Predicting Life Expectancy of Concrete Septic Tanks Exposed to Sulphate and Biogenic Sulphuric Acid Attack

A thesis submitted in fulfilment of the requirements for the degree of Masters of Engineering

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August 2009
DECLARATION

This thesis is a presentation of my original research work and it has not been submitted previously, in whole or in part, to qualify for any academic award. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature, and acknowledgement of collaborative research and discussions.

Md Saeed Hasan
ACKNOWLEDGEMENTS

I would like to express my appreciation and sincere gratitude to my supervisor, Associate Professor Sujeeva Setunge for her valuable guidance, advice and encouragement throughout the course of this thesis. I thank her from the bottom of my heart.

I would like to thank Dr. Tom Molyneaux and Dr. David W. Law for their continuous support and suggestions to accomplish my research.

I would like to thank Ms. Pradeepa Adihetty, the Project Manager, Country Towns, of the Department of Sustainability and Environment (DSE) for her contribution to and support of this thesis.

I would like to thank all technicians, secretaries and personnel in the School of Civil, Environmental and Chemical Engineering at RMIT University.

I wish to express my sincere gratitude to my family members, both at home in Bangladesh and overseas, for providing me with the encouragement to carry out research for the last two years. Special thanks are due to my brother, sisters and sister-in-law.

Last but by no means least, I would like to thank my dear parents, the late Md Abdul Momen and Tahmina Begum. Nothing I can say can adequately express my gratitude for the adoration, support and encouragement they provided throughout my life. I am grateful to Omnipotent God for the gift of such caring parents.
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Abstract
The prediction of the expected long-term performance of concrete exposed to sewage and similar materials can be difficult as it is affected by a large number of parameters. In addition, the deterioration process in concrete is generally slow. Deterioration of concrete in sulphate environments takes a number of years to reach the ultimate failure state. Accelerated test methods permit application of more severe environmental conditions to laboratory samples, thus reaching ultimate failure stage within a short period of time. With the use of data from more severe conditions a generalized model can be developed to predict deterioration. If such a model is validated with field data, it becomes a powerful tool that can predict the deterioration for a longer term exposure under lesser concentrations of sulphates. Previous research has shown that such a method is appropriate for the prediction of the deterioration of sewer pipes.
Since the focus of the study was to ascertain the life expectancy of concrete septic tanks located in rural Victoria, an investigation was conducted to identify typical suppliers of concrete and typical mix proportions. Taylex Concrete Suppliers provided typical mix proportions used during the period of interest. Three different mix designs were used to cover the range of desired strength of concretes used in septic tanks in the state of Victoria prior to 1990.
In developing the accelerated test method, ASTM C 192, ASTM C 452, ASTM C 1293 and ASTM C 109 standard procedures were adopted wherever possible. Samples were removed from moulds after 24 hours from casting and cured in a saturated lime water chamber where a temperature of 23± 2°C was maintained. After 28 days the samples were removed from the lime water and the compressive strengths of 3 similar samples of each mix were tested using the ASTM C157/ C157M. After 28 days of saturated lime curing, the concrete bar specimens were placed into three different
concentrations of sodium sulphate solutions, namely 2%, 4% and 5.5%, and into two
different sulphuric acid solutions, pH 3 and pH 4.

From the analysis of mass change data after 350 days, it was found that the mass
change rate for concrete in sulphate solutions increases with the increase of
concentration of Na$_2$SO$_4$ solution. The weights of the samples in Na$_2$SO$_4$ solution
increased with time, whereas the control specimens lost weight as a result of heating
cycles. The probable reason for weight increase in Na$_2$SO$_4$ solution was hypothesized
as the formation of gypsum (CaSO$_4$.2H$_2$O) and ettringite (3CaO.Al$_2$O.3CaSO$_4$.32H$_2$O),
which is confirmed from microstructural analysis. The rate of weight gain was higher at
the beginning and reduced with time. The stronger the concentration of Na$_2$SO$_4$ the
stronger was the weight gain or expansion of mass. All the samples in sulphate
solutions attained their maximum weight at around 250 days.

For the specimens in sulphuric acid solutions weight loss was observed to be higher for
higher concentrations. The lower the pH of the acidic solutions, the larger was the
weight loss. The weight loss of specimens in acidic solutions exceeded the control
specimen after 250 days. The reason for the loss of weight of the samples in sulphuric
acid may be the decalcification of C-S-H gel within the concrete, and as a consequence
the loss of cementitious structure.

Comparison of the corrosion of concrete and also microstructural examination of field
samples confirmed that the deterioration mechanism is similar to that observed in the
laboratory. The accelerated testing adopted here offers a realistic method of predicting
the deterioration of septic tanks under biogenic sulphuric acid corrosion. Two equations
have been proposed to predict deterioration due to sulphate attack and sulphuric acid
attack as mass loss (or gain) with time.
Chapter 1

Introduction

1.1 Background

Worldwide there is a heavy reliance on concrete septic tanks in small capacity waste-water treatment systems due to the inherent qualities of concrete such as strength, long service life and cost effectiveness. Deterioration of concrete due to sulphate attack is a major durability problem for structures exposed to sulphate-rich soil and groundwater such as septic tanks, sewage pipes and water treatment plants. Under continuous exposure to a sulphate-rich environment, concrete loses its strength and durability resulting in a reduction of the designed service life. The widespread occurrence of sulphate attack and the destruction caused by it have attracted researchers over the years into the study of the deterioration mechanism and methods to combat it. However, different theories about the mechanism still exist and the mechanism is not yet well understood.

In Victoria, sewage is treated either through reticulated systems or individual on-site (non-reticulated) systems. A reticulated system comprises a network of collection pipes, sewer mains and pumping stations that transport wastewater to a treatment plant. On-site systems stand alone, and all waste should be treated and contained on-site, within the property boundaries. The septic tank is the most common type of on-site system. Septic tanks have been extensively used since the 1950s, when they were an approved method of sewage disposal for domestic properties. In 1973, a planning directive from the then Melbourne and Metropolitan Board of Works required all new
subdivisions and developments to contain their waste on-site or connect to the sewer. At this time, the number of backlog properties in Melbourne peaked at 173,000. Backlog properties are the properties identified as requiring reticulated sewerage disposal but still using septic tanks. Across Victoria, around 250,000 septic tanks are currently in use. A centralized concrete pipe sewerage system was started in Melbourne in early 1892. The septic tank sewerage system was first introduced in Melbourne in early 1939 to cover the more spacious outer suburbs such as the Mornington Peninsula. Construction of this initial system was the envy of other towns. By the early 1960s, problems of water pollution caused by the waste from septic systems led to the formation of a number of sewerage authorities in the city. These sewerage authorities soon began replacing septic systems with reticulated sewerage systems. Australia's major urban water authorities are currently responsible for 89,500 km and 81,000 km of water and sewer pipelines respectively. In country Victoria and some metropolitan areas there are places where the households are still not connected to the main sewer pipeline. For example, statistics from Manningham City Council indicate approximately 4620 properties in Manningham are not connected to a sewer. These properties utilise septic tank systems to treat domestic wastewater. Of these, approximately 60% of properties discharge treated effluent directly to storm water, with the remaining 40% of properties containing effluent on-site using absorption trenches or other methods of irrigation. There are other city councils where there are a good number of properties not connected to main sewers. Such unsewered developments in Australia use septic tank systems to treat and dispose of sewage. In many cases these septic tanks are not replaced after being installed on site. Hence some sewers are more than half a century old. Currently, an estimated 42,000 properties are included in the metropolitan backlog program, with cost estimates in the order of $550 million for the provision of new infrastructure and a 40-year time frame (CAMERON, 2006). The equivalent numbers, costs and time frames for rural properties are unknown.
In much of the research literature, the deterioration of concrete in sulphate environment is categorized as two phenomena: chemical sulphate attack and physical sulphate attack (Neville, 2004, Santhanam, August 2001). However, some researchers like to classify them as internal and external sulphate attack. Deterioration of concrete sewerage pipes also takes place due to microbially-induced concrete corrosion (MICC) which is also called internal acid attack. Researchers have observed extensive MICC in sewers, in both pipes and at pipeline junctions (Cho and Mori, 1995, Diercks et al., 1991, Mori et al., 1992, Parker, 1945). Since these initial reports of corrosion in sewage collection systems, MICC has been shown to occur in other types of concrete facilities. Some of these are wastewater treatment facilities (Redner et al., 1991) swimming pools (Chandra and Berntsson, 1988), cooling towers (Zherebyateva et al., 1991), and hydraulic facilities (Zherebyateva et al., 1991). The most rapid cases of deterioration occur in areas with elevated hydrogen sulphide (H$_2$S) concentrations, moisture, and oxygen in the atmosphere. These conditions are commonly found in sewage collection systems.

Sulphate attack in concrete is a complex phenomenon whereby sulphate mainly reacts with the hydration products of cement. The primary products of sulphate attack in concrete are gypsum and ettringite. There is a controversy concerning the role of gypsum in concrete deterioration by sulphate (Tian and Cohen, 2000a). Decalcification of calcium silicate hydrate (C-S-H) gel and deterioration of the cementitious structure occur at the second stage. Deterioration of concrete by sulphate attack is found to be irregular in nature and varies with the type of sulphate solution containing different cations (Torii and Kawamura, 1994a, Santhanam et al., 2001b). The results also change with some other parameters such as permeability, initial curing condition, cement type and content and temperature (Khatri et al., 1997, Mangat and Elkhathib, 1992).
Naturally present sulphur in source water in the form of sulphates or sulphides can be transformed into hydrogen sulphide ($H_2S$) by the anaerobic bacteria present inside the pipe (Islander et al., 1991, Roberts et al., 2002). If this $H_2S$ is exposed to either oxygen in incoming water, oxidising bacteria or air present in the tank, it is converted into sulphuric acid ($H_2SO_4$). Conversion is accelerated by the presence of oxidising bacteria, which grow and attach themselves to the surface of the concrete. Sulphuric acid is highly reactive and reacts with the calcium compounds in the concrete, resulting in deterioration of the surface. This deterioration involving bacteria is named biogenic sulphuric acid corrosion of concrete or acid attack in concrete. The detrimental effect of corrosive sulphuric acid attack on concrete in sewers can be of the order of several mm per year (Mori et al., 1991). A similar type of attack is expected in septic tanks.

In country Victoria septic tanks installed prior to 1980 could be in a critical condition after experiencing severe sulphate attack for a long time. These tanks should be now assessed to predict their remaining service life to ensure that environmental contamination does not occur. Regular inspection and monitoring is essential to avoid costly and environmentally-damaging collapses and spills from septic tank systems. Sewage and effluent can contain a variety of human disease-causing micro-organisms and parasites. Disease can be spread to humans from this material by direct contact or indirectly by consumption of contaminated food or water. However, there is no precise methodology to inspect concrete septic tanks to locate cracks and deterioration inside the tanks. No reported work has covered concrete septic tank deterioration under sulphate exposure. From the literature on concrete sewerage pipes an initial idea of the deterioration process can be established. However, the internal environment of septic tanks would have less oxygen than sewer pipes where half-filled gravity flow allows a continuous flow of oxygen.
1.2 Aims and Objectives

The research presented in the thesis was conducted to establish the life expectancy of concrete septic tanks located in rural Victoria, when exposed to external and internal environments encountered in practice.

