.5 Conclusion

Acid resistance of sewer pipe concrete is vastly improved with the use of calcium aluminate materials. Concrete consisting entirely of CAC and alag™ aggregate is best suited for use in the severely corrosive conditions at Virginia. Acid resistance of the CAC/dolomite aggregate concrete is good and suited for use in an aggressive sewer environment. Concrete containing dolomite aggregate such as that conventionally used in the manufacture of sewer pipes is not suited for use in very corrosive environments such as that at Virginia. Siliceous aggregate concrete deteriorates at a substantially faster rate in sulphuric acid environments encountered in sewers.

Attack in sewer environments is complex and mainly depends on concrete composition. Composition influences the growth of the thiobacillus colony ultimately responsible for the rate of attack and acid resistance of the concrete. A sewer pipe concrete of good acid resistance (as measured using the hydrochloric acid solution method) as well as toxicity towards the thiobacillus bacteria, is best suited for use in severely corrosive sewer environments. Concrete consisting entirely of calcium aluminate (CAC/alag™) resist an acidic environment such as that generated from the absorption of hydrogen sulphide and more importantly provides a surface entirely toxic towards the thiobacillus bacteria. CAC/dolomite concrete is attacked at a significantly faster rate in an acidic environment as the lower toxicity allows sites suiting the growth of the thiobacillus bacterial colony and thiobacillus thiooxidans to develop, which results in the corrosion of the concrete substrate. Concrete containing dolomite aggregate neutralises the sulphuric acid generated but subsequently allows sites to be created that permit the growth of the thiobacillus colony and thiobacillus thiooxidans leading to corrosion within 5 months. Small amounts of biocides added to the dolomite aggregate concrete prove ineffective presumably because the sulphuric acid generated is sufficient to attack the surface and mask the toxic effects of the biocide.

Solubility of the concrete significantly assists in improving the resistance of the concrete in a biologically induced sulphuric acid environment. Soluble dolomite aggregates neutralise and slow the activity of the thiobacillus bacteria eliminating the preferential dissolution of the cement binder portion. A highly soluble dolomite such as that from the Western Cape proves more effective in the severe conditions and spreads the attack over the surface eliminating the faster dissolution of the cement binder occurring in concrete containing the less soluble dolomite from Gauteng. Attack on siliceous aggregate concrete is far more severe. Attack is concentrated on the cement binder leading to stone particle fall-out.

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CHAPTER 6

CONCLUSIONS, LIMITATIONS AND FUTURE RESEARCH

6.1 Introduction

The primary objective of the research was to develop a test method with which to study the acid resistance of concrete, namely that containing dolomite aggregates, which are used in the manufacture of sewer pipes subjected to biologically-induced sulphuric acid environments. Such a test is necessary to assist with the development of a concrete mixture that can resist the severely corrosive environments (pH of less than 2,00) encountered in sewers throughout South Africa. The secondary objective was to develop an understanding of the development, growth and activity of the thiobacillus bacterial colony in a sewer and the manner in which the concrete substrate influences these factors.

The scope of this chapter is to document and discuss:-

- findings of the research
- limitations and shortcomings of the research
- future research objectives

Acid attack mechanisms pertaining to the research were documented to highlight the similarities and differences between the attack on sewer pipe concrete in a sulphuric acid solution, a hydrochloric acid solution and a biologically-induced sulphuric acid solution encountered in sewers. Assessing the acid resistance of concrete using the hydrochloric acid test was discussed, and advantages and disadvantages of the method were documented. Acid resistances of sewer pipe concretes measured using the hydrochloric acid test method were documented and compared to the acid resistances of similar concretes in a biologically-induced sulphuric acid environment. A flow-chart was developed to highlight the importance of the concrete constituents on the acid resistance of the sewer pipe concretes.

The limitations of the research, which stem from the complex nature of the sulphuric acid attack in sewers, were documented and discussed. Future research required to further understand the complex nature of the biologically-induced sulphuric acid attack and develop a test method to simulate the acid attack in sewers was documented and discussed.

6.2 Acid attack mechanisms

From the research it was concluded that attack in a hydrochloric acid solution was similar to the sulphuric acid attack at the average daily sewage level region of a concrete sewer pipe, where attack is often worse owing to the continuous removal of the corrosion products and exposure of the concrete substrate. Attack on concrete specimens in a hydrochloric acid solution was also similar to that on similar concrete specimens inserted above the average daily sewage level region in an experimental sewer section at Virginia. Although the extent and nature of attack on the concrete specimens appeared similar the mechanisms of attack in the hydrochloric acid solution, sulphuric acid solution and biologically-induced sulphuric acid environment differed significantly.

Attack in a mineral acid solution, which is not biologically induced, depends on concrete composition, acid strength (i.e. hydrogen ion concentration) and acid type. Acid type determines the reaction products (i.e. salts) that form on dissolution of the concrete, the solubility of which dictate the mechanism of attack. Although the stability and dissolution of acid-soluble compounds in the concrete depends on the hydrogen ion concentration, the spontaneity of the dissolution depends on the reaction products that form.

At similar hydrogen ion concentrations, the dissolution potential and stability of the acid--soluble compounds in a sulphuric acid solution and a hydrochloric acid solution are similar implying a similar rate of dissolution. Calcium sulphate, the main salt that forms on reaction of concrete with sulphuric acid, is sparingly soluble and rapidly saturates the sulphuric acid solution. After saturation, the calcium sulphate precipitates out of the solution directly onto the concrete. Saturation opposes the dissolution of the acid-soluble compounds and the calcium sulphate layer forming on the concrete acts as a diffusion barrier through which the ions involved in the attack mechanism need to move, which slows dissolution. At this point, the attack is diffusion controlled and depends on the mobility of the ions through the layer, which depends on the bulkiness of the ions and characteristics of the layer such as density and thickness. Attack ceases to depend on the hydrogen ion concentration and on solubility (i.e. stability) of the concrete compounds in the sulphuric acid solution. The deposited layer isolates the concrete from the solution and stifles the dissolution of the acid-soluble compounds.

Attack in a hydrochloric acid solution effectively remains dependant on the dissolution of the acid-soluble compounds and depends on the strength of the hydrochloric acid solution, which determines the dissolution potential and stability of the concrete compounds. Calcium chloride, the main salt that forms on reaction of the concrete with hydrochloric acid is readily soluble and remains dissociated in the solution. Acid-soluble compounds freely dissolve into the solution at a rate dependant on the hydrogen ion concentration leaving a layer of corrosion debris on the surface, which offers little resistance to the diffusion of the ions involved in the acid attack mechanism.

Attack in a biologically induced sulphuric acid environment is more complex and depends not only on the strength of the solution and the stability of the acid soluble compounds but also on the growth of the thiobacillus colony, which depends on the temperature and hydrogen sulphide concentration of the sewer atmosphere and the composition of the concrete pipe substrate. Attack on the crown of sewers is similar to that in a sulphuric acid solution in that a layer of calcium sulphate forms. At the average daily sewage level region however, attack is similar to that in a hydrochloric acid solution as the calcium sulphate layer is continually removed due to abrasion and dissolution into the flowing sewage.

Studying attack on the concrete specimens in the experimental sewer section at Virginia suggests that the sulphuric acid attack in such a corrosive environment is similar to that in the hydrochloric acid solution. Blisters that formed on the surfaces of the specimens contained an acidic milky liquid which freely ran out once ruptured, that is the calcium sulphate forming during the reaction weakly adhered to the concrete surface and remained suspended in the sulphuric acid solution. Such attack was similar to that observed in the concentrated sulphuric acid solutions (i.e. pH of less than 0) in which the calcium sulphate layer that forms was porous and easily removed form the surface of the specimens tested (Section 3.2). This implies that the sulphuric acid generated by the thiobacillus bacteria in the Virginia sewer is concentrated which is feasible as the pH of less than 1,00 recorded in the blisters, was measured after the sulphuric acid generated by the thiobacillus bacteria reacted with the concrete substrate.

6.3 Assessing acid resistance of sewer pipe concrete

From the research it was concluded that the acid resistance of sewer pipe concrete is successfully measured using the hydrochloric acid test method. Acid resistance is measured in a hydrochloric acid solution maintained at a pH of 1,00 on cylindrical test specimens prepared in a manner similar to that of the concrete pipe or on cored specimens taken directly from the concrete pipe. Specimen mass loss and hydrogen ion consumption measurements are used to determine the integrity and neutralisation capacity of calcareous or dolomite aggregate concrete in sulphuric acid environments encountered in sewers. Visual inspection of the specimens gives a good indication of the manner in which the concrete is attacked, which is required to assess the integrity of concrete containing poor quality dolomite aggregate or siliceous aggregate in the acidic environments.

A hydrochloric acid solution test is capable of assessing the integrity of a concrete in acidic environments. Attack in a hydrochloric acid solution is representative of that at the average daily sewage level region of a pipe where corrosion products are removed continuously and expose the concrete substrate to the sulphuric acid environment. Attack at the average daily sewage level region is severe and usually determines the life span of the concrete pipe. Attack in this region compares to that in a hydrochloric acid solution as the concrete is continuously exposed to the sulphuric acid environment and the attack depends on the strength of the acid solution and acid solubility of the concrete compounds. Acid solubility depends on concrete composition, which sewer pipe manufacturers can change to develop a concrete of suitable resistance and/or neutralisation capacity to withstand the corrosive sewer conditions.

Assessing attack at the average daily sewage level region in a sulphuric acid solution requires continuous renewal of the solution to dissolve the calcium sulphate and constantly expose the concrete to the solution simulating the conditions in a sewer. Such a test method is impractical. Substituting the sulphuric acid solution with a hydrochloric acid solution provides a straightforward easy-to-use method with which to assess the acid resistance of sewer pipe concrete. Control of pH and continuous brushing of the specimens to remove corrosion debris ensures the attack remains a function of the concrete composition and conditions remain constant.

Maintaining the pH at 1,00 generates results with which to assess the acid resistance of dolomite aggregate concrete within 96 hours (or sometimes even within 48 hours). Such aggressive environments are common throughout South Africa and testing at a pH of 1,00 is essential to develop mixtures to resist these corrosive conditions, which are of a concern to concrete sewer pipe manufacturers. The influence of the chemical and physical properties of concrete on acid resistance is clearly seen as test specimens are prepared in a manner similar to that of concrete pipes. Adjusting these parameters by altering the composition of the concrete assists with the development of a mixture to resist these severely corrosive sewer environments. Concrete in these environments must not only slow or stifle the growth of the thiobacillus bacterial colony leading to the sulphuric acid generation but also offer good resistance to the sulphuric acid generated.

Assessing acid resistance in a biologically-induced sulphuric acid environment is also necessary to ensure the development of a successful mixture. Concrete composition significantly influences the activity and growth of the thiobacillus colony responsible for the generation of the sulphuric acid. A number of different concrete mixtures aimed at resisting an acid environment are easily and quickly tested using the hydrochloric acid test; however the success of the mixtures can only be monitored in a biologically induced sulphuric acid environment. Mixtures that offer good resistance generally contain compounds affecting the activity and growth of the thiobacillus bacteria such as dolomite aggregates, CAC and metallic biocides that are toxic towards the thiobacillus bacteria. These must be assessed in a biologically induced environment.

6.4 Acid resistance of sewer pipe concrete

From the research it was concluded that aggregates have a more profound influence on the acid resistance of sewer pipe concrete than the cement binder portion (Figure 6.1). Concrete consists mostly of coarse and fine aggregates, the properties of which determine the nature of the acid attack. Alag™ aggregate concrete resisted the hydrochloric acid solution and biologically-induced sulphuric acid environment at Virginia significantly better than a concrete containing a dolomite aggregate. A dolomite concrete was readily attacked in the hydrochloric acid solution and biologically-induced sulphuric acid environment at Virginia but resisted these environments better than a siliceous aggregate concrete. Although siliceous aggregate concrete reflected a lower mass loss and hydrogen ion consumption in the hydrochloric acid solution than the dolomite aggregate concrete this was only due to the entrapment of corrosion debris between the siliceous aggregate particles, which stifled attack on the cement binder. In the biologically-induced sulphuric acid environment at Virginia, the mass loss of siliceous aggregate concrete was similar to that of dolomite aggregate concrete. Attack was however concentrated on the cement binder portion of the siliceous aggregate concrete, which equates to a substantially higher depth of attack on the siliceous aggregate concrete compared to that on the dolomite aggregate concrete. A similar situation would result in the hydrochloric acid solution if the corrosion debris sandwiched between the siliceous aggregate particles was removed concluding that a siliceous aggregate concrete gives poorer resistance in acidic environments than a dolomite aggregate concrete.