The major objectives of the work can be summarised as to:

a. Develop a method of accelerated testing to ascertain deterioration of concrete septic tanks.

b. Establish parameters affecting the deterioration of concrete septic tanks.

c. Identify types of concrete used in septic tanks in country Victoria and assessing the structural conditions of concrete, which includes testing concrete in the laboratory with established aggressive environments found within the septic tanks.

d. Conduct accelerated tests in the laboratory.

e. Develop a model for predicting the remaining life of concrete in terms of deterioration of concrete under the aggressive environment conditions of sulphate found in septic tanks.

f. Support the developed model with data from field samples.

1.3 Outline of the Thesis

This dissertation is organized into the following chapters, with additional detailed information included as appendices:

- Chapter 2 presents a review of existing literature on sulphate attack on concrete.
- Chapter 3 describes the planning of the research project, the properties of the various materials used in the project as well as the experimental schedule and procedures.
• Chapter 4 summarizes the findings of various microstructural investigations on concrete exposed to sulphate-rich environments. The results of different laboratory tests are also described in this chapter.
• Chapter 5 describes the findings of concrete deterioration in sulphuric acid environments.
• Chapter 6 presents the development of a model to predict life expectancy and its validation using field samples.
• Chapter 7 briefly summarizes the main conclusions from this study and highlights additional research needs that were beyond the scope of this project.
Chapter 2

Previous Work

2.1 Introduction

The deterioration of concrete exposed to sewerage may be caused by chemical and physical processes or their combination as a result of exposure to sulphate and sulphuric acid. Sulphate attack represents a major challenge. The sources of sulphate can be internal, such as delayed ettringite formation (DEF) or external, and the manifestations of distress can either be chemical or physical in nature. The objective of the work presented in this thesis is to understand the deterioration mechanisms of concrete septic tanks when exposed to sewerage. In order to achieve this it is important to understand the underlying chemical reactions and the current state-of-the-art knowledge on deterioration of concrete when exposed to sulphates. In this chapter a review of the existing theories and hypotheses about sulphate attack on concrete is presented. A brief discussion of different forms of sulphate attack and their consequences along with the chemical reactions are presented.

In planning the experiments, the understanding of the possible mechanisms of deterioration established in this chapter were utilised. In addition, a review of predictive models which have been developed to predict the deterioration of concrete sewer pipes is also presented.
2.2 Mechanism of Sulphate Attack

2.2.1 What is Sulphate Attack

The chemistry of sulphate attack is complex and involves numerous overlapping reactions. Because of this complexity, one of the problems encountered in the relevant literature on concrete durability is the question of the definition of sulphate attack. *Sulphate attack* is the term used to describe a series of chemical reactions between sulphate ions and the components of hardened concrete, principally the cement paste, caused by exposure of concrete to sulphates, oxygen and moisture (Skalny, 2002). In many research papers, the deterioration of concrete in sulphate environments is categorized as two phenomena: chemical sulphate attack and physical sulphate attack (Neville, 2004, Santhanam, August 2001). However, some researchers like to classify these as internal and external sulphate attack respectively. As is the case with other aggressive chemicals, sulphates are potentially most deleterious to concrete when present in gaseous or liquid form, the latter situation being the most common; attack by solid sulphate-containing chemicals is rare. One school of research considers sulphate attack to have taken place if sulphates are involved, regardless of the mechanisms of deterioration (Neville, 2004). The other school of research limits the concept of sulphate attack to the consequences of chemical reactions between sulphate ions and hydrated cement paste, so that chemical changes in the paste take place. However, if sulphates interact with cement and cause damage to it, but the action is physical, and a similar action can occur with salts other than sulphates, then the damage is considered to be a physical attack or physical sulphate attack (Neville, 2004).

2.2.2 Chemical Sulphate Attack

According to ACI’s Guide to Durable Concrete (ACI 1992), there are two mechanisms that can be considered to be sulphate attack: formation of gypsum and formation of ettringite (Skalny, 2002). Chemical sulphate attack is considered to be the result of
chemical reactions involving sulphate anion, $\text{SO}_4^{2-}$. Some of the visible examples of damage caused by reactions of concrete components with sulphates include spalling, delamination, macro cracking and, possibly, loss of cohesion. All of these phenomena are consequences of chemical processes invisible to the naked eye, including adsorption–desorption phenomena, dissolution–precipitation of colloidal and crystalline phases and recrystallization. The primary products of chemical sulphate attack in concrete are ettringite and gypsum, due to the chemical reaction between sulphate solutions and the cement hydration products. Sodium sulphate reacts with calcium hydroxide to form calcium sulphate, better known as gypsum according to Equation 2.1. Depending on the surrounding environmental conditions, these reactions proceed to a greater or lesser extent. In flowing water conditions with a constant supply of sulphate ion which also ensures removal of calcium hydroxide, the reactions may continue until all calcium hydroxides are leached. On the other hand, in a steady environment with the presence of a fixed amount of sulphate the reaction may reach equilibrium. There is a controversy regarding the expansion theory of concrete due to the formation of gypsum (Tian and Cohen, 2000a). According to Tian and Cohen (2000b) (Tian and Cohen, 2000b) gypsum formation is expansive in nature and the tensile stresses during gypsum formation may be the cause of expansion and subsequent cracking. However, some other researchers do not agree with this theory and have found no evidence of expansion during the formation of gypsum (Mather, 1997).

\[ \text{Ca(OH)}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} + 2\text{NaOH} \text{ Gypsum} \]

\[ 4\text{CaO.Al}_2\text{O}_3\cdot13\text{H}_2\text{O} + 3\text{CaSO}_4\cdot2\text{H}_2\text{O} + 14\text{H}_2\text{O} \rightarrow 3\text{CaO.Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O} \text{ Ettringite} \]

\[ 2\text{Na}^+ + \text{SO}_4^{2-} + 10\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O(solid)} \text{ } \]
Calcium sulphate or gypsum can subsequently react with hydrated calcium aluminates (4CaO Al₂O₃ 13H₂O), hydrated calcium sulfoaluminates (4CaO Al₂O₃ SO₃ 12-18H₂O) or unhydrated tricalcium aluminate (C₃A) to produce ettringite (3CaO.Al₂O.3CaSO₄.32H₂O) according to Equation 2.2. Ettringite is said to be expansive in nature, though the expansion mechanism is not yet fully understood (Mehta, 1983a, Cohen, 1983b). Some researchers do not agree with the theory that ettringite formation is expansive (Odler and Gasser, 1988a). The most accepted theory is that the expansion is due to crystal growth pressure during the formation of ettringite. Another theory is based on the swelling of ettringite by water absorption (Cohen, 1983b). Ettringite is unstable in low pH (11.5 – 12.0) at high sulphate concentrations (Biczok, 1967a). When pH falls to such low values ettringite may break down to form gypsum (Santhanam, 2001). There is another term related to the deterioration of concrete in sulphate environment: delayed ettringite formation (DEF). DEF is the formation of ettringite in a cementitious material by a process that begins after significant completion of hardening and in which expansion of concrete occurs in the absence of external sulphates (Taylor et al., 2001).

The secondary effect of chemical sulphate attack is the decalcification of C-S-H gel and loss of cementitious structures of concrete which begins in low pH (<10) environments. This secondary effect of decalcification of C-S-H gel is found only when Mg is present as a cation in the solution (Jan Skalny, 2002). Thaumasite is also formed during sulphate attack at low temperatures (0 to 5 °C). Thaumasite formation occurs as a result of the reaction between C-S-H gel and SO₄²⁻, CO₂ or CO₃²⁻ and water. Thaumasite has also been reported to form as a result of the interaction of ettringite with the C-S-H gel in the presence of CO₂.
2.2.3 Physical Sulphate Attack

Physical sulphate attack, also called sulphate salt crystallization or salt hydration distress, usually occurs due to repeated crystallization and recrystalization from sodium sulphate decay-hydrate into sodium sulphate anhydreite and vice versa, as per Equations 2.3 and 2.4 (Jan Skalny, 2002). This temperature-dependent process of crystallization-recrystallization of sodium sulphate solution may occur within the concrete matrix, which leads to the fatigue of the cement paste and consequently loss of cohesion and mass.

A common form of physical salt attack in concrete occurs when sodium sulphate penetrates into concrete and phase changes occur between anhydrous sodium sulphate (thenardite) and decahydrate sodium sulphate (mirabilite). These phase changes, typically triggered by changes in temperature, lead to significant crystallization pressures that can impart stresses and cracking in concrete. Neville (2004) reported that this transformation of thenardite to mirabilite can result in tensile hoop stresses the range of 1450-2900 psi (10-20 MPa). This stress is quite high and could easily damage concrete (Neville 2004). The tensile strength of normal strength concrete is around 3 to 5 Mpa.

Folliard and Sandberg (1994) proposed that crystallization of sodium sulphate within concrete, triggered by temperature changes, was the predominant cause of distress due to physical salt or sulphate attack.

Since the 1940s, the Portland Cement Association (PCA) has studied the long-term durability of concrete specimens stored in outdoor environments in Sacramento, California. The PCA study has included four research phases since its inception and has focused on the areas of cement content, cement composition, cement types, water to cementitious ratio (w/c), and various types of coatings. The fourth phase, initiated in
1982, included research on mineral admixture replacements, w/c, and coatings. Concrete beams measuring 6 in x 6 in x 30 in (150 mm x 150 mm x 760 mm) were cast and shipped to Sacramento, California one year after being cast. The beams were then halfway submerged in soil containing 10% sodium sulphate. The beams were annually inspected and assigned a rating between 1-5, with 5 indicating the most severe deterioration (Stark, 1989). The first PCA bulletin report in 1989 reported that the most important parameter influencing sulphate resistance was the w/c of concrete (Stark, 1989). It was also reported that cement type (e.g., Type I vs. Type II vs. Type V) had minimal influence on sulphate resistance for concrete mixtures with either low or high w/c, but a significant difference was noted for mixtures with intermediate w/c values. Interestingly, mixtures containing fly ash or GGBFS showed reduced sulphate resistance in 29 of 30 mixtures, when compared to a control mixture. Beams with coatings were reported to behave well, but it was proposed that this protection may only be temporary as the epoxy coating showed signs of peeling away from the concrete (Stark, 1989). The distress reported in concrete beams was attributed to external, chemical sulphate attack in the 1989 bulletin, and there was no mention of other distress mechanisms.

In 2002, a second bulletin on the PCA site determined that damage to the concrete beams was only occurring above the soil level, and that very little damage was reported below ground or in parallel tests in which beams were stored indoors (without substantial variations in temperature). Stark (2002) proposed that the main mechanism of distress was physical sulphate (or salt) attack, a form of distress that had been identified as being a key deterioration factor in various papers published between the 1989 and 2002 PCA bulletins. The main findings from the 2002 bulletin suggest that physical sulphate attack is a much more significant form of distress in field concrete than had been previously reported and the overall topic of sulphate attack is even more complex than ever.
2.2.4 Biogenic Sulphuric Acid Attack

Another form of sulphate attack is acid attack which mainly occurs in sewage and water treatment plants. Naturally-present sulphur in source water in the form of sulphates or sulphides can be transformed into hydrogen sulphide (H$_2$S) by the anaerobic bacteria present inside a sewer (Islander et al., 1991). If this H$_2$S is exposed to either oxygen in incoming water, oxidising bacteria or air present in the tank, it is converted into sulphuric acid (H$_2$SO$_4$). Conversion is accelerated by the presence of oxidising bacteria, which grow and attach themselves to the surface of the concrete. Sulphuric acid is highly reactive and reacts with the calcium compounds in the concrete, resulting in deterioration of the surface. This deterioration process involving bacteria is named biogenic sulphuric acid corrosion of concrete or acid attack in concrete. The detrimental effect of corrosive sulphuric acid attack on concrete in sewers can be of the order of several mm per year (Mori et al., 1991). The deterioration of concrete by sulphuric acid within septic tanks is primarily due to corrosion caused by hydrogen ion attack followed by sulphate ion attack similar to that of external sulphate attack. Sulphuric acid reacts with free lime [Ca(OH)$_2$] in the concrete and forms gypsum. Some researchers have reported that this gypsum produces a corroding layer on the concrete surface (M. Atkins, 1992, Monteny et al., 2000). However, most other researchers oppose this. According to other researchers, newly-formed gypsum through sulphuric acid attack softens the concrete by leaching of charge-compensating cations and ejection of tetrahedral aluminum with no gypsum deposition (Allahverdi and Skvara, 2006). This biogenic corrosion of concrete in sewer pipes is a combination of sulphate-acid attack. The corrosion rate depends on the rate of biogenic acid production, which is directly related to the presence of Thiobacilla bacteria which transform sulphur into sulphuric acid inside the sewer networks, and the amount and flow conditions of the sewage in a pipe.
Thiobacillus thiooxidans is a sulfur-oxidizing bacterium that produces sulfuric acid. The sulfuric acid can then react with the highly alkaline concrete, forming materials, such as ettringite and gypsum, that provide little or no structural support to the concrete pipe.

Parker (1947) isolated *Thiobacillus concretivorus* (*thiooxidans*) from the corroded layer of concrete and concluded that microbial activity was the cause of the deterioration of the concrete. Since Parker’s initial study, numerous other sulfur-oxidizing bacteria have been determined to be involved in the corrosion process (*T. thioparus*, *T. novellus*, *T. neapolitanus*, *T. intermedius*) (Parker, 1947; Islander et al., 1991).

This microbiologically-influenced corrosion (MIC) in concrete sewer pipes is a problem that has been shown to cause degradation and eventual failure of concrete. MIC is caused by sulphuric acid generated by a very complex microbial ecosystem existing along the inner surface of the concrete pipe. This ecosystem is created by the interactions inside the sewer pipe between the ambient environment (temperature, humidity), the sewer stream (flow rate, chemical makeup), and the composition of the concrete itself. Due to the growth of various strains of bacteria, there is a macroscopic reduction of the pH on the exposed inner surfaces of the concrete that steadily occurs, thereby causing the normally alkaline surface of the concrete to slowly become acidic. Immediately after the pipe is produced, its surface begins to carbonate. The carbonation process lowers the pH to a level that will allow microbial life to be sustained (Daczko et al., 1997). Once the pipe is placed into service, a succession of bacteria, each of which flourishes at a given pH, begins to grow. As a result, the pH of the concrete surface is systematically lowered by each bacterium, which produces the sulphuric acid necessary to alter their environment and promote the subsequent growth of the next bacterial strain in this biological succession. Over time, the local pH near the concrete surface decreases from highly alkaline to highly acidic.
The corrosion process is initiated by the conversion of sulphate to sulfide in the sewage by sulphate-reducing bacteria. Sulfide then forms either bisulfide or hydrogen sulfide based on the pH equilibrium (pKa₁=7.1, pKa₂=14). Because sewage is typically acidic, hydrogen sulfide will predominate. Hydrogen sulfide is typically a gas at the temperature and pressure normally associated with sewer conditions and partitions primarily into the gaseous phase. Another factor that can contribute to this partitioning into the gaseous phase is turbulent flow of the sewage. Concrete initially exhibits pH in the range of 11-13, which is too alkaline for the growth of most bacteria. The initial step in reducing the pH involves the abiotic neutralization of the concrete. This neutralization is brought about by reaction of the cementitious material and carbon dioxide, also known as carbonation (Ismail et al., 1993), or reaction with other acidic gases that may be present, such as hydrogen sulphide. This abiotic neutralization can reduce the pH of the concrete to as low as nine. Islander (1993) grew various thiobacilli in laboratory cultures and developed a theory which suggests that neutrophilic thiobacilli can grow at pH 9 and further reduce the surface pH to four. At this lower pH, bacteria that are capable of producing vast amounts of sulfuric acid can flourish (T. thiooxidans). These can further reduce the surface pH to one or two.

2.3 Deterioration from Sulphate Attack

2.3.1 Formation of Ettringite

2.3.1.1 Mechanism of Ettringite Deterioration

Ettringite is a complex mineral that forms due to the reaction between calcium, aluminium and sulphate. Ettringite naturally forms during the early hydration process of cement, while the concrete is still plastic. Formation of ettringite at early stages of hydration is not harmful to the concrete; rather it works as a skeleton providing early stage strength (Ramadan, 2000). The early ettringite may decompose and reform at a
later stage, after months or years, a process which is called delayed ettringite formation (DEF).

Two possible mechanisms have been suggested for the reactions between ions in pore solutions and cement paste components to form ettringite. They are topochemical (Chatterji and Jeffery, 1963, Cohen, 1983a) (replacement of pre-existing mineral phases) and through solution (Chatterji, 1976, Fu et al., 1997) (direct precipitation from solution). Hansen (1976) concluded that ettringite must have formed by a topochemical reaction because tricalcium aluminate does not dissolve in an aqueous medium and, consequently, could not be an aluminum ion source. He proposed that ettringite forms radially around residual topochemically-reacting C\textsubscript{3}A particles (Cohen, 1983a). If the ettringite-forming reaction is topochemical, then there should be a definite relationship between the crystal structures of the reacting particles and that of ettringite (Mehta, 1976b, Mehta, 1976a). Because of large differences in the crystal structures of ettringite (hexagonal) and anhydrous calcium aluminate (C\textsubscript{3}A; cubic) or tetracalcium monosulfoaluminate (C\textsubscript{4}A\textsubscript{3}S; hexagonal), the topochemical reaction is considered by many researchers to be kinetically difficult at normal temperatures (Deng and Tang, 1994, Mehta, 1983b). Mehta (Mehta, 1976b) believed that the formation of ettringite on the surfaces of reacting particles and its random deposition in other locations is an indication of a through solution mechanism for precipitation rather than a topochemical one. Deng and Tang (1994) assumed that the bonds of Ca–O and Al–O of aluminate are broken when polar H\textsubscript{2}O molecules and/or OH\textsuperscript{−} ions interact with aluminate particles, and eventually, Ca\textsuperscript{2+} and Al(OH)\textsuperscript{4−} ions form in pore solutions. As a result of reactions between these ions and SO\textsubscript{4}\textsuperscript{2−} ions in solution, secondary ettringite preferentially precipitates in open spaces, such as voids and cracks as needle-like (acicular) crystals, whenever pore solutions are critically supersaturated (Fu et al., 1995, Mehta, 1976b). Fu and Beaudoin (1995;1996) concluded that ettringite crystallization rates are
controlled by the degree of supersaturation required to form critical sized nuclei of ettringite.

2.3.1.2 Delayed Ettringite Formation (DEF)

Delayed ettringite formation may be defined as the formation of ettringite in a cementitious material by a process that begins after hardening is substantially complete and in which none of the sulphate comes from outside the cement paste (Taylor et al., 2001). Ettringite formed in cementitious materials can be partially or fully destroyed if the material is heated at elevated temperature above 70°C. Ettringite can re-form gradually in the concrete after a period of time when the concrete is stored at room temperature in a moist atmosphere and this process is called DEF. Sometimes it is also referred to as secondary ettringite formation. DEF can produce expansion and destruction of concrete.

The mechanism of ettringite causes expansion is a controversial issue. There are two principal theories; the ettringite crystal growth theory and the uniform paste expansion theory (Ludwig, 1987). The ettringite crystal growth theory attributes the expansion to the pressure exerted by the growth of ettringite crystals in the micro-cracks between the cement paste and aggregate which widens the cracks and causes expansion. The uniform paste expansion theory suggests that DEF expansion is caused by the uniform expansion of the cement paste leaving gaps around the aggregate. Newly crystallizing ettringite fills the gaps produced by this expansion, resulting in ettringite band formation. In this case, ettringite band formation does not contribute directly to the expansion. According to the researchers the width of the ettringite bands around the aggregate is proportional to the size of the aggregate and this is attributed to uniform paste expansion.

The exact mechanism of DEF is a controversial issue. The presence of insoluble sulphate in cement clinker has been reported as a potential cause of DEF by many
researchers (Day, 1992). Other researchers including (Diamond, 1996) concluded that high temperature curing causes the primary ettringite formed during the initial cement hydration to break down and reform at a later stage after the concrete has hardened. Alcali silica reactions (ASR) or other micro-cracking-based mechanisms have also been suggested as potential causes of DEF.

2.3.1.3 Damage Due to DEF

According to Day (Day, 1992), the earliest possible reported damage to cast-in-place concrete by DEF was observed by Kennerley in 1965. Kennerley investigated a deteriorated cold-joint in the Roxburgh Dam in Otago, New Zealand and noticed a white deposit, ettringite. In 1980, Pettifer and Nixon recorded several cases of concrete deterioration possibly caused by ettringite. These cases included concrete bases of substations in the English midlands and the Pirow Street Bridge in Cape Town, South Africa. The pores and voids of the substation concrete were filled with ettringite, even though there was a minimal amount of sulphates in the soil. The Pirow Street Bridge showed cracking only four years after completion and required repairs after nine years. The concrete was composed of reactive aggregates and low alkali cement. Also in the early 1980s, Volkwein was examining 12 to 80-year old concrete bridges for carbonation, chloride penetration, deterioration and corrosion. Volkwein (1980) found needle-shaped crystals in cracks and around aggregates in concrete contaminated by Cl ions. He concluded that, since the sulphate content did not change in the concrete, the chloride ions caused the formation of the ettringite. This conclusion is contradictory to the laboratory results of Attiogbe (1990), who found that DEF would not form in concrete prisms soaked in sodium-chloride solution.

Premature cracking was first noticed in pre-cast concrete in railway ties and cladding panels in Germany and Scandinavia during the 1960s and 1970s. The cracking initiated at the corners and edges of the panels and migrated into the interior. Studies
indicated the cracking occurred due to frost, loads, and premature or improper heating. These migrating cracks caused a separation of the aggregates and cement matrix. Petrographic examination confirmed the existence of ettringite crystals in the cracks. Heat-treatment was the likely cause of failure of the ties in Germany. A Research Institute (1990) report noted that heat treatment had two major impacts: (1) inadequate pre-treatment allowed internal damage through debonding of the aggregate and cement matrix, and (2) heat treatment interrupted the normal formation of ettringite which eventually continued when the concrete hardened. The Scandinavian ties were fabricated with high early strength cement and cured at 75-85°C. A report by Tepponen (1987) noted visible damage after 15 years and thin section analysis revealed ettringite in the cracks. However, subsequent studies concluded that poor frost resistance and not ettringite was the main reason for the deterioration. Furthermore, publications and experiments by Hienz and Ludwig (1987) noted damage to pre-cast units manufactured with high-early-strength cement and heat treatment during production. They noticed that damage always occurred on units exposed to the weather and subjected to moisture saturation. They concluded that the damage was caused by the reformation of ettringite in hardened concrete following heat-treatment.