Although the cement binder has a lesser influence on acid resistance, modifications of the binder are significant and very important in aspiring to develop an acid resistant sewer pipe concrete (Figure 6.1). CAC failed to improve on the resistance of dolomite aggregate concrete in the hydrochloric acid solution but substantially improved the resistance of the concrete in the biological-induced sulphuric acid environment at Virginia. Silica fume improved the resistance of concrete containing a poor quality dolomite and concrete containing siliceous aggregates in the hydrochloric acid solution but failed to improve the resistance of concrete to the biologically-induced sulphuric acid environment at Virginia. Slag, fly ash and meta-kaolin failed to improve resistance of siliceous aggregate and dolomite aggregate sewer pipe concretes in the acidic environments. Acid resistances of OPC dolomite aggregate concretes were not improved with the addition of biocides containing metals such as nickel, copper, zinc and silver.

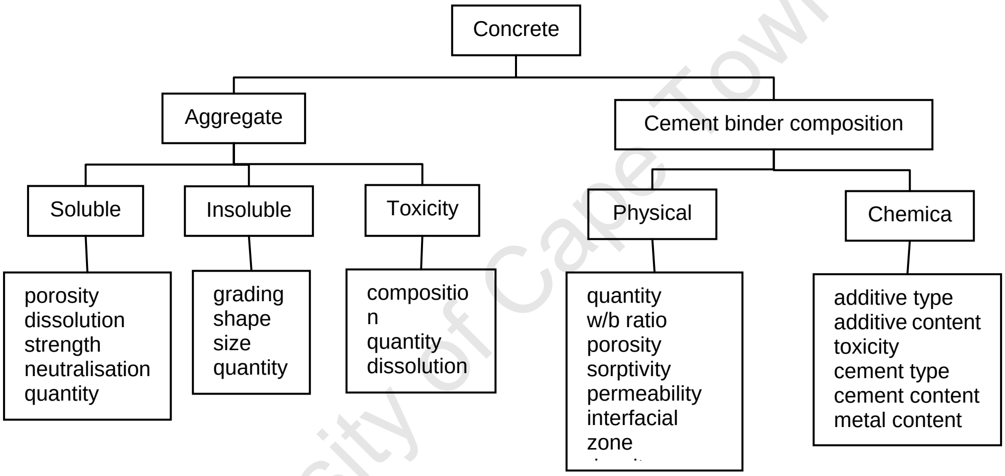

Figure 6.1 Flow diagram showing influence of constituents on the resistance of sewer pipe concrete to sulphuric acid environments encountered in sewers

Alag™ aggregate substantially improved the acid resistance of CAC concrete. Alag™ concrete reflected a low mass loss and hydrogen ion consumption in the hydrochloric acid solution indicating that the concrete was resistant to an acidic environment, which is related to:-

- slow dissolution rate of the alag™ aggregate in the hydrochloric acid solution (a good-quality dolomite aggregate dissolved twice as fast in the hydrochloric acid solution than the synthetic alag™ aggregate)
- good bonding between the alag™ aggregate particles and the CAC binder, which eradicates the influence of the interfacial zone that exists between the dolomite aggregate and cement binder
- entrapment of corrosion debris between the slow dissolving alag™ aggregate particles hindering the acid attack on the CAC binder

Attack on the alag™ aggregate concrete in the biologically-induced sulphuric acid environment at Virginia was also negligible in comparison to the dolomite and siliceous aggregate concretes owing to the good acid resistance, neutralisation of sulphuric acid generated and more importantly toxicity of the calcium aluminate materials towards the thiobacillus colony, which slows the development, growth and activity of the thiobacillus bacterial colony.

A good quality dolomite aggregate in the hydrochloric acid solution dissolved at a similar rate to the cement binder avoiding the preferential dissolution of the binder, which is responsible for siliceous aggregate fall-out. Aggregate fall-out creates cavities substantially reducing the cover to reinforcing and service life of the siliceous aggregate concrete structure. A poor quality dolomite that fractures or is of a high porosity offered poor resistance to the hydrochloric acid solution. Aggregate stone particles dissolved at a faster rate than the binder portion causing cavities that substantially reduces the cover to reinforcing. By contrast, in the biologically-induced sulphuric acid environment at Virginia, the higher solubility of the poor quality dolomite aggregate particles appeared to neutralise the acidic conditions better than concrete containing a good quality dolomite aggregate. Attack was spread more evenly over the surface of the poor quality dolomite aggregate concrete improving the integrity of the concrete in the sewer environment. Attack, which is speculated to initiate on the cement binder portion, more readily occurred on the cement binder of the concrete containing the good quality aggregate stone particles leaving them standing proud of the attacked surface.

Although mass loss and hydrogen ion consumption measurements indicate that siliceous aggregate concrete resists the hydrochloric acid solution better than a dolomite aggregate concrete it is clear in the biologically-induced sulphuric acid environment at Virginia that the siliceous aggregate concrete is of substantially poorer acid resistance. A siliceous aggregate is acid-insoluble and attack is not spread over the entire surface of the concrete but concentrated on the cement binder portion. Fine aggregate particles such as crusher and filler sand particles are rapidly exposed and fall-out, which leads to the fall-out of siliceous stone particles that reduce the cover to reinforcing of the structure. Activity of the thiobacillus bacterial colony in sewers remains high due to the poor neutralisation capacity of the siliceous aggregate concrete and a corrosive sulphuric acid environment develops at a much faster rate than that on a dolomite aggregate concrete. A comparison to the attack in the hydrochloric solution can only be done once the test method is modified to ensure that corrosion debris sandwiched between the siliceous aggregate particles is continuously removed.

Siliceous aggregate grading, particle shape and particle size significantly influenced the resistance of the concrete in the hydrochloric acid solution. A tightly packed network of aggregate particles entraps corrosion debris and limits fall-out of the aggregate particles, which improved the resistance of the siliceous aggregate concrete in the hydrochloric acid solution. Irregular angular-shaped fine aggregate particles entrap corrosion debris to a larger extent than rounder-shaped fine aggregate particles and interlock to limit fine particle fall-out improving acid resistance of the siliceous aggregate concrete in the hydrochloric acid solution. Siliceous aggregates of a larger size take longer to fall-out and mask the attack on the cement binder better than the aggregates of a smaller size improving resistance of the concrete in the hydrochloric acid solution. In the biologically-induced sulphuric acid environment at Virginia, the shape and size of the siliceous aggregates negligibly influenced the resistance of the concrete. Attack on the cement binder is not affected due to the liquid nature of the corrosion products that form.

Acid resistance of a dolomite aggregate concrete containing CAC is significantly better in the biologically-induced sulphuric acid environment at Virginia than a dolomite aggregate containing OPC due to the toxicity of the CAC, which slows the development, growth and activity of the thiobacillus bacterial colony. In the hydrochloric acid solution, the CAC binder is more vulnerable to the attack and dissolves at a faster rate than the dolomite aggregate particles. The reason for the faster rate of attack is not clear as the CAC and OPC concretes have similar acid solubility and transport properties. Calcium aluminate is readily soluble at a pH of 1,00 and aluminium hydroxide only precipitates above a pH of 3,00, which then forms an alumina gel that improves the acid resistance of the CAC concrete. A possible explanation for the higher solubility for the CAC at a pH of 1,00 is that the CAC contains more un-hydrated particles, which fall-out with the acid attack or that CAC is more prone to attack due to the expansive conversion reaction associated with the calcium aluminate after hydration (the hydrated cubical structure converts to a stable hexagonal structure).

The reason why silica fume improves acid resistance of OPC concrete containing a poor quality dolomite and OPC concrete containing a siliceous aggregate is not entirely sure. Silica fume results in pore refinement improving the transport properties of the cement binder portion and improves the density of the interfacial zone between the aggregate and binder resulting in the slower dissolution of the binder. Slower dissolution of the cement binder masks the dolomite aggregate particles form the acid solution slowing the dissolution of dolomite aggregate particles which usually dissolve at a substantially faster rate than the cement binder thereby reducing the mass loss and hydrogen ion consumption of the concrete specimens.

Such an effect is less pronounced with concrete specimens containing a good quality aggregate. Slowing the dissolution of the cement binder, which usually dissolves at a faster/equal rate to the good-quality dolomite aggregate, fails to mask and reduce the area of dolomite (which forms a large percentage of the concrete specimen) exposed to the acid solution and therefore negligibly affect mass loss and hydrogen ion consumption of the concrete specimens. Improvements in the acid resistance of the siliceous aggregate concrete specimens relate directly to the slower dissolution of the silica fume binder, which prolongs the fall-out of fine and coarse aggregate particles and therefore significantly reduces the mass loss of the concrete specimens with time.

Slag, fly-ash and meta-kaolin do not significantly improve the properties of the binder. The decrease in the calcium hydroxide in the cement binder, which only forms a small percentage of the concrete, is too slight to affect mass loss and hydrogen ion consumption of the concrete specimens with time.

6.5 Limitations of research

Assessing acid resistance in a sulphuric acid solution was impractical and this prevents the development of a method, which simulates the attack in sewers and evaluates the use of materials that react with the sulphuric acid to form corrosion debris resistant to a sulphuric acid environment. A possible solution in developing an acid resistant concrete is to create a binder that on dissolution forms a barrier, which is completely insoluble in the sulphuric acid solution and prevents further attack.

A direct comparison between the acid resistance of concrete containing dolomite aggregate and that containing siliceous aggregate was not possible. A direct comparison can only be obtained by constantly removing the corrosion debris between the siliceous aggregate particles and then assessing and comparing the depth of attack with that of dolomite aggregate concrete. A mathematical factor to compare acid resistance of the concretes, which compensates for the interference of the corrosion debris, could not be formulated from the data collected. A more intensive investigation into the rates of attack on the different components of the concrete is required to develop such a factor.

Assessing acid resistance of concrete in a hydrochloric acid solution at a pH of 1,00 fails to recognise inherent chemical and/or physical properties of a concrete that afford resistance to milder mineral acid solutions. Concrete in less corrosive environments can effectively neutralise and stifle the activity of the thiobacillus bacterial colony.

A limited investigation into the acid resistances of sewer pipe was done in biologically induced sulphuric acid environments. A suitable biological method is required to test the effectiveness of concrete, which gives good resistance in the hydrochloric acid test solution, in simulated sulphuric acid sewer environments.

6.6 Future research requirements

A number of aspects require further investigation in order to develop a method with which to accurately assess the resistance of sewer pipe concrete in biologically induced sulphuric acid environments. A suitable method requires:-

- a mineral acid solution test
- a biologically-induced sulphuric acid solution test
- an experimental sewer test site

A mineral acid solution test such as the hydrochloric acid test method is crucial in determining the composition of concrete mixtures suitable for use in a sulphuric acid environment encountered in sewers. Assessing the acid resistance of the mixtures in the hydrochloric acid solution is quick and easy. Acid resistance is sensitive to the physical and chemical composition of the concrete, which accurately assesses the integrity of the concrete in acidic environments. A thorough understanding of the mechanisms of attack in the different acidic environments and on the different concretes of interest was achieved, specifically that relating to the problem of sewer corrosion, which formed the basis of the research. Some findings from the research were not conclusive requiring further investigations.

Analysis of the attack mechanism in weaker acidic solutions (i.e. pH greater than 2,00) is required to formulate an overall understanding of the solubility of the concrete compounds and develop a rate equation that can be related to the overall corrosion rate in sewers. A suitable laboratory method to measure resistance of concrete to weaker acidic solutions is required. Attack in the weaker environments not only relies on the acid solubility of the concrete but also on the absorption of the acid solution into the concrete. Additives improve the transport properties of concrete, which affects the absorption of fluids and influences the attack mechanisms in the weaker acidic solutions. Calcium aluminate cements form insoluble compounds at higher pHs, which increase the resistance of the concrete to less aggressive acidic environments. Weaker acidic environments are relevant to the conditions in the moisture layer on the concrete walls in sewers, which attack the concrete creating the conditions for the manifestation of the thiobacillus thiooxidans responsible for the corrosion.

A reliable laboratory method is required to assess the biological sulphuric acid attack on concrete mixtures identified for the manufacture of sewer pipes in the hydrochloric acid test solution. Validation of such a method requires substantial field-work in sewers throughout South Africa. Sites with different corrosive conditions that is, severe (pH less than 1,00) to weak (pH greater than 5,00) are necessary. Continuous long-term testing is required to accurately relate acid resistance of the concrete to the factors responsible for the corrosive conditions. A system such as the experimental section in the Virginia sewer is ideal but requires meticulous monitoring to establish the conditions in the sewage, sewer atmosphere and concrete walls above the sewage level responsible for the severe attack. Relating such factors to the corrosion rates monitored on the concretes of interest allows for the formulation of a real-life rate of attack equation. Correlating such an equation with that developed in the laboratory methods allows for the development of a model which estimates the service life of concrete in any sewer environment.

APPENDIX A

METHOD OF TITRATION

A.1 Introduction

A titration is an analytical procedure for determining the concentration of an ionic substance in a solution. A volume of the solution is accurately measured into a conical flask using a pipette. A standard solution containing an ionic substance which completely reacts with the test solution is prepared in a volumetric flask. Small amounts of the standard solution are added to the solution in the conical flask using a burette. On completion of the reaction that is, titration end or equivalence point the concentration of the test solution is calculated. A titration end-point is detected by a sharp change in electrical conductivity (conductance).

A.2 Acid-base titrations

An acid-base titration determines the acid concentration from the amount of a standard base solution added to attain neutralisation. Acids such as sulphuric or hydrochloric liberate hydrogen ions (Equations 1 and 2), which react with the hydroxide ions liberated from a base such as sodium hydroxide (Equation 3) to form the stable water molecule (Equation 4). At the end-point the hydroxide ions neutralise the hydrogen ions.

$H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + 2SO_4^{2-}$ (1.1)
$HCl + H_2O \rightarrow H_3O^+ + Cl^-$ (1.2)
$NaOH + H_2O \rightarrow Na^+ + OH^-$ (1.3)
$H_3O^+ + OH^- \rightarrow 2H_2O$ (1.4)

Conductance decreases uniformly with the addition of the hydroxide ions due to the neutralisation of the highly mobile hydrogen ions. After the end-point that is, neutralisation of the excess hydrogen ions the highly mobile hydroxide ions added increase the conductance of the solution uniformly.

A sharp increase in pH occurs at the end-point of the titration of a sulphuric or hydrochloric acid solution against a sodium hydroxide solution. On addition of the sodium hydroxide the pH changes negligibly. A sharp increase occurs at approximately 3,0 after which the addition of a few drops drastically increases the pH to 11,0 (Figure 1.1) denoting the equivalence point at a pH of 7,00 (Ebbing, 1984). Acid-base indicators, substances that change colour within a small pH range, detect the titration end-point. A number of indicators are available such as methyl orange (red in acids turning orange at pH 3,0 and yellow at pH 4,0), phenolphthalein (colourless in acids turning pink at pH 8,0) and bromothymol blue (yellow in acids turning blue at pH 6,0).

A.3 Assessing accuracy of the titration method

Aim of the investigation was to assess the accuracy of bromothymol blue in determining the end-point of the titration of sulphuric acid against sodium hydroxide. Assessing the indicators available revealed that the colour change of bromothymol blue from yellow to blue was easily distinguished in the acid solutions polluted with the corrosion debris of the concrete. Colour changes of phenolphthalein and methyl orange indicators were not as distinct and masked by the cloudiness of the solutions.

A.3.1 Experimental method

A 0,1 % solution of the bromothymol blue indicator was prepared by dissolving 0,1 g of bromothymol blue powder into 100 mℓ of ethanol. A sulphuric acid solution (0,05 mol/ℓ) was prepared by weighing 5,3 g of sulphuric acid (1,84 g/cm^3) into a conical flask (1 ℓ) containing deionised water. A standard sodium hydroxide solution (0,110 mol/ℓ i.e. 4,400 g in 1,000 ℓ) of a hydroxide ion concentration (0,01 mol/ℓ) similar to that of the hydrogen ion concentration was prepared in a conical flask (1ℓ).

Aliquots of the sulphuric acid solution (20 mℓ) were transferred (using a pipette) into three separate conical flasks (100 mℓ) adding three drops of the bromothymol blue indicator to each. Small portions (1 to 3 mℓ) of the sodium hydroxide solution were measured (using a burette) into each of the conical flasks. At an indication of a colour change from yellow to blue the sodium hydroxide was added drop wise (0,05 to 0,10 mℓ) until a definite colour change to blue occurred. After the addition of each portion of sodium hydroxide the pH of the mixture was measured. Volume of sodium hydroxide to reach the end-point was determined from a plot of pH versus sodium hydroxide added and compared to the volume after the addition of one drop changed the colour of the solution to blue.

A similar titration was conducted using a standard sodium hydroxide solution (0,203 mol/ℓ) with a hydroxide ion concentration approximately twice that of the hydrogen ion concentration to speed-up the method.

A.3.2 Results and discussion

Volume of the standard sodium hydroxide solution (18,93 mℓ) graphically determined (Figure A.1) at the equivalence point (pH = 7,00) was slightly higher than the volume (18,24 mℓ) detected from the colour change of the solution. Small differences results from the colour change occurring at a pH of 3,00, which underestimates the amounts of sodium hydroxide required to reach the actual equivalence point. After the colour change a few more drops (± 0,8 ml) of sodium hydroxide are required to increase the pH to 7,00.

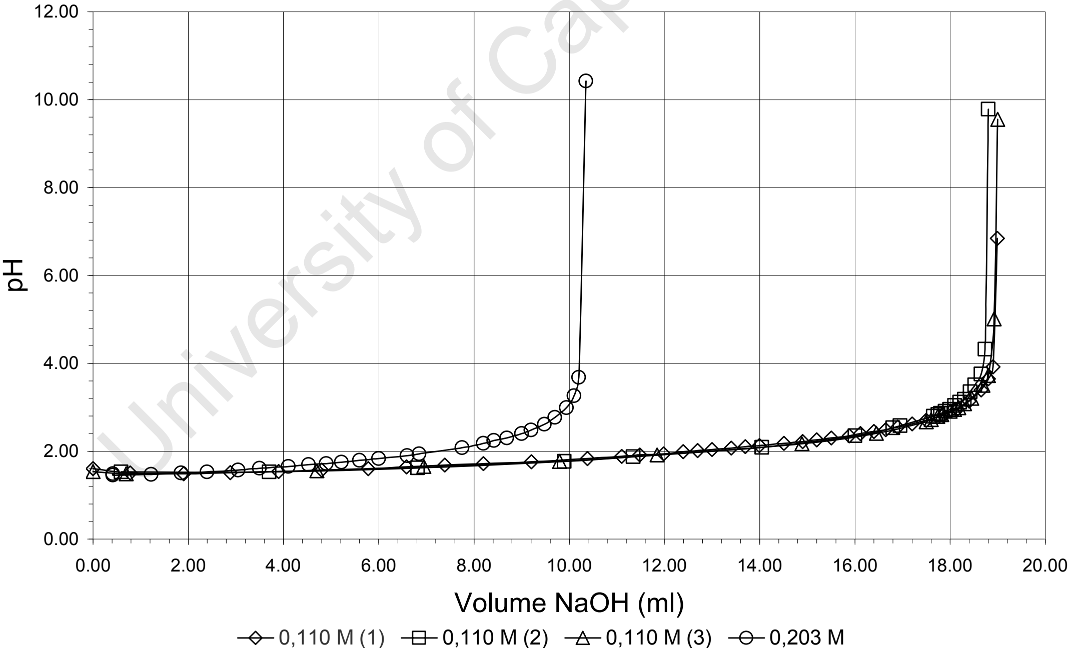

Figure A.1 Change in pH with volume (mℓ) of standard sodium hydroxide solution added in titration to determine concentration of a sulphuric acid solution

Sulphuric acid concentrations (C_a) calculated from the averages of graphical and indicator determined volumes of the sodium hydroxide solution compare favourably (0,052 mol/ℓ and 0,050 mol/ℓ respectively) illustrating the reliability of using the bromothymol blue indicator to determine the hydrogen ion concentration (0,104 mol/ℓ and 0,100 mol/ℓ respectively) and pH (0,98 and 1,00 respectively) of the sulphuric acid solution (Section 1.3.4).

Graphical and indicator volumes determined using the stronger standard sodium hydroxide solution (0,203 mol/l) were similar (10,25 mℓ and 10,10 mℓ respectively). Sulphuric acid concentrations calculated (0,052 mol/ℓ and 0,051 mol/ℓ respectively) compare favourably with those calculated using the weaker solution volumes that is, the stronger solution reliably determines hydrogen ion concentration and pH of the sulphuric acid solution.

A.3.3 General discussion

Colour change of the indicator at a pH of 3,00 prior to the equivalence point at a pH of 7,00 minimises effects of iron and aluminium ions (liberated from the concrete) in determining acid concentrations. Such ions form hydroxides that precipitate out of solution (iron hydroxide at a pH greater than 2,00 and aluminium hydroxide at a pH greater than 4,00) necessitating further addition of the standard sodium hydroxide solution to reach the equivalence point or colour change of the titration. Meticulously adding the sodium hydroxide solution allows detection of a blue colour change at a pH of approximately 2,00 and limits precipitation of iron hydroxide and prohibits precipitation of aluminium hydroxide. Such practice is crucial when determining the hydrogen ion concentrations of acid solutions in which calcium aluminate materials are tested. A margin of safety (approximately 1,00 mℓ) exists when using bromothymol blue to detect the equivalence point, which compensates for any extra sodium hydroxide added as a result of iron hydroxide that precipitates.

Stronger sodium hydroxide solution is a more reliable method for determining the equivalence point as the appearance of the blue colour is more easily noticeable and smaller amounts (± 0,2 ml) of the sodium hydroxide gives the colour change.

A.3.4 Typical calculation

Calculation of acid concentration (C_a) depends on the concentration (C_b) and volume (V_b) of sodium hydroxide, volume (V_a) and nature of acid (moles of hydrogen ions per mole of acid).

A mole of sulphuric acid dissociates to yield 2 moles of hydrogen ions ($H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$) implying that 1 mole reacts with 2 moles of sodium hydroxide:

$SA = C_{sa} \times V_{sa}$ and $SB = C_{sb} \times V_{sb}$

SA = moles of sulphuric acid and SB = moles of sodium hydroxide

$SB = 2SA$ that is $C_{sb} \times V_{sb} = 2(C_{sa} \times V_{sa})$

$\therefore C_{sa} = (C_{sb} \times V_{sb}) / 2V_{sa}$

A mole of hydrochloric acid dissociates to yield 1 mole of hydrogen ions ($HCl \rightarrow H^+ + Cl^-$) implying that 1 mole reacts with 1 mole of sodium hydroxide:

$\therefore C_{ha} = (C_{sb} \times V_{sb}) / V_{ha}$

A.3.5 Conclusion

A bromothymol blue indicator is a reliable and accurate means of detecting the equivalence point at pH of 7,00 of a titration of strong acids such as sulphuric and hydrochloric acids polluted with the metallic ions liberated from the concrete, against a strong base namely sodium hydroxide. Colour change is easily detected in the titration solution and indication of a change at a pH of 2,00 eliminates the interferences of hydroxides precipitating out of the solution.

APPENDIX B

METHOD STATEMENT FOR PREPARATION OF CONCRETE SPECIMENS

B.1 Introduction

Accurate determination of acid resistance of sewer pipe concrete requires a specimen preparation method to obtain concrete representative of that in sewer pipes manufactured using the roller suspension compaction method. Acid resistance depends on physical and chemical composition of the concrete, which the compaction significantly influences, for example, mixtures containing a low-strength dolomite aggregate that tends to fracture.

The objective of this appendix is to discuss the experimental methodology to develop the specimen preparation procedure:-

- a compaction method developed using a siliceous aggregate concrete mixture
- an investigation into the fracturing of dolomite aggregate particles during specimen and pipe compaction
- an investigation to reduce the fracturing of lower strength dolomite aggregate particles during specimen compaction

B.2 Development of the compaction method

The aim of the investigation was to develop a compaction method giving concrete of similar quality to that in sewer pipes manufactured using the roller suspension method, which entails the compaction of dry mixtures (w/c ± 0,36) via layers into steel pipe moulds and then steam curing the pipe in the mould after 4 hours at 50 °C for a further 4 hours.

B.2.1 Experimental method

Concrete specimens were prepared from a mixture consisting of a 13,2mm siliceous stone (53 %), siliceous filler sand (30 %) and normal portland cement (17 %). Aggregates were air dried for 30 days prior to mixing. Water was added to the raw materials in a pan mixer to obtain a dry mixture of consistency similar to that of sewer pipe mixtures (w/c ± 0,36). Concrete mixtures were compacted into steel cylindrical moulds (80 × 150 mm) via 4 layers tamping (20 times) each layer with a steel rod (15 × 600 mm) prior to compacting each layer using a 2 kg hammer (25 strokes) onto a steel rod with a square base (20 × 350 mm) followed by (5 strokes) onto a solid steel cylinder (75 × 300 mm). Specimens were removed from the moulds after 4 hours and steam cured for a further 4 hours at 50 °C. Specimens were stored in a conditioning room maintained at a temperature of 26 °C and relative humidity of 60 % for 28 days and some (on average 3) were cured in water at a temperature of 23 °C for 28 days.

After 28 days, standard tests namely relative density (SANS 6251, 1994) and compressive strength (SANS 5863, 2006), and durability index tests (Alexander et al, 1999) namely oxygen permeability, water sorptivity and porosity were done on concrete specimens and cores extracted from concrete pipe sections to assess the success of the compaction method.

Compressive strength tests (average of six determinations) were done on cylindrical specimens (80 × 80 mm cut from the specimens cured in water and 40 × 40 mm cut from cores extracted from the pipe sections). Cut edges were ground smooth and parallel. Specimens were saturated in water for 5 days prior to testing.