2.3.2 Thaumasite form of Attack

Thaumasite formation has often been confused with ettringite formation due to the close chemical composition of the expansive phases (Drimalas, 2007). Thaumasite formation is known to occur when C-S-H is in contact with either calcium, carbon dioxide, carbonates, sulphates, or moisture at temperatures between 32-59 ºF (0-15 ºC) (Bensted, 1999b). Thaumasite (CaSiO₃·CaCO₃·CaSO₄·15H₂O) belongs to the family of ettringite-type crystal hydration products. Its crystalline structure, X-ray diffraction (XRD) pattern, microstructural features and many of its optical properties are similar to those of ettringite (Yang and Buenfeld, 2000). Such similarities create difficulties in
differentiating thaumasite and ettringite. Optical microscopy and XRD analysis (Crammond, 1985) may be used to identify thaumasite in large quantities in a concrete sample. However, for samples with thaumasite present at relatively low levels or concentrated in small areas, the usefulness of optical microscopy is limited by its resolution. The d-spacings of thaumasite (Powder diffraction file 25-127, JCPDS) and ettringite (Powder diffraction file 9-414, JCPDS) are sufficiently similar that the XRD peaks of thaumasite in small quantity may be overwhelmed by the adjacent strong peaks of ettringite. Consequently, the identification of thaumasite by XRD analysis is difficult, and especially so at low thaumasite or high ettringite content.

It has been found that thaumasite is more stable at lower temperatures. It has been suggested by Bensted (Bensted, 1999a, Bensted, 2000) that silicon tends to adopt the octahedral co-ordination found in thaumasite more easily at lower temperatures. Nevertheless, thaumasite is formed also at temperatures around 20 °C and above, as reported for buildings in Southern California (Diamond, 2003) and Italy (Collepardi, 1999). Once thaumasite has formed it remains stable up to 30 °C (Macphee and Diamond, 2003).

Thaumasite has been found in cement systems with both high and low C₃A contents (Blanco-Varela et al., 2006, Brown and Hooton, 2002, Nobst and Stark, 2003). Thaumasite itself contains no alumina but it has been proposed that the presence of aluminium promotes thaumasite formation (Nobst and Stark, 2003). In contrast, Blanco-Valera et al. (Blanco-Varela et al., 2006) found that low C₃A cements produce higher amounts of thaumasite.

The formation of thaumasite needs a source of carbonate which can be supplied from the limestone contained in the cement itself, from carbonate-containing aggregates, ground waters, soils or the air (CO₂). The presence of limestone used as filler in cement has been found to influence the type of AFM phase present; monocarbonate
(C$_3$A · CaCO$_3$ · 11H$_2$O) forms instead of monosulphate (C$_3$A · CaSO$_4$ · 12H$_2$O) in the presence of calcite (Kuzel and Pöllmann, 1991).

Thaumasite has been observed in the presence and absence of portlandite (Ca(OH)$_2$). It has been found that alkaline conditions (pH $\geq$ 12.5) enhance thaumasite formation (Hobbs and Taylor, 2000), while during strong leaching at low pH levels (pH $\leq$ 8.0) gypsum becomes the dominant sulphate phase and the amount of thaumasite decreases (Zhou et al., 2006). However, Gaze and Crammond (Gaze and Crammond, 2000) showed that once thaumasite forms, it remains stable at pH levels as low as 6–8.

Beside needing a source of carbonate, high amounts of sulphate are a prerequisite for the formation of thaumasite. It has been found that both the addition of gypsum (Gaze, 1997) or the presence of a sulphate rich solution can lead to thaumasite formation in carbonate containing cements.

However, the exact mechanisms of thaumasite formation are still not known in detail.

2.3.3 Formation of Gypsum

2.3.3.1 Controversy Regarding Role of Gypsum

Work on sulphate attack conducted by Thorvaldson et al. (1945) during the early part of the last century has been described by Hansen and Tian (Hansen, 1966, Tian and Cohen, 2000a). Thorvaldson et al. used mortar-bar specimens made of one part C$_3$S with five parts sand and others made of one part C$_2$S with five parts sand. Thorvaldson et al. found that mortar expanded less than 0.01% after 22 years exposure in 2% Na$_2$SO$_4$ solution. However, in 8% Na$_2$SO$_4$ solution, the mortar began to expand slowly after 3 years and reached an expansion of 0.9% at the end of 22 years. They concluded that this expansion was attributed to a slow alkali-silica reaction on the quartz sand and the specimens expanded no more than those stored in water.
Hansen (Hansen, 1966, Hansen, 1963) presented a possible scenario about the role of gypsum formation during sulphate attack. He pointed out that if gypsum formation is expansive, the source of expansion should be due to volume increase during the reaction of CH with sulphate ions to form gypsum. He did not believe that the gypsum generated by a through-solution mechanism can form solid reaction products in a capillary cavity to occupy a larger volume than that of the cavity plus the volume of the solid CH that dissolves and takes part in the reaction. If the gypsum formed in a capillary cavity occupies a larger volume than that of the cavity plus the volume of the solid CH consumed in the reaction, it is only possible when gypsum crystals form in situ or on the surfaces of CH particles (i.e., by topochemical reaction). He also believed that the precipitation of gypsum in the gel pores may not cause swelling of the pores by absorbing water, since the surface of the gypsum formed may not be appreciably greater than that lost by the dissolution of CH crystals. He noted that if there is a force exerted, it is due to hydraulic pressure but not due to crystal growth.

Mather (Mather, 1996) does not believe that gypsum formation is always destructive. He also does not agree that gypsum formation during sulphate attack on cement paste causes expansion. He supports Hansen's theory and points out that gypsum formation results primarily from the reaction of sulphate ions and calcium ions by a through-solution mechanism. Gypsum forms from the supersaturated solution by evaporation and subsequent precipitation. During this process, no expansion would be expected. Mather, (1996) uses an analogy to support his argument: “You cannot break a bottle full of saturated solution by removing the cork and letting the water evaporate.”

2.3.3.2 Literature Supporting that Gypsum Formation is Expansive

Mehta (Mehta, 1992) stated that gypsum formation causes expansion and spalling based on his experimental study on alite paste. However, in his testing (Mehta et al.,
1979) alite mortar prisms were exposed to a 10% sulphate solution (5% Na₂SO₄ + 5% MgSO₄) and only short-term (75 days) expansion data were provided. The data showed no obvious expansion. The long-term results showed that the loss of adhesion and strength was more evident than expansion.

Nielsen (Nielsen, 1966) conducted microscopic examination of thin sections of cement paste exposed to each of 0.07 M Na₂SO₄, MgSO₄, and FeSO₄ solutions for 2 months. He gave no information on the C₃A content of the cement. He found that gypsum was the predominant reaction product, while ettringite was rarely formed in an amount sufficient to be reasonably considered as a source for the formation of cracks. In Na₂SO₄ solution, the ettringite crystals found in cracks formed after the occurrence of the cracks.

Bonen and Cohen (Bonen and Cohen, 1992a, Bonen and Cohen, 1992b) conducted microstructural analyses on Portland cement paste exposed to magnesium sulphate solution for one year. They observed the formation of a “surface double-layer” that was composed of brucite and gypsum layers and a sequential formation of inner layers of gypsum, similar to the occurrence of lisegang bands. Ettringite and monosulphate were found only in minor amounts.

Bonen and Sarkar (Bonen and Sarkar, 1993) studied the replacement of portlandite by gypsum in the interfacial zone (a zone between the aggregates and bulk paste) along the boundaries of the aggregate particles. They found that thick deposits of gypsum up to 50 μm wide precipitate by a through-solution mechanism. The crystallization pressure of gypsum produced tensile stresses and caused disruptive expansion. Their conclusion contradicted Hansen’s (Hansen, 1966) suggestion that gypsum forming by a through-solution mechanism cannot cause expansion.
Yang et al. (Yang et al., 1996) also studied the process of sulphate attack and the role of the interfacial zone during the attack process. Their conclusion is similar to that of Bonen and Sarkar’s (date) that sulphate reacts with CH and AFM in the interfacial zone, leading to expansion and cracking.

Wang (Wang, 1994) reported the results of X-ray diffraction (XRD) examination of the solid phases present at different depths in Portland cement paste attacked by Na_2SO_4 solution. He considered that more physical damage was caused by the formation of gypsum than by the formation of ettringite.

Gonzalez and Irassar (González and Irassar, 1997) investigated the sulphate attack mechanism on four cements with low-C_3A content (three cements containing 0% C_3A, and one cement containing 1% C_3A). The C_3S content in these cements varied from 40 to 74%. Their data showed greater expansion for the cement mortar specimens with higher C_3S content. The mortar made with 74%-C_3S cement reached an expansion of 0.112% after 180 days of exposure. Their XRD analysis showed that gypsum had formed in those specimens after 90 days of sulphate immersion. These gypsum peaks may suggest a correlation between expansion of the specimens and gypsum formation. However, they still attributed the expansion to the formation of ettringite, which was only observed by XRD in those specimens after 360 days of sulphate exposure. Gonzalez and Irassar (González and Irassar, 1997) concluded that “The great expansion was measured for high C_3S-content cement and the expansive formation of ettringite in this case was attributable to localized gypsum formation.”

Ping and Beaudoin (Ping and Beaudoin, 1992a, Ping and Beaudoin, 1992b) suggested a theory based on the principles of chemical thermodynamics. They pointed out that the expansive force resulted from crystallization pressure. There are two conditions for the occurrence of crystallization pressure: (1) the solid product should form and grow in
a confined space; (2) the activity product of reactants in the pore solution should be greater than the solubility product of the solid products under atmospheric pressure. Theoretically, any solid product—not only ettringite—may produce crystallization pressure and cause expansion if the above two conditions are met. They suggested that in theory gypsum formation can be one of the principal causes of expansion during sulphate attack.

2.4 Parameters Affecting Sulphate Attack

2.4.1 Cation Type

The complexity of sulphate attack begins first with the variety of sulphates that can damage concrete. The most common sulphates that interact with concrete are calcium, sodium and magnesium sulphate, which are listed in order of their aggressiveness. Calcium sulphate (gypsum) is generally believed to be the least aggressive of the three sulphates, mainly due to its lower solubility. The solubility of gypsum is approximately 1440 ppm, which is significantly less than that of sodium sulphate and magnesium sulphate. Specifically, as shown in Equation 2.5, calcium sulphate will react with monosulfoaluminate and water to form ettringite, which can result in expansion and cracking. Calcium sulphate also reacts with tricalcium aluminate to form ettringite, as shown in Equation 2.6.

\[
\begin{align*}
C_{3}A\left(C\overline{S}\right)H_{12} + 2C\overline{S}H_{2} + 16H & \rightarrow C_{3}A\left(C\overline{S}\right)H_{32} \quad \text{...2.5} \\
C_{3}AH_{4} + 3C\overline{S}H_{2} + 12H & \rightarrow C_{3}A\left(C\overline{S}\right)H_{32} \quad \text{...2.6}
\end{align*}
\]

Where C is CaO, A is Al₂O₃, \(\overline{S}\) is SO₃, and H is H₂O. Attack from sodium sulphate is more complex than attack from calcium sulphate because more phases are affected. Sodium sulphate may attack concrete in two different ways. The first form of attack
(Equation 2.7) involves sodium sulphate reacting with calcium hydroxide (portlandite) to form gypsum. Gypsum can then react with monosulfoaluminate (Equation 2.8) to form ettringite. Once the calcium hydroxide is depleted, gypsum formation will discontinue. Once the monosulfoaluminate becomes depleted, excess gypsum will form in the system and ettringite formation will cease (Gollop, 1992). The second form of attack (Equation 2.9) involves sodium sulphate reacting with tricalcium aluminate to form ettringite.