Concrete discs (approximately 25 mm thick) for relative density measurements (average of six determinations) were cut from the specimens cured in air and cores extracted from pipe sections. Conditioning involved oven drying the discs at 50°C to a constant mass followed by saturation in water for approximately 5 days. Suspension of the saturated disc in water and noting the change in mass measured the volume (density of water ± 1,00 g/cm^3) required to determine the relative density (dry mass/water mass change).

Similar discs (approximately 25 mm thick) were cut for determination of durability indices (average of six determinations). Conditioning involved oven drying at a temperature of 50°C and relative humidity of 15 % to a constant mass (approximately 14 days). Oxygen permeability was measured from the pressure decay with time as oxygen permeates through a concrete disc in a falling head permeameter (approximately 5 hours). Oxygen permeability index (OPI) is the negative logarithm of the Darcy coefficient calculated from the pressure decay rate. A high OPI value represents a relatively impermeable material. OPI values range from 9,0 for a poor, permeable material to 10,5 for a dense, impermeable material.

Concrete discs were re-conditioned (drying for 12 hours at a temperature of 50°C and relative humidity of 15 %) to determine water sorptivity. Several layers of absorbent paper were placed in a plastic tray and covered with a saturated calcium hydroxide solution. Sides of the discs were sealed to allow uniaxial absorption. Absorption of the solution into the discs was measured with time (approximately 120 minutes). After absorption, the discs were vacuum saturated in the calcium hydroxide solution.

Water sorptivity is the rate of movement of a waterfront through a porous material. Absorption is the dominant mechanism controlling the rate of water ingress into unsaturated or partially saturated concrete, which results from the capillary action of the pore structure. A lower water sorptivity represents a better, lower absorbent material. Water sorptivity values range from 15 mm/√h or more for poor, highly sorptive materials to 6 mm/√h or less for dense, low-sorptivity materials.

B.2.2 Results and discussion

Comparable values indicate that the specimen preparation method gave concrete of similar to slightly higher quality to that of sewer pipes manufactured using the roller suspension method (Table B.1). Values are typical that of dense, impermeable concrete. Oxygen permeability of the specimen concrete was significantly higher than that of the pipe concrete suggesting that the laboratory compaction is more forceful explaining the higher relative density and compressive strength values.

Table B.1 Relative density, compressive strength and durability index values of specimen and pipe concrete containing siliceous aggregates

Specimen	Density (g/cm^3)	Strength (MPa)	Permeability (OPI)	Sorptivity (mm/√hr)	Porosity (%)
Pipe	2,39	79	9,35	6,97	9,14
Specimen	2,45	83	10,12	6,21	9,17

B.2.3 Conclusion

Specimen preparation using hand compaction generates concrete of a slightly higher quality to that manufactured using roller suspension compaction.

B.3 Assessing quality of dolomite stone

The aim of the investigation was to determine quality of the dolomite stone used in manufacture of the five different sewer pipes throughout South Africa. Compaction of the mixtures fractures the stone particles, which alters the properties and performance of the concrete in corrosive environments. Stone of a sound nature minimises fracturing during compaction.

B.3.1 Experimental method

Standard tests namely relative density (SABS method 844, 1994) to assess porosity and 10 % fine aggregate crushing test - FACT (SABS method 842, 1994) to assess strength were done on dolomite stone sourced from the Olifantsfontein, Wadeville and Roodepoort factories in the Gauteng Province and the Kuilsriver and Blackheath factories in the Western Cape Province.

B.3.1 Results and discussion

Relative density values of the stone were comparable, which imply the stone are of a similar mineralogy porosity (Table B.2). Aggregate crushing values varied considerably indicating stone strengths differ significantly (Table B.2). Stone from Olifantsfontein, Wadeville and Roodepoort factories were of substantially higher 10 % FACT value than stone from the Kuilsriver and Blackheath factories. Stone from Kuilsriver (160 kN) and Blackheath factories (130 kN) were of similar values. Stone from the Olifantsfontein factory (354 kN) was of a significantly higher value than that from the Roodepoort (246 kN) and Wadeville (235 kN) factories.

Table B.2 Relative density and 10 % FACT values of dolomite stone sourced from factories in Gauteng and Western Cape

Dolomite stone	Relative density (g/cm^3)	10 % FACT (kN)
Olifantsfontein	2,87	354
Wadeville	2,81	235
Roodepoort	2,86	246
Kuilsriver	2,79	160
Blackheath	2,79	130

An aggregate crushing test determines the general quality of the aggregate and is a measure of abrasion resistance expressed as the compressive strength to crush stone particles of a certain size. Attrition during handling and mixing of aggregates that cause excessive fines is not desirable. Aggregate crushing values are a representative measure of the dolomite stone strengths in sewer pipe mixtures. Sizes of the stone particles tested (13,2 to 9,5 mm) are nominally the same as that used in sewer pipe manufacture. Significantly lower aggregate crushing values of the stone from the Western Cape Province accounts for the higher fines content and severe fracturing on compaction. Such stones are acceptable in standard concrete mixtures but undesirable in high performance and compaction mixtures.

B.3.2 Conclusion

Quality of the dolomite stone sourced from a lime processing plant in the Western Cape Province is poor in comparison to the dolomite stone sourced from the quarries supplying the factories in the Gauteng Province. Significantly lower strength of the Western Cape stone results in severe fracturing of the particles during compaction, which alters the properties of the concrete. Stone fracturing impacts on the reliability of the specimen preparation method as stone fractures to a different extent during roller suspension compaction.

B.4 Evaluation of specimen preparation method

The aim of the investigation was to compare fracturing of dolomite stone particles in the specimen preparation and roller suspension methods. Cracks in the stone particles reduce compressive strengths of the concrete and increase the area of stone exposed to corrosive environments.

B.4.1 Experimental method

A sewer pipe mixture containing a low strength dolomite stone (10 % FACT = 130 kN) was compacted at the Blackheath factory using the method documented above (Section 2.2.1) to prepare specimens and the roller suspension method to prepare pipe sections. A representative portion (8 kg) of the mixture was graded before and directly after the compaction of specimens and pipe sections by consecutively washing the portions through sieve sizes of 19,0, 13,2, 9,5, 6,7, 4,75 and 2,36 mm. Amounts of aggregate particles passing through the respective sieves were recorded and compared.

B.4.2 Results and discussion

Specimen and roller suspension compaction methods substantially fractured the dolomite stone particles with more fracturing in the specimen compaction method (Figure B.1). Specimen compaction fractured 3 % more of the 13,2 mm stone particles (fracturing 9 % compared to 6 % of the particles), 5 % more of the 9,5 mm (14 % compared to 9 %), 6 % more of the 6,7 mm (15 % compared to 9 %), 6 % more of the 4,75 mm (15 % compared to 9 %) and 2 % more of the 2,36 mm (4 % compared to 2 %).

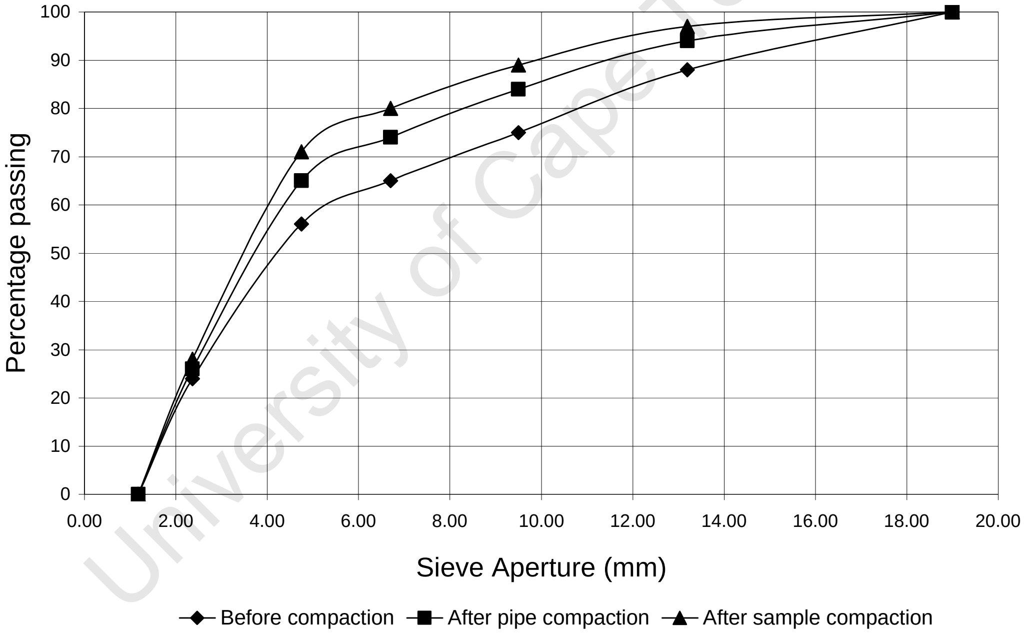

Figure B.1 Sieve analysis of Blackheath mixture before and directly after specimen and pipe compactions

Specimen compaction is significantly more destructive increasing fracturing of the 13,2 and to a larger extent the 9,5 mm stone, which gives the specimen concrete a different physical composition to that of the pipe concrete. Area of dolomite exposed to the acidic solutions increases, which effectively increases solubility of specimen concrete in comparison to that of pipe concrete.

B.4.3 Conclusion

Accurate determination of acid resistance requires concrete of similar quality, which necessitated the modification of the specimen preparation method to minimise fracturing of dolomite stone and obtain concrete representative of that in sewer pipes manufactured using the roller suspension method.

B.5 Modification of specimen preparation method

The aim of the investigation was to modify specimen compaction to decrease fracturing of low strength dolomite stone (10 % FACT less than 160 kN) and simulate the extent of stone particle fracturing during roller suspension compaction of sewer pipe mixtures.

B.5.1 Experimental method

Specimens and pipe sections were compacted from a mixture prepared at the Blackheath factory. Cylindrical specimens were prepared using a similar compaction procedure as that documented above (Section 2.2.1) the only exception was to replace the square-based rod (20 × 350 mm) with a solid steel rod with flat ends (32,8 × 350 mm). Stone fracturing after specimen and pipe compactions was assessed and compared in a manner similar to that above (Section 2.4.1).

B.5.2 Results and discussion

Compaction of the mixture using the rod with a larger surface area (11,46 compared to 4,00 cm^2) significantly reduces the fracturing of the dolomite stone particles and fractures the stone particles to a similar extent as that during the roller suspension compaction (Figure B.2). Amounts of 13,2 mm stone particles fractured during the modified specimen compaction method decreases (7 % compared to 9 %) and is similar to that fractured during the roller suspension compaction (6 %). Amounts of 9,5 mm (8 % compared to 14 %), 6,7 mm (7 % compared to 15 %), 4,75 mm (6 % compared to 15 %) and 2,36 mm (4 % compared to 0 %) stone particles fractured were significantly reduced and were fractured less than that during roller suspension compaction leaving a margin for error. Significant reduction in the fracturing of the stone particles smaller than 13,2 mm was crucial as the stone mainly consists of the smaller particle sizes.

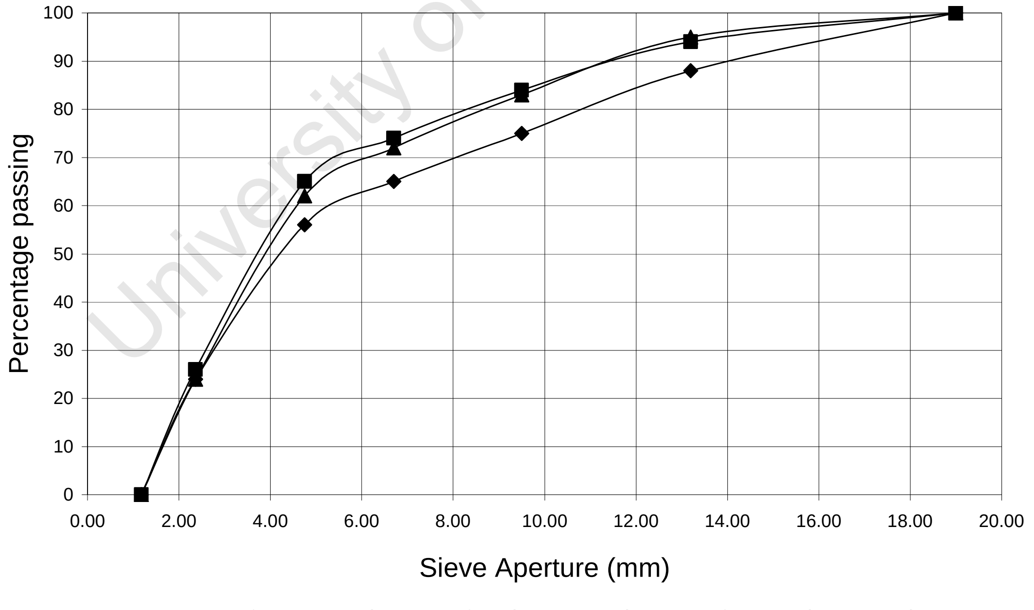

Figure B.2 Sieve analyses of Blackheath mixture before and directly after modified specimen and roller suspension pipe compactions

B.5.3 Conclusion

Compaction with the larger surface area rod successfully reduces fracturing of aggregate particles allowing for the formulation of the method statement for the preparation of specimens to investigate the acid resistances of sewer pipe concretes manufactured using the roller suspension compaction method documented below (Section 2.6).

B.6 Standard specimen preparation method

Aim of the specimen preparation method is to prepare cylindrical concrete specimens from dry mixtures simulating the manufacture of concrete sewer pipes using the roller suspension method.

B.6.1 Apparatus

1. Steel cylindrical moulds designed to withstand heavy mechanical compaction. Cylindrical part of mould (80 mm inside diameter, 150 mm in height) consists of two halves bolted together, which is inserted into a recess on a base plate and bolted down (Figure B.3).
2. A steel tamping rod (15 mm in diameter, 600 mm in length) with rounded edges (Figure B.4).
3. A steel compacting rod (32,8 mm in diameter, 350 mm in length) with flat end faces, acting as a piston.
4. A 10 kg steel compacting cylinder (75 mm in diameter, 300 mm in height) with flat end faces.
5. A 2 kg steel hammer.
6. A suitable steam generator.
7. Steam compartment. Temperature is regulated by a thermocouple positioned at the centre of the compartment. Thermocouple is attached to a thermostat, which is connected to the steam generator.

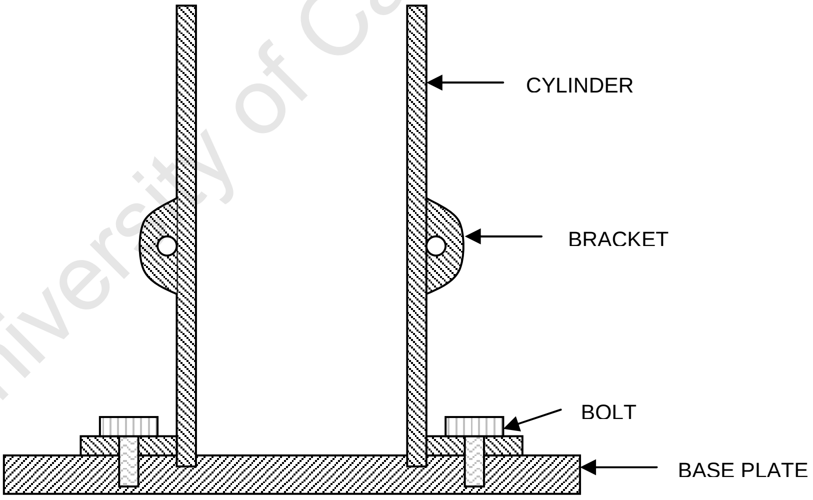

Figure B.3 Schematic arrangement of a steel cylindrical mould illustrating the layout of the components

B.6.2 Mixture design

A standard mixture is based on that in industry for concrete pipes manufactured using the roller suspension method. A dry mixture with no slump specifically designed for compaction is used. Approximately 2 kg of the mixture is required per specimen (80 mm in diameter, 150 mm in height). Raw materials are obtained from sewer pipe manufacturers. A typical sewer pipe mixture in South Africa consists of dolomite stone (41- 55 %), dolomite crusher sand (21 - 41 %), siliceous filler sand (0 - 17 %) and rapid hardening normal portland cement (16 - 18 %).

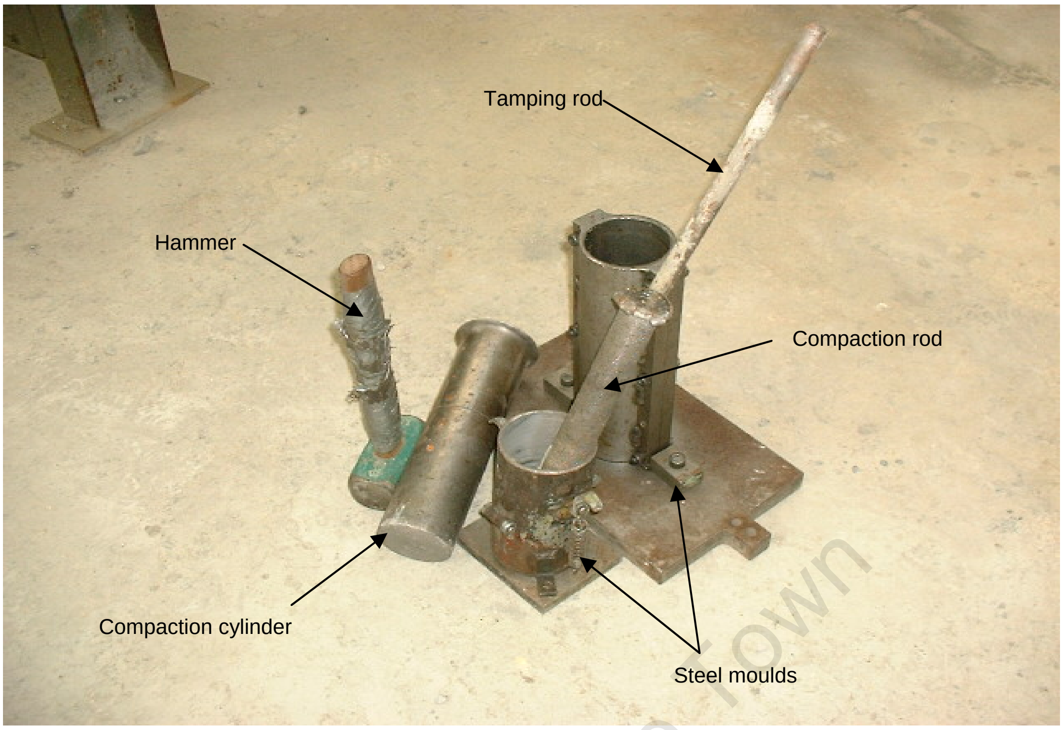

Figure B.4 Compaction apparatus required for the preparation of cylindrical concrete specimens

Standard tests are done on the raw materials. Physical and chemical nature of the raw materials influences the acid resistance of the concrete specimens. Grading (SABS method 829, 1994) and acid insolubility (SABS method 6242, 2002) of the aggregates are measured (Table B.3). Size and acid insolubility of the aggregates affects the rate of attack on concrete specimens subjected to the dynamic hydrochloric acid test. Size indicates ease of aggregate fall-out. Acid insolubility reflects the dissolution potential of the aggregates. A 10 % FACT (SABS method 842, 1994) determines the fracturing potential of the aggregates on compaction. Stone with a 10 % FACT value of 160 kN or less fractures readily; that with a value of between 250 kN and 350 kN is resilient towards fracturing. Stone fracturing easily on compaction affects the rate of attack on concrete specimens subjected to the dynamic hydrochloric acid test. An acid-soluble stone (calcareous) dissolves rapidly. An acid insoluble stone (siliceous) falls-out readily.

Table B.3 Typical SABS acid insolubility and particle size of aggregates used in manufacture of concrete pipes in South Africa

Raw materials	**Acid Insolubility** (%)	**Sieve size** (mm)
Dolomite stone	2 - 16	2,36 - 13,2
Dolomite crusher sand	3 - 25	0,00 - 2,36
Siliceous stone	97 - 99	4,75 - 13,2
Siliceous filler sand	70 - 98	0,00 - 0,60

Concrete materials are mixed dry for approximately 3 minutes in a pan mixer and for a further 5 minutes after adding water. Aggregates are air-dried. Water is added to obtain a mixture of consistency similar to that in industry. A w/c ratio of 0,36 is not exceeded in standard mixtures obtaining a dry mixture with no slump. Air-drying the aggregates and a w/c ratio of 0,36 ensures hydration of cement is similar for all concrete specimens prepared. Modifying the mixture with mineral extenders and/or chemical additives requires the addition of more or less water. Water is added to obtain a modified mixture that allows for heavy-mechanical compaction.

B.6.3 Specimen compaction

1. Oil and assemble the cylindrical mould.
2. Add approximately 400 g of the wet concrete mixture to the mould.
3. Tamp the layer twenty times evenly over the entire surface using the tamping rod.
4. Compact the tamped layer using the steel compacting rod. Hammer the rod down with twenty well-struck blows over the entire surface of the tamped layer.
5. Compact the layer further using the steel piston. Hammer the piston down with five well-struck blows to ensure a solid finish.
6. Repeat steps 2 to 5 until the mould is filled (approximately four to five layers).
7. Cover the fully compacted mould with moist sacking cloth (Hessian) and allow to cure for four hours at room temperature.
8. Remove the concrete specimen from the mould.
9. Cure the concrete specimen in wet steam at approximately 50°C for four hours.
10. Store the steam-cured concrete specimens at a temperature of 25°C and relative humidity of 60 % for 28-days prior to testing.

B.6.4 Standard testing of specimens

Standard tests are done on the concrete specimens to ensure that sufficient compaction has been obtained and to determine the acid dissolution potential of the concrete material.

Compaction is assessed by measuring oxygen permeability, water sorptivity and porosity of 28 day old concrete specimens (Alexander et al 1999). Density (SABS method 1251, 1994) and compressive strength (SABS method 863, 1994) of the 28 day old specimens are also measured. Acid dissolution potential of the material is assessed by doing an SABS acid insolubility test (SABS method 1242, 1994) on the 28 day old concrete specimens. Measurements are compared to that of similar sewer pipe materials (Table B.4).

Table B.4 Typical measurements on sewer pipe materials prepared using either the hand-compaction method or the roller suspension method

Measurements	Sewer materials
Oxygen permeability index	10,00 – 11,00
Water sorptivity (mm/√hr)	4,00 – 6,00
Porosity (%)	8,00 – 10,00
Density (g/cm^3)	2,40 – 2,60
Compressive strength (MPa)	60,0 – 80,0
Acid insolubility (%)	5,00 – 10,00

Concrete specimens prepared using mixtures containing mineral extenders and/or chemical additives are subjected to additional tests, which assess the suitability of the material in the manufacture of concrete pipes using the roller suspension method. Splitting strength (SABS method 1253, 1994) and the compressive strength (SABS method 863, 1994) of concrete specimens are measured after steam curing (approximately 8 hours after preparation).

APPENDIX C

METHOD STATEMENT FOR THE HYDROCHLORIC ACID SOLUTION TEST

C.1 Introduction

A dynamic hydrochloric acid solution test requires a detailed standard procedure, which ensures similar test conditions to consistently measure and reliably compare acid resistances of cylindrical sewer pipe concrete specimens. Standardising of the method involves establishing specific limits for variation of test parameters such as pH, solution changes and specimen cleaning. A constant pH requires strict control to ensure specimens are exposed to similarly corrosive hydrochloric acid solutions. Solution renewals limit accumulation of suspended solids and dissolved ions allowing accurate titration measurements of hydrogen ion concentration. A competent cleaning/brushing technique allows similar and adequate removal of the corrosion debris and ensures the specimens remain in constant contact with the hydrochloric acid solution.

C.2 Standardising the pH of the hydrochloric acid solution

The aim of this investigation was to establish the limits in which the pH varies without significantly affecting the mass loss and hydrogen ion consumption measurements.

C.2.1 Experimental method

Olifantsfontein specimens (three air-cured for 28 days) from the batch prepared for the validation of testing in a hydrochloric acid solution (Chapter 3 - Section 3.9.1) were immersed each in hydrochloric acid solutions (50ℓ) in which pH of one solution was allowed to vary between 1,00 to 1,50 and that of the remaining two strictly controlled between specific limits namely 1,00 to 1,05 for one and 0,95 to 1,00 for the other. Specimens were continuously brushed (using the soft-PVC-bristles) during rotation, removed and cleaned (under running water using the soft-nylon-bristle brush) once every hour prior to weighing. Hydrogen ion concentrations of the solutions were determined prior to the re-immersion of the specimens. Dimensions of the specimens were measured once every 8 hours. Solutions in which pH was controlled were renewed after 24 hours. Mass losses and hydrogen ion consumptions of the specimens were recorded with time for 32 hours.

C.2.2 Results and discussion

Specimen mass loss and hydrogen ion consumption rates in the solution in which pH varied from 1,00 to 1,50 continuously decreased with time (Figure C.1 and C.2). Specimen mass loss rates in the solutions in which the pH was controlled remained constant with time and hydrogen ion consumption rates increased with time. After 32 hours, mass loss and hydrogen ion consumption of the specimen in the solution at pH 0,95 to 1,00 (21,4 % and 12,67 mg/cm^2) was similar to that of the specimen in the solution at pH 1,00 to1,05 (19,8 % and 11,55 mg/cm^2). Mass loss and hydrogen ion consumption of the specimen in solution of pH varying from 1,00 to 1,50 was significantly lower (13,7 % and 7,94 mg/cm^2).