Once the monosulfoaluminate becomes depleted, excess gypsum will form in the system and ettringite formation will cease (Gollop, 1992). The second form of attack (Equation 2.9) involves sodium sulphate reacting with tricalcium aluminate to form ettringite.

Tian and Cohen (2000) studied the expansion of alite (C₃S) caused by the formation of gypsum. In the case of a pure alite paste, no aluminium should be available to form ettringite. Cement pastes made with and without silica fume were placed in a 5% sodium sulphate solution. After 360 days in sodium sulphate, the alite paste, without silica fume, began to expand, and x-ray diffraction analysis showed that this expansion was due to gypsum formation (Tian and Cohen, 2000b). These findings suggest that gypsum formation can, in fact, lead to expansion, in addition to the loss of mass or cohesion that is typically observed when gypsum forms.

\[
\text{CH} + \text{N}_2\text{SH}_{10} \rightarrow \text{C}_2\text{SH}_2 + 2\text{NH} + 8\text{H} \tag{2.7}\]

\[
\text{C}_2\text{A(CS)}\text{H}_{32} + 2\text{C}_2\text{SH}_2 + 16\text{H} \rightarrow \text{C}_5\text{A(CS)}\text{H}_{32} \tag{2.8}\]

\[
2\text{C}_3\text{AH}_6 + 3\text{N}_2\text{SH}_{10} \rightarrow \text{C}_5\text{A(CS)}\text{H}_{32} + 2\text{AH}_3 + 6\text{NH} + 5\text{H} \tag{2.9}\]

Where C is CaO, A is Al₂O₃, S is SO₃, N is Na₂O, CH is Ca(OH)₂ and H is H₂O. Magnesium sulphate is the most complex of the three types of sulphates. It can react with all hydrated cement products and is generally considered to be the most damaging form of sulphate. Magnesium sulphate will react with calcium silicate to form gypsum plus magnesium hydroxide and a silica gel, as shown in Equation 2.10. This formation of magnesium hydroxide (brucite) is known to form a barrier which may provide
protection to the concrete and it also tends to internally affect pore solution pH. Brucite formation does have its downfall in that it needs a high amount of calcium hydroxide to form. Once the portlandite is depleted, the magnesium sulphate will seek more calcium. In this case, decalcification of the C-S-H will occur, due to the removal of calcium (Gollop, 1992).

$$3\text{CaO} \cdot 2\text{SiO}_2 + \text{MgSH} \rightarrow 3(\text{CSH}_2) + 3\text{Mg(OH)}_2 + 2S$$ ........................................2.10

### 2.4.2 Sulphate Ion Concentration

Sulphate ion concentration is a primary parameter used to describe the severity of sulphate attack. Limits for design specifications for concrete in sulphate environment have been specified on the basis of sulphate concentration in soil and water by several agencies. Recommendations for sulphate resistance, as specified in ACI 201.2R-92, are shown in Table 2.1. The boundary between moderate and severe forms of attack is 1500 ppm SO$_4^{2-}$ in water and 2000 ppm SO$_4^{2-}$ in soil. Xu et al. (Xu et al., 1998) discussed some other limits on sulphate concentration as specified by different organizations. The international organization CEMBUREAU set 600 mg SO$_4^{2-}$/l in water and 6000 mg SO$_4^{2-}$/kg in soil as the upper limits for moderate attack. Based on these limits, the European Prestandard ENV 206 states 500 ppm and 3000 ppm in soil as the limits for moderate levels of attack.

There is a need for a better understanding of the mechanisms of sulphate attack as a function of sulphate ion concentration. Different mechanisms of sulphate attack have been proposed at different concentrations of sodium and magnesium sulphates (Cohen and Mather, 1991). In the field, the issue of varying sulphate concentrations becomes critical when a concrete column is exposed to different concentrations in different portions due to the development of wetting and drying fronts (Santhanam et al., 2002).
As sulphate ion concentration increases, sulphate attack is primarily due to gypsum formation. If sulphate ion concentration is less than about 1000 ppm in sodium sulphate solution and less than about 3200 ppm in magnesium sulphate solution, then damage occurs by expansion of ettringite (Biczok, 1967b). Above 6000 ppm of sulphate ions in magnesium sulphate solution, attack occurs by gypsum formation. Xu et al. (Xu et al., 1998) suggest that if the concentration of sodium sulphate is high enough, then it can react with alumina-bearing phases to form ettringite. Mehta and Monteiro (Mehta and Monteiro, 1993) observe that whether ettringite or gypsum is formed during early hydration depends on the aluminate-to-sulphate ratio and the reactivity of the alumina-bearing phases. In an investigation of practically-no-C₃A Portland cements subjected to a high sodium sulphate concentration of 5% (corresponding to 33,800 ppm sulphate ions), Gonzalez and Irassar (Gonzalez and Irassar, 1997) proposed that ettringite formation occurred at a much later stage. The unhydrated C₄AF phase and its hydration products reacted to form ettringite. It therefore appears that even though alumina-bearing phases and sulphate ions were available, due to the low reactivity of C₄AF, ettringite formation occurred at a later stage of sulphate exposure.

Heller and Ben-Yair (1964), as cited in Gollop and Taylor (Gollop and Taylor, 1995), found that much more ettringite was formed in a paste exposed to a 10% sodium sulphate solution than in pastes exposed to weaker solutions, but there was no direct relation between the amount of ettringite formed and the degree of expansion.

2.4.3 Permeability

Concrete with a low w/c yields a microstructure with reduced porosity and permeability which reduces the rate of ingress of sulphate ions. Cement paste with a w/c of 0.7 is approximately 10 times more permeable than a comparable mixture with a 0.55 w/c (Powers et al. 1954). A significant correlation between higher permeability and greater expansion was reported with concretes exposed to 5% sodium sulphate (Khatri et al.,
1997), and Al-Amoudi (Baghbra Al-Amoudi, 2002) reported similar findings for concrete exposed to sodium sulphate, but not with magnesium sulphate solutions. To achieve low permeability, one must not only use a low w/c (i.e., less than 0.45) but also ensure adequate curing. As described later, the incorporation of supplementary cementitious materials (SCM) into concrete mixtures is the most powerful method of reducing sulphate ingress.

### 2.4.4 Water to Cement Ratio

The water to cement ratio (w/c) of a concrete mix affects the permeability of hardened concrete and hence also sulphate attack. A higher w/c leads to higher permeability of concrete and hence a lower resistance to penetration of aggressive agents, including sulphate ions. Various agencies recommend the use of a judicious combination of cement composition and w/c to improve resistance of concrete to sulphate attack, as evident from Tables 2.1 and 2.2. For instance, ACI 201.2R-92 recommends the use of ASTM type V ($C_3A$ content less than 5%) Portland cement and a maximum w/c of 0.45 for severe sulphate attack (sulphate ion concentration in water of 1500-10,000 ppm).

Monteiro and Kurtis (Monteiro and Kurtis, 2003) analysed long term data on expansion under sulphate attack and concluded that the time to failure for concrete was influenced by w/c and the $C_3A$ content of the cement. As both quantities increased, time to failure decreased. Even for concrete mixtures with $C_3A$ contents of up to 8%, the use of w/c of lower than 0.45 improved the performance of concrete. After a summary of case studies Mehta (Mehta, 1992) concluded that it was the permeability of concrete rather than the mineralogical composition of cement that appeared to be the most important factor governing sulphate attack.
Table 2.1: Recommendations for normal weight concrete subject to sulphate attack (ACI 201.2R-92)

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Water soluble sulphate* (SO₄) in soil, %</th>
<th>Sulphate* (SO₄) in water, ppm</th>
<th>Cement</th>
<th>Water-cement ratio, maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild</td>
<td>0.00-0.10</td>
<td>0-150</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Moderate</td>
<td>0.10-0.20</td>
<td>150-1500</td>
<td>Type II, IP (MS), IS (MS)</td>
<td>0.50</td>
</tr>
<tr>
<td>Severe</td>
<td>0.20-2.00</td>
<td>1500-10,000</td>
<td>Type V</td>
<td>0.45</td>
</tr>
<tr>
<td>Very severe</td>
<td>Over 2.00</td>
<td>Over 10,000</td>
<td>Type V+ pozzolan or slag</td>
<td>0.45</td>
</tr>
</tbody>
</table>

* Sulphate expressed as SO₄ is related to sulphate expressed as SO₃ as in reports of chemical analysis of cement as SO₃ x 1.2 = SO₄.

Table 2.2: Sulphate aggressiveness to concrete specified by CEMBUREAU

<table>
<thead>
<tr>
<th>Aggressiveness</th>
<th>SO₄²⁻ in water (ppm)</th>
<th>SO₄²⁻ in soil (ppm)</th>
<th>Cement</th>
<th>Water-cement ratio, maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1</td>
<td>&lt;200</td>
<td>&lt;0.2</td>
<td>-</td>
<td>0.55</td>
</tr>
<tr>
<td>Class 2</td>
<td>200-600</td>
<td>0.2-0.6</td>
<td>-</td>
<td>0.55/0.50</td>
</tr>
<tr>
<td>Class 3</td>
<td>600-3000</td>
<td>0.6-1.2</td>
<td>Sulphate resisting cement</td>
<td>0.50</td>
</tr>
<tr>
<td>Class 4</td>
<td>3000-6000</td>
<td>&gt;1.2</td>
<td>Sulphate resisting cement</td>
<td>0.45</td>
</tr>
<tr>
<td>Class 5</td>
<td>&gt;6000</td>
<td></td>
<td></td>
<td>0.45 + protection</td>
</tr>
</tbody>
</table>

2.4.5 Cement Composition

Cement composition affects the resistance of concrete and other cement-based materials to sulphate attack. It must be noted that the influence of cement composition and permeability as governed by w/c needs to be examined simultaneously while testing the performance of concrete under sulphate attack.

The sulphate resistance of concrete structures can be improved by controlling sulphate permeation into concrete, and sulphate attack can be prevented either by changing cement from ASTM Type I to Type II or Type V or by introducing pozzolans such as fly ash, blast furnace slag, volcanic ash (VA) and finely ground volcanic pumice (VP) in concrete (Hossain and Lachemi, 2006, Kalousek et al., 1972, Naik et al., 1996).
ASTM Type V cement with a low C₃A is recommended in structures placed in such environments. Typically, ASTM Type I cement contains between 8% and 12% C₃A, whereas Type II cement contains less than 8% C₃A and Type V cement less than 5% C₃A. Significant development in cement chemistry over the past two decades has resulted in cements with a high C₃S/C₂S content (Mehta, 1991). This increase in C₃S/C₂S ratio results in increased calcium hydroxide content in the hardened cement concrete, thereby enhancing the susceptibility of such cements to the softening type of sulphate attack (Rasheeduzzafar et al., 1990). Irassar et al. (Irassar et al., 2000) reported that a low C₃S/C₂S ratio is a significant positive factor in the choice of cement for good sulphate resistance. Sulphate permeation can also be controlled by increasing compactness, lowering water-to-cement ratio, proper curing, surface treatment, and use of precast concrete in place of cast-in-situ concrete (Hossain, 1999, Miyagawa, 1991).

It has been reported that the limitation of C₃A content is not the ultimate answer to the problem of sulphate attack (Kalousek et al., 1972, Rasheeduzzafar et al., 1990). Mehta (1992) has pointed out that Type V cement addresses only the problem of sulphate expansion associated with ettringite formation. Therefore, Type V cement can be particularly efficacious when calcium sulphate is the attacking medium, although it could be beneficial with respect to the prevention of the formation of gypsum owing to the action of sodium sulphate. Thus, Type V cement is of no avail in the attack of calcium hydroxide and C–S–H and the subsequent loss of strength (Mehta, 1992). The use of blended cement made with supplementary cementitious materials such as fly ash, silica fume, and blast furnace slag is therefore recommended in sulphate environments (Frigione and Sersale, 1989, Naik et al., 1996).
2.5 Predicting Deterioration in Sulphate Attack

Since there is little work published on septic tanks, the author was guided by previous work published on the deterioration of sewerage pipes. The rate of corrosion of concrete pipes depends on the strength and density of the concrete, the degree of acid penetration, the acid value and the circulation of hydrogen sulphide in the atmosphere. Non-accelerated laboratory testing was started by the U.S. Bureau of Reclamation (USBR) to establish the influence of concrete-mix parameters on sulphate resistance over 50 years ago. Concrete specimens were monitored at regular intervals with field exposure conditions of sulphate concentrations. Kurtis et al. (Kurtis, 2002) conducted statistical analysis of a portion of the data to predict the expansion of the concrete as a function of time, w/c ratio, and C₃A content. According to Pomeroy (Pomeroy, 1977), the theoretical corrosion rate prediction equation is given by,

\[
CR = 11.4 \times k \times \phi_{sw} \times \left(1 / a \right) \tag{2.11}
\]

Where

CR = average rate of corrosion of concrete by acid (mm per year)

k = coefficient for acid reaction, accounting for estimated fraction of acid remaining on wall

0.8 for S (increase of sulphide concentration) ≤ 1.0

0.7 for 1.0 ≤ S ≤ 5.0

0.6 for S > 5.0

\(\phi_{sw}\) = flux of hydrogen sulphide to pipe wall (g/m² * h)

a = coefficient for alkalinity of concrete, normally 0.16.

The rate of corrosion of concrete pipes has been expressed by Thistlethwayte (Thistlethwayte, 1972) using the theoretical Equation 2.12.
\[
CR = 19.9 \times 10^7 \times \frac{K_{sa} \times P_{H_2S} \times A_{sa}}{z \times \rho \times A_{aw}}
\]

Where

- \(K_{sa}\) = rate of absorption of H\(_2\)S on pipe wall (kg/m\(^2\) * h)
- \(P_{H_2S}\) = partial pressure of H\(_2\)S (ppm)
- \(A_{sa}\) = ratio of surface width of waste stream to exposed perimeter of pipe wall above water surface (m\(^2\)/m)
- \(z\) = of cement content of concrete (kg/m\(^3\))
- \(\rho\) = density of concrete (kg/m\(^3\))
- \(A_{aw}\) = exposed perimeter of pipe wall above water surface (m\(^2\)/m).

Both expressions indicate that the corrosion rate is usually measured as mm/year and that it is a function of the acid concentration, coefficient of alkalinity of concrete (or the cement content), exposed area of pipe above sewerage and the pressure of H\(_2\)S. In the experiments conducted in the present study, some of these parameters are constants, leaving acid concentration, cement content of concrete and age as the main variables.

### 2.6 Conclusions

The comprehensive literature review presented in this chapter has identified possible mechanisms of the deterioration of concrete when exposed to sulphate-rich environments. Table 2.3 summarises the findings. The research program presented in subsequent chapters was developed with the aim of identifying which mechanisms are predominant in septic tanks.
<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Required Conditions</th>
<th>Signs of Deterioration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gypsum Formation</strong></td>
<td>Presence of sulphate ions; calcium hydroxide is required. Sulphate attack is generally attributed to the reaction of sulphate ions with calcium hydroxide and calcium aluminate hydrate to form gypsum.</td>
<td>Gypsum in XRD and SEM, Mass loss</td>
</tr>
<tr>
<td><strong>Ettringite Formation</strong></td>
<td>Presence of sulphate ions, gypsum, calcium hydroxide is required. Ettringite crystals may grow by combining calcium hydroxide and aluminium sulphate solutions. When gypsum reacts with anhydrous calcium aluminate in a through-solution reaction and acts as a set retarder in Portland cement mixtures, then ettringite forms. Ettringite is not stable in low lime environments when the pH falls below 11.5-12.0.</td>
<td>Expansion or mass gain, Spalling of the concrete, Ettringite in XRD and SEM</td>
</tr>
<tr>
<td><strong>Thaumasite Formation</strong></td>
<td>Thaumasite formation is generally associated with concretes exposed to carbonate and sulphate at low temperatures. The formation of thaumasite requires the presence of calcium silicate, sulphate ions, carbonate ions and a wet, cold (&lt;15 °C) environment. Some researchers suggest that thaumasite is formed only at pH above 10.5.</td>
<td>softening of the cement paste matrix into a white, mushy incohesive mass, Thaumasite in XRD</td>
</tr>
<tr>
<td><strong>Delayed Ettringite Formation (DEF)</strong></td>
<td>If heat curing is done at initial stage, later the concrete starts forming ettringite. It occurs when environmental sulphate (from water or soil) penetrates concrete</td>
<td>Expansion or mass gain, Spalling of the concrete, Ettringite in XRD and SEM</td>
</tr>
<tr>
<td>Physical Sulphate Attack</td>
<td>Presence of sodium sulphate in pore solution. This process is temperature-dependant. Ground waters with high concentrations of sulphate, chloride and other ionic species may cause this form of attack. Ground water and the ionic species present in it enter and penetrate concrete by one or more of the following mechanisms: adsorption, vapor diffusion, liquid assisted vapor transfer, saturated liquid flow, or ionic diffusion under saturated conditions.</td>
<td>Mass gain due to absorption of water and loss of cohesion</td>
</tr>
</tbody>
</table>
Chapter 3

Experimental Method and Materials

3.1 Introduction

The possible deterioration mechanism and signs of deterioration as reported by previous researchers have been identified in the previous chapter. This chapter presents the development of an experimental methodology to ascertain the deterioration of concrete septic tanks. The materials utilised in this project, the examination of samples under different testing conditions, and the experimental methods and procedures used throughout the course of the investigation are described in detail.

A primary interest of many engineers and researchers is macroscopic changes in concrete structures due to sulphate attack. Standard tests for the evaluation of concrete performance under sulphate attack are usually based on observation of macroscopic responses and/or engineering properties such as length change, changes in mass, compressive strength and permeability. These can be readily measured in laboratories without the need for sophisticated sample preparation techniques and equipment such as that needed for scanning electron microscopy (SEM), x-ray microtomography (microCT) or x-ray diffractron (XRD). However, information provided by such tests alone, is often not sufficient to establish relations between the sulphate
environment, concrete composition and mechanisms of damage with time of exposure (Tian and Cohen, 2000b).

To complete experimentation within a reasonable period, accelerated testing was selected as a method during the course of this work.

### 3.2 Planning of the Accelerated Tests

Accelerated test methods for the evaluation of the performance of cement mortar or cement concrete in a sulphate-laden environment have been a subject of debate and discussion. Buenfeld and Hassanein (1996) argue that laboratory tests on concrete are helpful in understanding mechanisms of deterioration, but have limitations in determining the rates of deterioration for a number of reasons which include the following:

- Accelerating deterioration may distort the mechanisms of sulphate damage.
- Laboratory tests involving studies over a short duration may not capture some long-term behaviour such as pore structure refinement by cementitious admixtures at later stages.
- It is not possible to exactly replicate the field conditions in the laboratory, for example thermal or humidity cycles.
- Common strategies employed in accelerating laboratory sulphate attack are to increase solution concentrations or temperatures, or to subject samples to intermittent exposure (wet/dry cycling). However, each of these approaches may influence not only the rate of reaction, but also the products formed and the mechanisms responsible for damage.

However, with proper calibration using field measurements, accelerated testing can provide a reasonable estimate of the expected deterioration progression in concrete
septic tanks for a limited time frame. The research presented here adopted two measurements of deterioration: length change and mass change under accelerated conditions.

Two accelerated laboratory test methods for the evaluation of sulphate performance of Portland cement mortars are ASTM C452 (Standard test method for potential expansion of Portland cement mortars exposed to sulphate) and ASTM C1012 (Standard test method for length change of hydraulic cement mortars exposed to sulphate solution). ASTM C1012 (2004) is one of the most common tests used in practice and is often included in specifications and guidelines for assessing sulphate attack on concrete. Loss in compressive strength has also been used by numerous researchers to identify whether sulphate attack has occurred (Ibrahim M., 1999). In a controlled experimental system monitored over a finite time span, compressive strength is not a good way of analysing samples as it is a destructive procedure in which the number of samples will reduce with each compressive strength test. In developing the experimental program covered here, ASTM C1012 (2004) was followed as closely as possible.

Acceleration of deterioration was achieved by exposing samples to a higher level of aggressive chemicals than encountered in practice and subjecting samples to heating and drying cycles. Applying wetting–drying cycles and raising the temperature and the concentration of solution are common methods of accelerating testing (Sahmaran et al., 2007). Hekal et al. (Hekal et al., 2002) investigated the sulphate resistance of hardened blended cement pastes exposed to 10% MgSO$_4$ solution under different exposure conditions (room temperature, 60 °C, and drying-immersion cycles at 60 °C). They concluded that only the method based on drying-immersion cycles at 60 °C could be considered an accelerated method. In another study, Mangat and Khatib (Mangat and El-Khatib, 1992) applied temperatures of 20 and 45 °C for curing in water during
the first 28 days and for curing in sulphate solution at later stages. However, the results depended on the initial curing conditions in water rather than the solution temperature. Considering the above findings, the accelerated tests developed as part of the study presented here included a drying and heating cycle to accelerate the tests. Heating and drying was applied immediately before the measurement of mass change was recorded to ensure that a constant mass measurement was taken at a base condition. Since the primary objective of the work is to measure the deterioration of concrete, all the tests were conducted on concrete and not mortar. It should be noted here that almost all of the reported work has explored sulphate attack on mortar and not concrete.

3.3 Materials and Exposure Solutions

3.3.1 Types of Concrete Used in Septic Tank

Prior to the commencement of the experiments, it was necessary to verify the types of concrete used in septic tanks in country Victoria. Since the focus of the study was to ascertain the life expectancy of concrete septic tanks located in rural Victoria, an investigation was conducted to identify typical suppliers of concrete and the typical mix proportions used. Taylex Concrete Suppliers provided typical mix proportions used during the period of interest. They use 350kg per m$^3$ in a standard 32 MPa mix where 330 kg is the VICROADS requirement. The extra cement enables them to pour and strip the next day. A blended cement will not provide the quick early strength they need. In this mix design Taylex use Sika admixtures such as 200 ml Sikamix per 100 kg cement and 200 ml Visco-10 per 100 kg cement. 80 mm slump is used for septic tank production using a 100% GP cement. The stone is natural river pebble recovered from the Goulburn River and the sand is also recovered from the Goulburn, washed, graded and classified as concrete sand. Taylex use 10 and 14 mm sizes for the aggregate and sand of fineness modulus 2.9.
Figure 3.1: Grading curve of fine aggregate

3.3.2 Mix Design

Three different mix designs were generated to match the criteria supplied by Taylex. The target 28 day mean strength of 32 MPa and the slump of 80 mm were used as specifications to prepare these three mixes. The three mixes are documented in Table 3.1. A set of trial mixes was completed prior to finalising these mix designs.