Steady increase in pH from 1,00 to 1,50 relates to a significant decrease in hydrogen ion concentration with time. Acid-soluble compounds tend to stabilise and dissolve at slower rates resulting in the decrease in mass loss and hydrogen ion consumption rates with time. Acid-soluble compounds dissolve at a steady rate due to the constant supply of hydrogen ions in the pH controlled solutions resulting in the constant mass loss rates with time. An increase in the hydrogen ion concentration rates with time was due to the exposure of the dolomite stone with time.

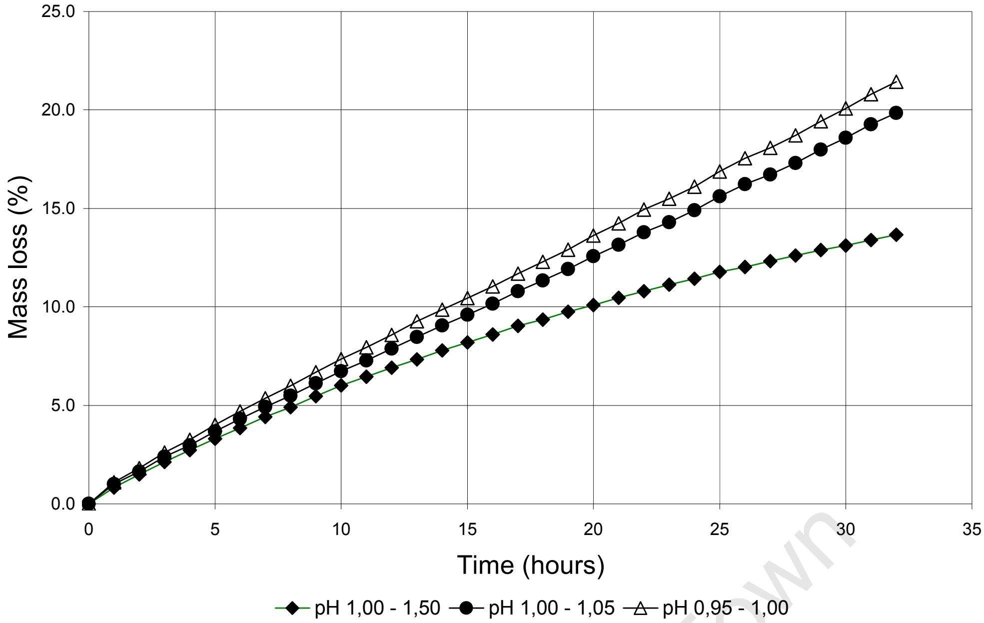

Figure C.1 Mass losses with time of Olifantsfontein specimens in hydrochloric acid solutions of different strengths to establish pH control limits

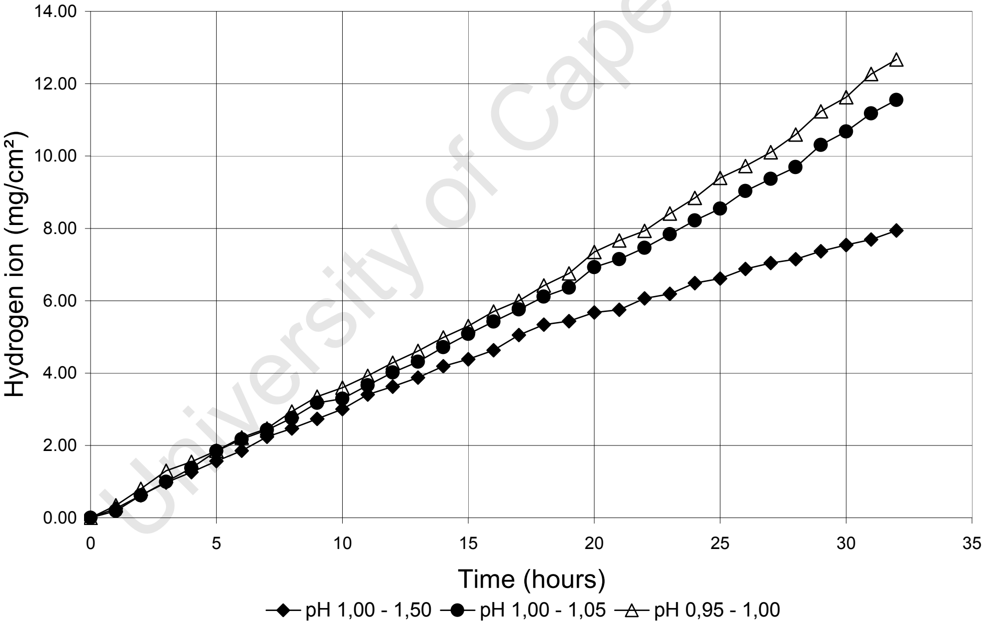

Figure C.2 Hydrogen ion consumptions with time of Olifantsfontein specimens in hydrochloric acid solutions of different strengths to establish pH control limits

Allowing pH of the hydrochloric acid solution to vary from 1,00 to 1,50 significantly decreases the aggressiveness of the solution. An acid-soluble concrete decreases the pH of the solution at a faster rate compared to that of a solution containing a concrete of a lower acid solubility. Such variation in the aggressiveness of the solutions results in misleading measurements of mass losses and hydrogen ion consumptions with time. Strictly controlling the pH of the solutions eliminates the variability. A steady attack rate is maintained allowing accurate comparisons of mass loss and hydrogen ion consumption rates to assess acid resistances. A steady attack rate is attained by preventing an increase in the pH to above 1,05 and decrease to below 0,95 that regularly occurs with the addition of hydrochloric acid to re-adjust the pH of the solutions.

Solution renewals after 24 hours successfully prohibited the murky conditions resulting from the corrosion debris and allowed for easy detection of the indicator colour change, which denotes the titration end-point. Solution renewal methods do not affect mass loss and hydrogen ion consumption rates and allows for accurate determination of the hydrogen ion concentrations.

C.2.3 Conclusion

A hydrochloric acid solution requires strict control of pH to ensure accurate comparison of measurements on sewer pipe concretes. A lower limit of 0,95 and upper limit of 1,05 minimises the effect of the pH on the acid resistance measurements. Solution renewal frequencies depend on the reactivity/solubility of the concretes. Solution renewals allows for accurate determination of hydrogen ion consumptions and control of pH.

C.3 Standardising the cleaning of specimens in the hydrochloric acid solution

The aim of this investigation was to establish a specimen cleaning/brushing technique that limits abrasion but removes corrosion debris accumulating on the concrete specimens. Successful removal of the debris ensures that the concrete specimens remain in direct contact with the hydrochloric acid solutions eliminating variability arising from different accumulation rates.

C.3.1 Experimental method

Concrete specimens were prepared using the standard method developed (Appendix 2 – Section 2.6) and sewer pipe mixture from the Roodepoort factory (Table 3.4). Dolomite crusher sand and siliceous filler sand was that used for the preparation of the Roodepoort specimens to validate testing in a hydrochloric acid solution (Chapter 3 - Section 3.9.3). Dolomite stone used was of a similar 10 % FACT (250 KN) to that of the Roodepoort stone but with smaller particle sizes (nominally 6,7 mm to 9,5 mm) and lower SABS acid in solubility (2,95 %).

Specimens (four air-cured for 28 days) were immersed and continuously rotated each in hydrochloric acid solutions maintained at a pH of between 1,00 and 1,05 for 32 hours. A specimen in one of the solutions was left without brushing to establish a standard with which to monitor the different brushing techniques in the remaining three solutions:-

- cleaning specimens hourly under running water with a soft-nylon-bristle brush
- continuously cleaning specimens during rotation with a soft-PVC-bristle brush
- cleaning specimens continuously and hourly with the respective brushes

Specimens were weighed once every hour and hydrogen ion concentrations of the solutions were determined by method of titration once every 4 hours. Solutions were renewed after 24 hours. Dimensions were determined once every 12 hours. Mass losses and hydrogen ion consumptions of the specimens were recorded with time.

C.3.2 Results and discussion

Specimen mass loss and hydrogen ion consumption rates remained constant with time (Figure C.3 and C.4). After 32 hours, mass loss and hydrogen ion consumption of the specimen continuously and hourly brushed (15,2 % and 10,57 mg/cm^2) and that of the specimen continuously brushed (14,1 % and 9,93 mg/cm^2) were similar. Mass loss and hydrogen ion consumption of specimen brushed hourly (12,1 % and 7,29 mg/cm^2) and that of the specimen without brushing (9,7 % and 6,50 mg/cm^2) were significantly lower.

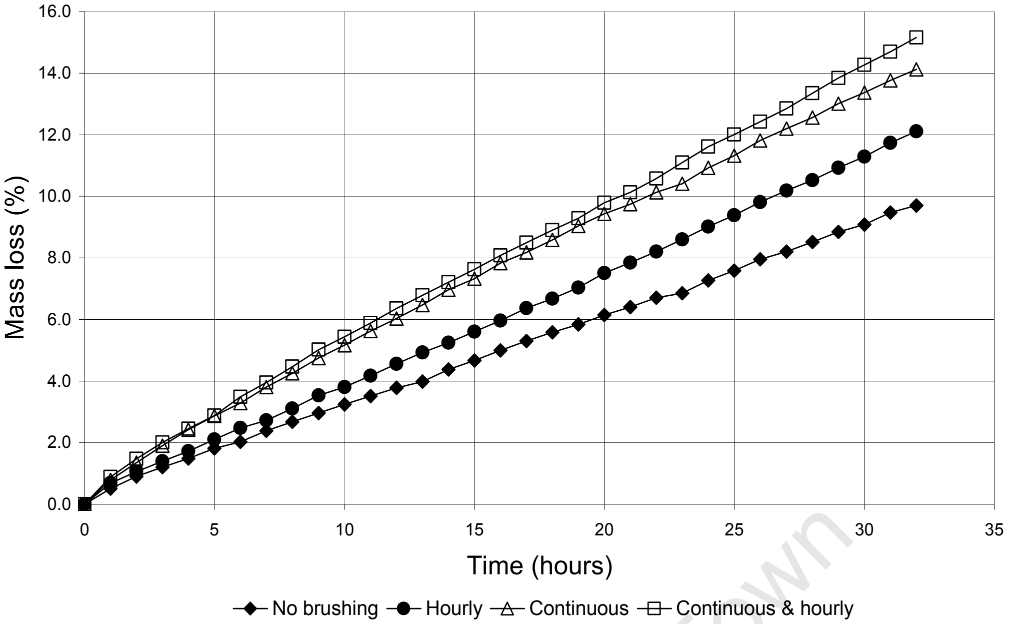

Figure C.3 Mass losses with time of concrete specimens in hydrochloric acid solutions maintained at a pH of 1,00 to 1,05 to monitor effects of brushing

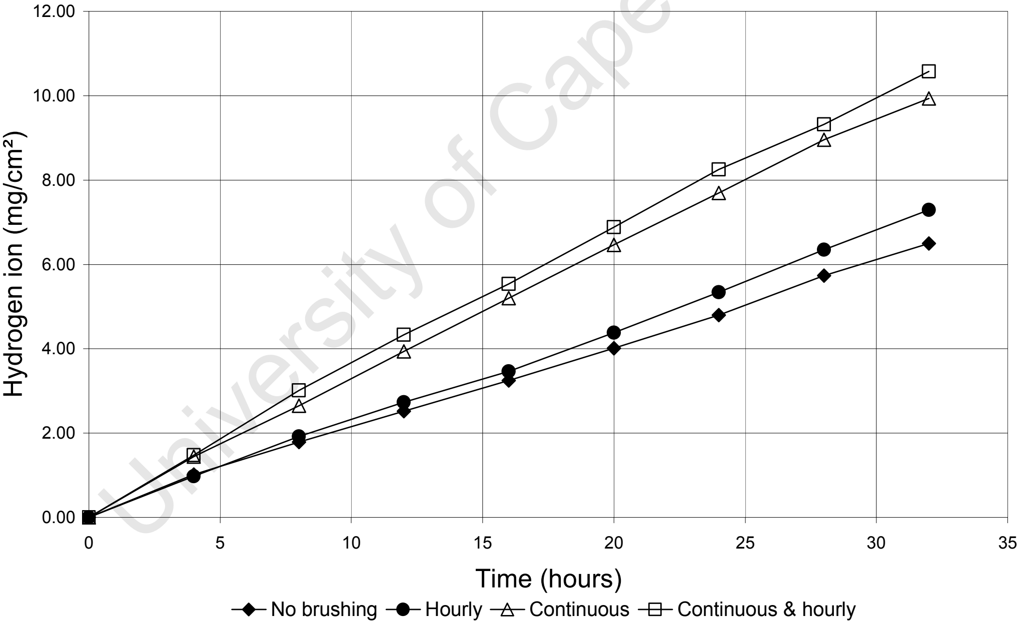

Figure C.4 Hydrogen ion consumptions with time of concrete specimens in hydrochloric acid solutions maintained at a pH of 1,00 to 1,05 to monitor effects of brushing

Corrosion debris accumulating on the surfaces of the specimens hinders the mobility of the ions involved in the hydrochloric acid attack mechanism. A gel-like layer consisting of acid-insoluble particles and water develops on the specimen without brushing and hourly intervals of the specimen brushed once every hour. Stagnant conditions in the layer slow influx of hydrogen ions from the solution and allow build-up of calcium chloride, aluminium hydroxide and iron hydroxide, which reduce dissolution rates of acid-soluble compounds into the hydrochloric acid solutions. Constant mass loss and hydrogen ion consumption rates are due to the porous nature of the gel, which negligibly affects the diffusion rate of the ions involved in the attack mechanism. Continuous brushing of the specimen during rotation removes the corrosion debris resulting in the higher mass loss and hydrogen ion consumption rates. Continuous and hourly brushing of the specimen removes any firmly bonded debris the gentle sweeping action of the soft-PVC-bristle brush cannot, which results in the slightly higher mass loss and hydrogen ion consumption rates.