Table 3.1: Mix Design of concrete used

<table>
<thead>
<tr>
<th>Name</th>
<th>Cement (Kg/m³)</th>
<th>Fine aggregate (Kg/m³)</th>
<th>Coarse Aggregate (Kg/m³)</th>
<th>W/C Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>7 mm</td>
<td>10 mm</td>
<td>14 mm</td>
</tr>
<tr>
<td>Mix A</td>
<td>415</td>
<td>825</td>
<td>420</td>
<td>525</td>
</tr>
<tr>
<td>Mix B</td>
<td>370</td>
<td>800</td>
<td>450</td>
<td>550</td>
</tr>
<tr>
<td>Mix C</td>
<td>350</td>
<td>900</td>
<td>450</td>
<td>550</td>
</tr>
</tbody>
</table>
3.3.3 Portland Cement

The cement used in this project was a Portland cement (Type GP), which was obtained from the Rockhampton Plant of Cement Australia Pty Limited. The physical properties and chemical composition data, as provided by the cement manufacturer, are presented in Tables 3.2 and 3.3 respectively.

Table 3.2: Physical properties of Portland cement

<table>
<thead>
<tr>
<th>Properties</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineness Index (m²/Kg)</td>
<td>390</td>
</tr>
<tr>
<td>Residue 45μ Sieve (%)</td>
<td>4.3</td>
</tr>
<tr>
<td>Normal Consistency (%)</td>
<td>27.5</td>
</tr>
<tr>
<td>Setting Time Initial (min)</td>
<td>120</td>
</tr>
<tr>
<td>Setting Time Final (min)</td>
<td>210</td>
</tr>
<tr>
<td>Soundness (mm)</td>
<td>1</td>
</tr>
<tr>
<td>Shrinkage 28 Days (μ Strain)</td>
<td>640</td>
</tr>
<tr>
<td>Compressive Strength 28 Days (Mpa)</td>
<td>55.9</td>
</tr>
</tbody>
</table>

Table 3.3: Chemical properties of Portland cement

<table>
<thead>
<tr>
<th>Chemical Entity</th>
<th>Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>63.8</td>
</tr>
<tr>
<td>SiO₂</td>
<td>20.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.4</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.5</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>3.0</td>
</tr>
</tbody>
</table>
3.3.4 Aggregates

Natural crushed stone of 7 mm, 10 mm and 14 mm sizes were used as coarse aggregate whose specific gravity was 2.64. River sand of specific gravity of 2.06 and fineness of 3.12 was used as fine aggregate.

3.3.5 Admixtures

To achieve similar mix designs to those used earlier in septic tank production, two typical admixtures were used. Sikamix was used as a mix enhancing admixture and Sika Viscocrete-10 as a high range water reducer retarder.

Inclusion of Sikamix in a mix,

- improves the cohesiveness, workability and lubrication of fresh concrete.
- reduces concrete bleed.

Inclusion of Sika Viscocrete-10 in a concrete mix leads to,

- high water reduction, resulting in high density, high strength and reduced permeability.
- reduced shrinkage and reduced creep when hardened.
- excellent plasticising effect, resulting in improved flow, soft placing and compaction characteristics.

3.3.6 Exposure Solutions

A major challenge faced by the author was determining the exposure conditions for the accelerated tests. From the published research, it was established that the deterioration of concrete exposed to sewage could occur due to sulphate attack, acid attack, or both. The other possible cause of deterioration of concrete septic tanks is exposure to sulphate-rich soil on the external surface of the tanks.

Considering the above facts, it was decided to test concrete under exposure to both sulphate and acid solutions. A heating and drying cycle was adopted to accelerate the
tests as well as to attain a constant weight at measurement of weight. Three samples from each mix design were stored in five different solutions of sulphate and acid. Three samples were kept as control specimens which were exposed to the room environment as well as heating cycles. The concentrations of the three selected sulphate solutions were 2%, 4% and 5.5% of Na$_2$SO$_4$ by mass, and two different 0.01M H$_2$SO$_4$ solutions where a constant range of pH was maintained to simulate quite severe conditions compared to actual field conditions. Field measurements indicated that the actual pH in septic tanks ranges from 6.0 in sewage-only tanks to 4.0 in all waste tanks. Figure 3.1 shows the typical conditions of the concrete septic tank that was visited. To accelerate deterioration a pH range between 2.5 and 4.5 was selected. The properties of solutions are listed in Tables 3.4 and 3.5.

**Table 3.4: Na$_2$SO$_4$ Solution properties**

<table>
<thead>
<tr>
<th>Solute</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Code</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>H</td>
</tr>
</tbody>
</table>

**Table 3.5: H$_2$SO$_4$ Solution properties**

<table>
<thead>
<tr>
<th>Name</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3</td>
<td>2.5 to 3.5</td>
</tr>
<tr>
<td>pH 4</td>
<td>3.5 to 4.5</td>
</tr>
</tbody>
</table>
3.4 Specimen Preparation

3.4.1 Specimens Size

Two types of casting moulds were used in the experiments: cylindrical moulds for specimens tested for compressive strength and mass change, and prism moulds for specimens tested for length change. Two different cylindrical moulds were used for the first set of experiments: 100mm diameter for compressive strength testing and 75 mm diameter for mass change testing. For the second set of experiments, 100 mm diameter cylindrical moulds were used for compressive strength tests and 75 mm x 75 mm x 285 mm prism moulds were used for length change tests. Prismatic beam samples were fitted with steel studs at the ends to enable measurement of the length change in a shrinkage apparatus. Before casting, moulds were cleaned and mould oil was applied so that sample could be demoulded without any damage while ensuring a smooth surface finish.

According to ASTM C39 / C39M 100 mm diameter and 200 mm long cylindrical specimens are to be used for tests of compressive strength. As per Australian
Standards AS 1012.9 (1999), 100 mm diameter and 200 mm long cylinders are required for measurement of compressive strength, provided that the maximum aggregate size is less than 20 mm and the approval of a structural engineer are obtained beforehand.

According to ASTM C157/C 157M the test specimen for concrete for length change, in which all of the aggregate passes a 2 inch (50mm) sieve, shall be a prism of 4 inch (100 mm) square cross-section and approximately 11.25 inches (285 mm) long. However, a prism of 3 inch (75 mm) square cross section shall be used if all of the aggregate passes a 1 inch sieve (25 mm) according to ASTM C 157/C 157M. The maximum size of aggregate used in this experimental work was 14 mm and therefore 75 mm square cross-section prism moulds were selected for length change testing. Pictures of cylindrical and prismatic moulds used in the experiment are shown in Figures 3.3 and 3.4.

Figure 3.3: Cylinder mould
3.4.2 Mixing Apparatus

All mixing was performed in a TTM 140 Turbo concrete mixer with a capacity of 0.2 cubic meters. The turbo mixer has a central rotating satellite on a vertical axle producing a force-feed mixing action. Before mixing it was sprinkled with water so that the inside surface was damp and would not absorb any of the mixing water. A picture of the mixing machine is shown in Figure 3.5.
3.4.3 Vibrating Table

All the specimens were vibrated using a vibrating table with a frequency of 50 Hz. It has a capacity up to 200 Hz and 24 100 mm diameter cylindrical moulds can be easily compacted at a time. A picture of the vibrating table is shown in Figure 3.6.

![Vibrating Table Image](image)

Figure 3.6: Vibrating Table

3.5 Experimental Procedure

3.5.1 Mixing

The materials were measured before starting the mixing according to the desired mix design. First the coarse and fine aggregates were mixed for 2 minutes in a dry state. Cement was then added to the mixer and mixed for another 2 minutes. Deionized water was used as the mix water and 90% of the measured mixing water was gradually added during the next 3 minutes. Finally, Sikamix and Sika Viscocrete 10 admixtures were added to the mix and the rest of the water added slowly to achieve a slump of 80 mm. Mixing was then continued for another two minutes. Immediately after the mixing process the specimens were cast and vibrated on the vibrating table. Casting of concrete was done in two layers for cylindrical moulds and one layer for prismatic moulds. All the specimens were vibrated on the vibrating table for not more than 2
minutes for each layer and the top surface was levelled off to obtain a smooth surface. All the task of casting was completed within the final setting time of 20 minutes.

3.5.2 Demoulding

The next day 24 hours after casting all the specimens were demoulded and placed in a lime water tank for 28 days for saturated curing. As the main objective of this experimental work was to study the deterioration of septic tanks located in rural Victoria, a minimum period of 28 days of curing was allowed. It has been noted that all the tanks are precast and only placed in the field after at least 28 days from manufacture.

![Figure 3.7: Saturated lime water tank](image)

3.5.3 Preparation of Specimen for Testing

After 7 days of saturated lime water curing, the edges of specimens were cut using a mechanical cutting tool. The compressive strength of the cylindrical specimens was determined after 7 and 28 days of curing using a MTS machine following the ASTM C39 / C39M standard test procedure. The mechanical cutting tools are shown in Figure 3.8.
3.5.4 Compressive Strength Test

Three cylindrical specimens from each mix design were tested in the MTS machine for compressive strength as at 7, 28 and 362 days according to the ASTM C39 / C39M. The loading rate of 20 MPa per minute was maintained while the testing was conducted under displacement as control. The failure pattern of the crushed cylinders was observed to see whether failure was due to primary compression and not to localized failure or end capping failure. Figure 3.9 shows the MTS testing machine.

Figure 3.9: MTS testing machine
3.5.5 Mass Change Test

A total of 18 cylinders of 75 mm diameter and 150 mm length were prepared from each mix design to test mass change in sulphate and acid solutions and 6 cylinders of 100 mm diameter were prepared to test compressive strength. For the mass change testing prismatic samples were not considered. Three cylindrical samples of 75 mm diameter from each mix design were stored in five different solutions of sulphate and acid. Three cylindrical samples of 75 mm diameter were kept as control specimens which were exposed to the room environment as well as heating cycles. The concentrations of the three selected sulphate solutions were 2%, 4% and 5.5% of Na₂SO₄ by mass and two different 0.01M H₂SO₄ solutions where a constant range of pH was maintained to simulate field exposure conditions. All samples were stored in an oven at a temperature of 105 °C for 24 hours after a 14 day wetting cycle in the solutions. After a heating cycle of 24 hours the weights of the samples were measured and all solutions were replaced with new solutions. For the 0.01M H₂SO₄ solution, a pH range of 1.5 to 2.5 and 2.5 to 3.5 was maintained by adding more 0.02M H₂SO₄ regularly. Regular visual inspections were carried out to observe spalling and cracking of concrete corners or surfaces. Mass change was calculated by the following equation,

\[ \varepsilon = \frac{M_t - M_o}{M_o} \times 100 \% \]

where:

\( \varepsilon = \) Change in mass as percentage

\( M_t = \) Mass at each measurement

\( M_o = \) Initial Mass of the specimen which is measured before specimen is exposed to the chemical solution.