C.3.3 Conclusion

A brushing technique to minimise the variability of the porous gel-like layer on mass loss and hydrogen ion consumption measurements requires a continuous brushing technique. Sweeping action due to the bending of the PVC bristles limits abrasion and allows a negligible amount of corrosion debris to accumulate. Cleaning of the specimen under running water using a soft-nylon-bristle brush removes any firmly bound debris.

C.4 Hydrochloric acid solution method

The aim of this method is to determine acid resistance of concrete containing dolomite intended for the manufacture of sewer pipes. Cylindrical specimens are prepared in a manner similar to that of the intended structure to ensure a concrete representative to that of the structure. A convenient size is 80 mm in diameter and 150 mm in height (surface area of approximately 478 cm^2). Cores of an adequate size and free from reinforcing taken from the concrete structure are also ideal for testing.

C.4.1 Description of testing rig

The rig consists of one or more compartments made out of 10 mm poly-vinyl chloride (PVC) sheeting (Figure C.5). The full-capacity of a compartment is approximately 72 ℓ (800 × 300 × 300 mm). Each compartment contains two rubberised rollers, a PVC brush and a PVC drain valve. Recommended mounting of the rig is on top of a metal frame (height 850 mm) allowing the rig to stand approximately 1150 mm above the ground. All materials in contact with the test solution are acid resistant. Compartments are covered with a PVC lid to avoid evaporation and contamination of the solution.

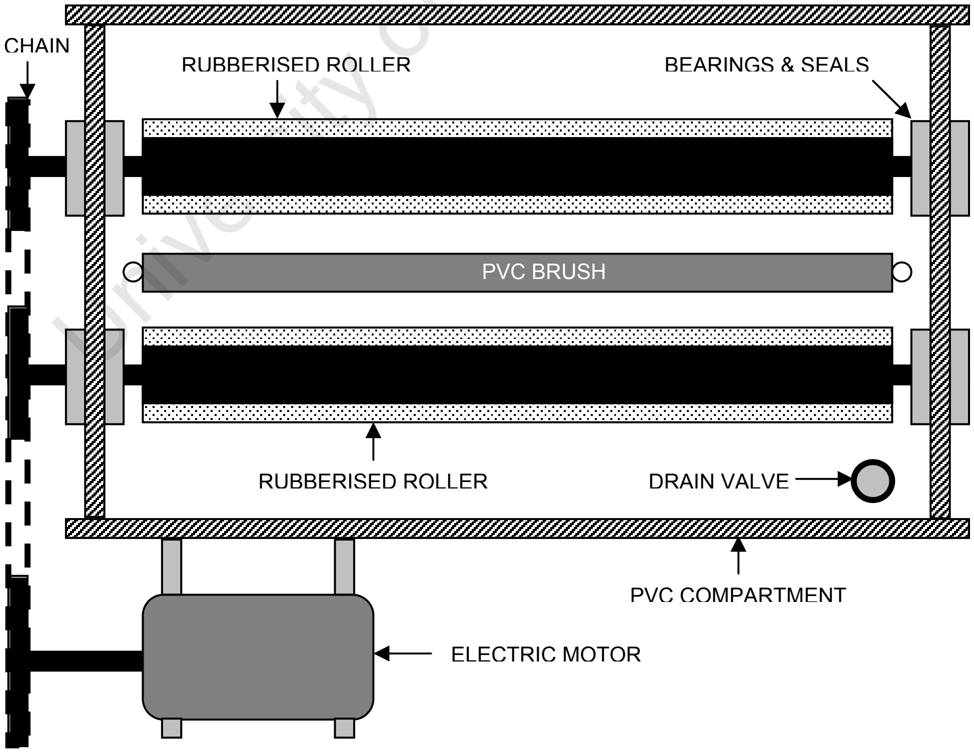

Figure C.5 Schematic arrangement of testing rig illustrating the plan of a compartment showing the layout of components (not to scale)

Rollers made of stainless steel rubberised with neoprene (50 mm in diameter) span the entire length of the compartment. Rollers are positioned 50 mm apart at the bottom centre of the compartment. Rollers are rotated via a chain driven by an electric motor. The chain runs over sprockets attached to the rollers on the outside of the compartments. The electric motor is required to run for long periods rotating a concrete specimen (80 mm in diameter) at approximately 16 revolutions per minute.

A brush (thickness of approximately 5,2 mm) spanning the entire length of the compartment is positioned at the top centre. The brush is raised or lowered on two stainless steel pins mounted on the base at the centre at each end of the compartment. The brush contains approximately 800 PVC bristles per centimetre. Bristles are soft and flexible approximately 100 mm long and 0,25 mm in diameter. Bristles sweep the surface of the specimen without applying pressure limiting abrasion (Figure C.6). A drain valve (25 mm in diameter) is attached to the underside of the compartment that is large enough to allow removal of the corrosion debris.

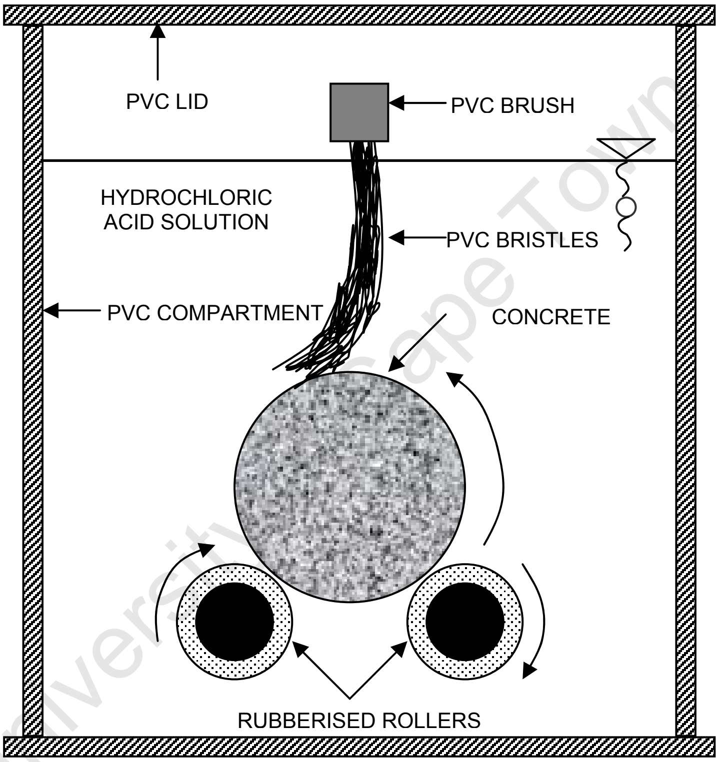

Figure C.6 Schematic arrangement of testing rig illustrating the end view of a compartment showing rotation and brushing of a concrete specimen on the rubberised rollers (not to scale)

C.4.2 Test procedure

A compartment is filled with approximately 50 ℓ of a hydrochloric acid solution (pH=1). A cylindrical concrete specimen (80 mm in diameter and 150 mm in height) approximately 2 kg in mass pre-saturated with water is immersed in the solution and rotated at 16 revolutions per minute. A PVC brush is lowered onto the surface of the specimen to sweep away the corrosion debris. Mass and exposed surface area of the specimen and hydrogen ion concentration of the solution are recorded with time. A pH of between 1,00 and 1,05 is maintained for the duration of the test. Solutions are renewed every 24 hours of running time to ensure accurate control of the hydrogen ion concentration. Attack is estimated by mass loss and hydrogen ion consumption with time. A test is run for a period sufficient to ensure the physical and chemical factors influencing the attack are reflected in mass loss and hydrogen ion consumption measurements. A recommended test period is approximately 96 hours of running time.

Testing four specimens made from the same raw materials gives reliable results. A rig consisting of four compartments is recommended allowing simultaneous testing of the four specimens each in respective compartments. Testing more than one specimen in a compartment at a time only permits mass loss as a measure of the acid attack rate. Testing a single specimen in a compartment allows determination of the hydrogen ion consumption of that particular specimen. Hydrogen ion consumption is important in assessing acid resistance of a specimen. Mass loss and acid solubility of concrete are not directly related. Mass loss is a function of the dissolution rate of the acid-soluble fraction and fall-out rate of the acid-insoluble fraction.

Renewals of the hydrochloric acid solutions are required to ensure precise control and measurement of hydrogen ion concentration. Frequency of solution renewals depends on the rate of attack. At higher rates of attack the solution is more rapidly saturated with insoluble particles and soluble ions such as aluminium, which affect the titration method. Cloudiness due to suspension of insoluble particles in the solution makes detection in the colour change of the indicator difficult. Soluble aluminium ions complex with the hydroxide ions added and precipitate out of solution masking the end-point of the titration. Solutions renewals do not affect the mass loss measurements. Solutions are renewed every time the colour change of the indicator is difficult to detect or on noticing a precipitate during the titration making the colour change sluggish.

Testing more than one concrete specimen in 50 ℓ of the hydrochloric acid solution makes control and measurement of the hydrogen ion concentration difficult. Solution is more rapidly polluted requiring frequent renewals (typically 12 hours for two specimens, 8 hours for three, 6 hours for four). Testing a single concrete specimen limits the build-up of corrosion products in the solution allowing on average renewals once every 24 hours to ensure accurate determination of the hydrogen ion concentration.

C.4.3 Test method

1. Pre-saturate the concrete specimen to be tested in tap water for a minimum of 4 days due to low porosity.
2. Measure the initial surface area of the specimen
   2.1. Measure the diameter (d) three times along the length of the specimen (at ends and centre) using a vernier.
   2.2. Measure the height (h) at four equally spaced positions around the circumference of the specimen using a vernier.
   2.3. Calculate the surface area ($A = \pi dh + \pi d^2/2$) of the concrete specimen.
3. Weigh and record the initial mass of the concrete specimen.
4. Fill the compartment with 50 ℓ of tap water.
5. Initially add approximately 500 mℓ of a 35 % hydrochloric acid solution to the 50 ℓof tap water and stir well.
6. Determine the hydrogen ion concentration (pH) of the solution by titration (Appendix A). Adjust pH to 1,00 by adding water if less than 0,95 and by adding hydrochloric acid if greater than 1,05. Re-determine hydrogen ion concentration.
   6.1. Pipette three 20 mℓ portions of the acid solution into separate conical flasks.
   6.2. Add one to three drops of the bromothymol blue indicator to each flask (solution obtains a yellow colour).
   6.3. Slowly add a standard sodium hydroxide solution using a burette to the acid solution until a single drop changes the colour from yellow to blue. (Note: Approximately 10 ml of a sodium hydroxide of approximately 0,200 M brings about the colour change. Care must be taken not to overshoot the end-point. Colour tends to change back to yellow after the end-point is reached especially once the acid solution is polluted.)
7. Immerse the concrete specimen in the hydrochloric acid solution by placing the specimen on the rollers.

8. Lower the PVC brush onto the specimen so that the bristles are in contact with the surface of the specimen along its entire length.
9. Turn on the testing rig.
    - 9.1. Remove the concrete specimen from the hydrochloric acid solution at four hourly intervals.
    - 9.2. Lightly brush end-faces of the concrete specimen with a soft bristle nylon brush under running tap water to remove any loose corrosion debris.
    - 9.3. Measure and record the mass and area of the concrete specimen (step 2).
    - 9.4. Determine hydrogen ion concentration (pH) of the hydrochloric acid solution (step 6).
    - 9.5. Add hydrochloric acid to re-adjust the pH of the solution to 1,00.
    - 9.6. Determine the re-adjusted hydrogen ion concentration (pH).
    - 9.7. Calculate mass loss and hydrogen ion consumption of the specimen for each of the four hourly intervals.
10. Renew the hydrochloric acid solution at least once every 24 hours of running time, sooner if the pollution level interferes with the titration method.
11. Run the test for a minimum of 96 hours. (Note: To suspend the test remove the concrete specimen and store in tap water. Re-immersed the specimen in the hydrochloric acid solution to continue the test.)
12. Calculate and plot the cumulative percentage mass loss and hydrogen ion consumption of the concrete specimen with time for the duration of the test.

C.4.4 Typical calculations

1. Hydrogen ion concentration (pH) of the hydrochloric acid solution:

   $[H^+] = C_b \times V_b \div V_a$

   $[H^+]$ = molar concentration of hydrogen ions (mol/ℓ)
   C_b = molar concentration of standard sodium hydroxide solution (mol/ℓ)
   V_b = volume of the standard sodium hydroxide solution (mℓ)
   V_a = volume of hydrochloric acid (mℓ)

   $pH = -\log [H^+]$

2. Quantity of hydrogen ions in the 50 ℓ hydrochloric acid solution:

   $Q_h = [H^+] \times MM_h \times V$

   Q_h = quantity of hydrogen ions (g)
   MM_h = molar mass of hydrogen (approximately 1,008 g/mol)
   V = volume of hydrochloric acid (ℓ)

3. Quantity of hydrochloric acid in the 50 ℓ aqueous solution:

   $Q_a = C_a \times MM_a \times V$

   Q_a = quantity of hydrochloric acid (g)
   C_a = molar concentration of hydrochloric acid (mol/ℓ)
   MM_a = molar mass of hydrogen chloride (36,46 g/mol)

(Note: Hydrogen concentration is equal to the hydrochloric acid concentration. In an aqueous solution 1 mole of hydrochloric acid dissociates to give 1 mole of hydrogen ions - Appendix 1.)

4. Initial quantity of hydrochloric acid added to 50 ℓ of tap water to obtain a pH = 1,00:

   $Q_o = C_a \times MM_a \times V = [H^+] \times MM_a \times V = 0{,}10 \text{ mol/ℓ} \times 50 \text{ l} \times 36{,}46 \text{ g/mol} = 182{,}3 \text{ g}$

Q_o = initial quantity of hydrochloric acid (g)

$V_o = Q_o \times v \div m$ = 182,3 g × 100 mℓ ÷ 35 g = 520,9 mℓ

V_o = initial volume of 35 % hydrochloric acid added to tap water (percentage by weight implying approximately 35 g of hydrochloric in 100 mℓ of distilled water)
m = mass of hydrochloric acid (35 g)
v = volume of distilled water (100 mℓ)

(Note: It is suggested to initially add approximately 500 mℓ of 35 % hydrochloric acid solution to the 50 ℓ of tap water. Amount of hydrochloric acid added to a fresh solution depends on the hardness of the tap water, the precise volume of tap water in the compartment and the purity of the hydrochloric acid solution. To accurately determine the quantity of hydrochloric acid required measure the amount needed to obtain a pH = 1,00 in 1 ℓ of the tap water.)

5. Quantity of hydrochloric acid consumed in 4 hour intervals:

$\Delta Q_a = Q_i - Q_f$

ΔQ_a = quantity of hydrochloric acid consumed in 4 hour interval (g)
Q_i = initial quantity of hydrochloric acid in solution (g)
Q_f = final quantity of hydrochloric acid in solution after 4 hours (g)

6. Volume of 35 % hydrochloric acid added after 4 hour intervals:

$\Delta V_a = \Delta Q_a \times v \div m$

ΔV_a = volume of acid added after 4 hour intervals (mℓ)

7. Quantity of hydrogen ions consumed in 4 hour intervals:

$\Delta Q_h = \Delta Q_a \div MM_a \times MM_h$

ΔQ_h = quantity of hydrogen ions consumed in 4 hour interval (g)

8. Rate of attack on concrete specimens:

8.1. Hydrogen ion consumption by concrete specimen per 4 hourly interval:

$HR = \Delta Q_h \div A$

HR = hydrogen ion consumption per 4 hours (g/cm^2)
A = average exposed surface area of specimen over 4 hour interval (cm^2)

$A = (A_i + A_f) \div 2$

A_i = exposed surface area of specimen at start of 4 hourly interval (cm^2)
A_f = exposed surface area of specimen at end of 4 hourly interval (cm^2)

8.2. Percentage mass loss of concrete specimen per 4 hourly interval:

$\Delta M = M_i - M_f$

ΔM = mass loss of specimen in 4 hour interval (g)
M_i = mass of specimen at start of 4 hourly interval (g)
M_f = mass of specimen at end of 4 hourly interval (g)

$ML = \Delta M \div M_o \times 100$

ML = mass loss of specimen (%)
M_o = original mass of specimen at start of test (g)

C.4.5 Precautions and health risks

Hydrochloric acid is a hazardous substance. Wearing proper acid resistant rubber gloves at all times is essential when working with acid solutions. Wearing a laboratory coat and eye protection is also advisable. Concentrated hydrochloric acid solution releases fumes requiring a well-ventilated area or fume cupboard when handling. A gas mask is recommended when working with the 35 % hydrochloric acid solution.

Hydrochloric acid test solutions are neutralised before discarding. Approximately 200 g of sodium hydroxide pellets are dissolved in 5 ℓ of water and added to the acid solution. Wearing of rubber gloves is required when handling sodium hydroxide pellets and solutions. Sodium hydroxide solutions are prepared in a well-ventilated area.

APPENDIX D

DEPTH OF ATTACK

D.1 Introduction

A measurement of depth of attack is a more reliable manner in which to compare acid resistance of siliceous aggregate concrete to that of dolomite aggregate concrete than percentage mass loss with time measured, which indicates that siliceous aggregate concrete specimens (approximately 10 % after 96 hours) resist acid attack better than dolomite aggregate concrete specimens (approximately 30 % after 96 hours). Siliceous aggregate specimens only show a comparable mass loss after 200 hours. Attack depth with time on siliceous aggregate concrete in practice is greater than that on dolomite aggregate concrete, which indicates that the siliceous aggregate concretes are more prone to the sulphuric acid attack in sewers.

Attack depth determines severity of acid attack on a concrete structure that contains steel reinforcing. Attack depth depends on:-

- dissolution rate of acid-soluble concrete constituents
- removal rate of acid-insoluble concrete constituents
- removal rate of corrosion debris

Aggregate type significantly influences the acid attack mechanism. Acid mainly attacks the binder portion of a siliceous aggregate concrete loosening the insoluble aggregate particles causing particle fall-out. Aggregate and binder of a dolomite aggregate concrete is dissolved at a similar rate.

D.2 Depth of attack measurements

Attack depth (d) on cylindrical dolomite aggregate concrete specimens is the difference between the initial radius (r_i) measured before and the final radius (r_f) measured after acid attack (i.e. $d = r_i – r_f$) as the entire surface is attacked uniformly (Figure D.1).

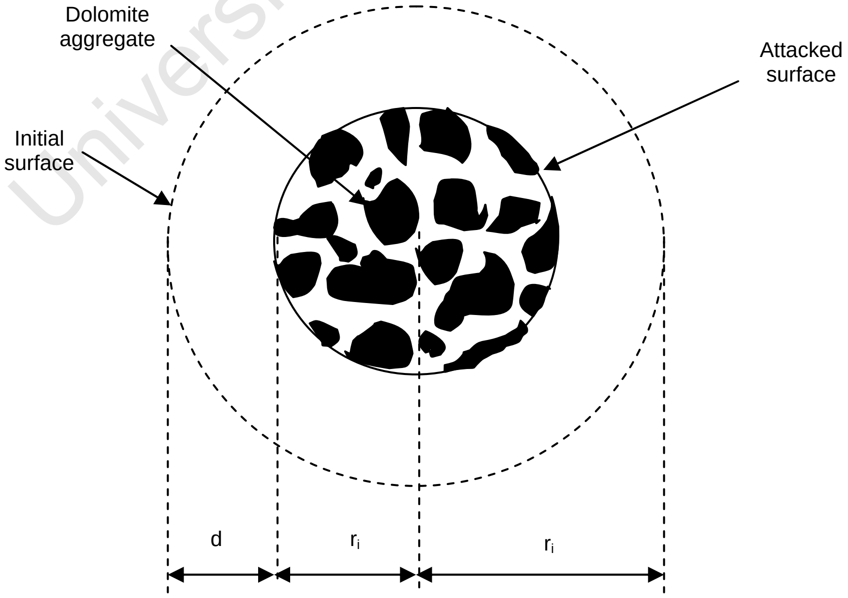

Figure D.1 Diagrammatic representation of a slice through a cylindrical dolomite aggregate concrete specimen illustrating the smooth surface after attack

Attack depth for cylindrical siliceous aggregate concrete specimens is the difference between the initial radius and the estimated radius measured with respect to the attacked binder portion sandwiched between the stone particles standing proud of the surface (Figure D.2).

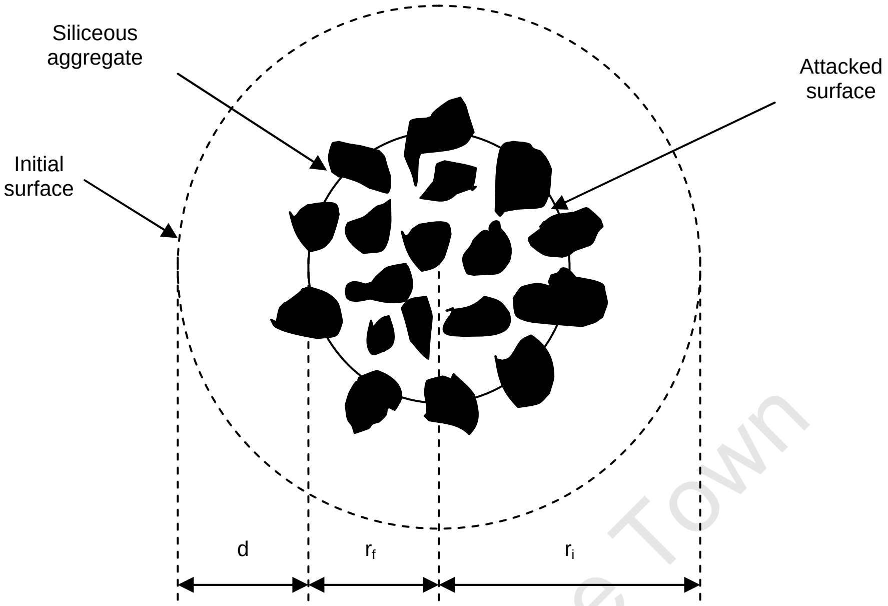

Figure D.2 Diagrammatic representation of a slice through a cylindrical siliceous aggregate concrete specimen illustrating the rough surface after attack

Variability in the depth of attack measurements over the surface of dolomite aggregate specimens was small due to smooth surface and efficient removal of the corrosion debris. Variability in the depth of attack measurements was significant in siliceous aggregate specimens namely if the mortar portion contains coarse irregular shaped siliceous sand particles. Measurements from between the protruding stone particles were difficult.

Attack depth was not successful in illustrating the poorer acid resistance of siliceous aggregate concretes. Attack depth measured after 96 hours indicate that the siliceous aggregate concrete specimens (0,29 cm) were more resistant to the hydrochloric acid solution at a pH of 1,00 than the dolomite aggregate concrete specimens (0,60 cm). Corrosion debris accumulating within the mortar portion of the siliceous aggregate concrete sandwiched between the stone particles significantly impedes the attack on the binder. A special dynamic hydrochloric acid method is required to compare relate the rate of attack on the dolomite aggregate concrete specimens to that on the siliceous aggregate concrete specimens. Continuous removal of the corrosion debris sandwiched between the siliceous aggregate particles is a necessity.

APPENDIX E

MEASUREMENT OF HYDROGEN SULPHIDE IN THE SEWER ATMOSPHERE

E.1 Introduction

Assessing the hydrogen sulphide content in the sewer atmosphere potentially indicates the aggressiveness of the sulphuric acid environment generated by the thiobacillus colony on the sewer walls above the sewage level. Activity of the thiobacillus bacteria directly relates to the amount of hydrogen sulphide in the sewer atmosphere. A hydrogen sulphide level of above 10 ppm is sufficient to sustain the growth of a thiobacillus colony capable of causing severe corrosion to concrete sewer walls.

E.2 Measurement of hydrogen sulphide in sewer atmospheres

A gas monitor (ATX 620 supplied by Scientific Industrial Instruments) used to monitor gas levels in mines) was used to measure the hydrogen sulphide content in the sewer atmosphere directly. A special sensor to monitor the hydrogen sulphide was inserted into the monitor and calibrated to record hydrogen sulphide levels of 0 ppm to 999 ppm. The monitor consists of a piston and cylinder which pumps the gas extracted from the sewer past the sensor. A data logger records the hydrogen sulphide levels with time.

Sewer air was extracted through an 8 mm hole drilled through the manhole covers. A 5 mm tube attached to the monitor was inserted into the sewer line directly above the sewage. Sewer air was extracted continuously and the hydrogen sulphide content was measured and logged with time. A daily hydrogen sulphide profile was generated from the data logged.