The mass data were measured in gm with an accuracy of 0.01 gm.
3.5.6 Length Changes Test

A second set of experiments was carried out using Mix A. A total of 8 prismatic samples of 75 mm square cross-section and 285 mm length were prepared with end studs to measure the length change of concrete under sulphuric acid attack, and 14 cylinders of 100 mm diameter were prepared to measure the compressive strength at 28 days and at the end of the period of exposure as given in Table 3.7. Three different pH solutions were prepared for this second set of experiments as given in Table 3.6. Two prismatic and two cylindrical samples were placed in each solution and they were kept in a controlled humidity chamber. Two prismatic and two cylinder samples were kept without exposure to any solution in the humidity chamber as control specimens to compare the length change of other specimens with respect to time. The length change or expansion was calculated using the following equation,

\[
\varepsilon = \frac{L_t - L_o}{L_o} \times 100 \%
\]

where:

\( \varepsilon \) = expansion

\( L_t \) = specimen length at each measurement

\( L_o \) = initial length of specimen, which is measured before specimen is exposed to solution

Table 3.6: Range of pH for length change experiment

<table>
<thead>
<tr>
<th>Name</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2.0</td>
<td>1.5 to 2.5</td>
</tr>
<tr>
<td>pH 3.0</td>
<td>2.5 to 3.5</td>
</tr>
<tr>
<td>pH 4.0</td>
<td>3.5 to 4.5</td>
</tr>
</tbody>
</table>
Length change was measured using the shrinkage comparator shown in figure 3.9. The comparator has an accuracy of ±0.001 mm.

![Shrinkage Machine for measuring length change](image)

**Figure 3.10: Shrinkage Machine for measuring length change**

<table>
<thead>
<tr>
<th>Mix Design Followed</th>
<th>Sample Classification</th>
<th>Exposure Type</th>
<th>No. of Specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A</td>
<td>Cylindrical 100 mm x 200 mm</td>
<td>pH 2.0</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH 3.0</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH 4.0</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Control (Exposed to humidity room temperature)</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Prismatic 75 x 75 x 285 mm³</td>
<td>pH 2.0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH 3.0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH 4.0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Control (Exposed to humidity room temperature)</td>
<td>2</td>
</tr>
</tbody>
</table>

### 3.5.7 Acid Penetration Test

Concrete is alkaline in nature when cast following general mix designs with no specific acidic admixtures. The deterioration of concrete by sulphuric acid within septic tanks reduces the alkalinity of concrete due to corrosion caused by hydrogen ion attack followed by sulphate ion attack similar to that of external sulphate attack. Sulphuric acid reacts with free lime [Ca (OH)₂] in the concrete and forms gypsum resulting in the
reduction of concrete alkalinity or increase in the acidity. To measure how much change has been done to the alkalinity of concrete due to the exposure to sulphate and sulphuric acid solutions, it was decided to carry out an acid penetration test, similar to the chloride penetration depth test. At the end of exposure to sulphate and sulphuric acid solutions acid base indicator solutions were applied on concrete surface to measure the pH of concrete. An acid base indicator is a substance that indicates the degree of acidity or basicity of a solution through characteristic colour changes. There are a lots of acid base indicators available among which a total number of six indicators were used for this test to cover the whole range of pH. The properties of these six indicators and the range of pH they cover are provided in Table 3.8.

Table 3.8: pH properties of acid base indicators

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Indicator Name</th>
<th>pH Range Covered</th>
<th>Distinctive Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>When Acid</td>
</tr>
<tr>
<td>1</td>
<td>Methyl Red</td>
<td>4.4 - 6.2</td>
<td>Red</td>
</tr>
<tr>
<td>2</td>
<td>Neutral red</td>
<td>6.8-8.0</td>
<td>Red</td>
</tr>
<tr>
<td>3</td>
<td>Thymol blue</td>
<td>8.0-9.6</td>
<td>Yellow</td>
</tr>
<tr>
<td>4</td>
<td>Phenolphthalein</td>
<td>8.0-10.0</td>
<td>Colourless</td>
</tr>
<tr>
<td>5</td>
<td>Bromphenol Blue</td>
<td>6.2-7.6</td>
<td>Yellow</td>
</tr>
<tr>
<td>6</td>
<td>Alizarin Yellow R</td>
<td>10.0-12.0</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

3.6 Microstructural Measurements

Based on the findings of previous researchers it was hypothesised that the success of accelerated testing can only be established by comparing the chemical compositions of the deterioration products observed from the accelerated laboratory tests and field measurements. Therefore, a number of methods of microstructural analysis were explored to identify the composition of the deterioration products.
3.6.1 SEM

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample, producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic x-rays, light (cathodoluminescence), specimen current and transmitted electrons. These types of signals all require specialized detectors for their detection that are not usually all present in a single machine. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about 1 nm to 5 nm in size. Due to the way these images are created, SEM micrographs have a very large depth of field, yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 25 (about equivalent to that of a powerful hand-lens) to about 250,000 magnifications, about 250 times the magnification limit of the best light microscopes.

Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic x-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 nm or 10 nm diameter, that would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell
and release energy. These characteristic x-rays are used to identify the composition and measure the abundance of elements in the sample.

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB₆) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded. The electron beam, which typically has an energy ranging from a few hundred eV (electron volt) to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster
scanning of the CRT display is synchronised with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor and saved to a computer's hard disc.

Figure 3.11: Working mechanism of SEM
3.6.2 EDX

Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF (X-ray fluorescence). As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other.

To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

There are four primary components of the EDS setup: the beam source; the X-ray detector; the pulse processor; and the analyzer. A number of free-standing EDS systems exist. However, EDS systems are most commonly found on scanning electron
microscopes (SEM-EDX) and electron microprobes. Scanning electron microscopes are equipped with a cathode and magnetic lenses to create and focus a beam of electrons, and since the 1960s they have been equipped with elemental analysis capabilities. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis.

3.6.3 XRD

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. When x-rays are incident on a sample, they are diffracted by the crystalline phase in the illuminated volume. X-ray diffraction (XRD) is governed by Bragg’s law as follows (Cullity, 1978):

$$\lambda = 2.d.\sin(\theta)$$

where, $\lambda$ = X-ray wavelength

$d$ = Spacing in the set of planes diffracting the x-rays

$\theta$ = Diffraction angle

Crystalline phases in a sample can be identified by x-ray diffraction. One way of doing so is by holding $\lambda$ constant (i.e., using a monochromatic beam) and varying $\theta$ to determine the values of $d$ spacing present. This is what is typically done in powder diffractometers. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the
sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s Law. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

Figure 3.12: X-ray diffraction theory in XRD analysis

3.7 Summary

The experimental methodology developed by the author was based on the findings of previous work as well as initial field measurements. In summary, three physical measurements: length change, mass change and compressive strength change were adopted as well as three microstructural measurements: SEM with EDX and XRD. Materials used in the preparation of specimens were similar to those of the concrete
used in septic tanks. It was hypothesised that the length change and mass change measurements would capture any expansion or corrosion of concrete and the microstructure examination would reveal the products of deterioration.
Chapter 4

Deterioration of Concrete under Exposure to Sodium Sulphate

4.1 Introduction

Based on the review of literature presented in Chapter 2, the deterioration of concrete exposed to sewage was attributed to sulphate attack, sulphuric acid attack or a combination. Therefore the experimental work presented in Chapter 3 concerned the observation of the deterioration of concrete under accelerated exposure to sulphate and sulphuric acid. This chapter presents the results of the experiments in which concrete deterioration under sulphate exposure was measured through mass change, SEM and XRD analysis. Chapter 5 covers deterioration under exposure to sulphuric acid.

The mechanism of sulphate attack was described in detail in Chapter 2. Sulphate exposure could lead to formation of gypsum, ettringite and thaumasite, which can be measured as mass gain/expansion or mass loss.

4.2 Previous Work on Sulphate Attack

Applying wetting–drying cycles and raising the temperature and the concentration of solution are common methods of accelerating tests (Sahmaran et al., 2007). Hekal et al. (Hekal et al., 2002) investigated the sulphate resistance of hardened blended
cement pastes exposed to 10% MgSO₄ solution under different exposure conditions (room temperature, 60 °C, and drying-immersion cycles at 60 °C). They concluded that only the method based on drying-immersion cycles at 60 °C could be considered an accelerated method. In another study, Mangat and Khatib (2002) applied the temperatures of 20 and 45 °C for curing in water during the first 28 days and for curing in sulphate solution at later stages. However, the results depended on the initial curing conditions in water rather than the solution temperature.

Shahmaran (Sahmaran et al., 2007) observed that when subjected to cyclic drying-wetting sulphate exposure with heating and cooling, all cements except SRPC, displayed similar behaviour; the compressive strength of mortars initially increased, then began to decrease and the specimens eventually disintegrated in less than 17 weeks. According to these researchers, due to the heating–cooling and drying–wetting cycles, the repetitive crystallization of sulphates by repeated hydration and evaporation produced expansion and internal stresses in the pores, leading to the formation of cracks. This process can also be called “physical sulphate attack”.

Santhanam (2001) found in PC mortars that at an early stage sodium sulphate attack results in the formation of gypsum and ettringite. He concluded that a considerable quantity of ettringite forms before any expansion of the mortar occurs and suggested that the mortar system initially can accommodate the products formed by the sulphate attack reactions. Then when the quantity of attack products reaches a certain level, expansion occurs. According to his findings in the case of PC mortar, the sudden increase in expansion occurs after the quantity of gypsum reaches almost 2% and the quantity of ettringite exceeds 8%.

Al-Dulaijan (Al-Dulaijan et al., 2003) conducted an experiment to evaluate the performance of plain and blended cements exposed to varying concentrations of
sodium sulphate for up to 24 months and found that the maximum deterioration, due to sulphate attack, was noted in Type I cement, followed by silica fume and Type V cements. They found that the mode of failure in Type I cement mortar specimens was mainly due to the formation of expansive cracking which is due to the formation of ettringite.

Rasheeduzzafar et al. (1990) investigated the influence of cement composition on sulphate resistance of cements with varying C$_3$A content of cement, and indicated that in addition to the C$_3$A content, the C$_3$S to C$_2$S ratio has a significant influence on sulphate resistance. After 150 days of accelerated sulphate exposure, Type I cement with higher C$_3$A was found to have a deterioration rate that was 2.5 times higher than that for the Type I Portland cement with lower C$_3$A content. Significant retrogression of strength was observed on immersion in a sulphate solution, even in a Type V (C$_3$A: 1.88%) cement that had a C$_3$S to C$_2$S ratio of 5.28. On the other hand, 20% silica fume blended with a Type I cement with a 14% C$_3$A content performed 1.4 times better than a Type V cement with a C$_3$A content of 1.88%.

Al-Amoudi (1998) conducted an experiment in which he examined the deterioration of reinforced concrete under 2.1% mixed sodium and magnesium sulphate solution for more than 44 months. He observed initially mass gain in the concrete samples followed by mass loss. He found that the silica fume and blast-furnace slag (BFS) cement concrete showed gain in the mass up to seven months, and ASTM Type I, Type V and fly ash showed mass gain up to 21 months. The maximum weight loss of 37.4% was observed after 44 months in BFS cement concrete followed by a weight loss of 23.1% in fly ash and a minimum weight loss of 1 % in plain cements (Type I and Type V).
4.3 Physical Properties of Observed Data

Figure 4.1 presents the data for mass change in concrete specimens stored in sulphate solutions. Raw data are given in Table B1 of Appendix B. The concrete specimens stored in sodium sulphate solutions showed a similar growth in mass for different concentrations of sodium. The percentage mass gain increased with time of exposure with a drop in the amount of growth rate at several points. The mass gain was higher for higher concentrations of sodium sulphate solution. The maximum mass gain rate was observed at 200 days, after which there was a slight decrease in the growth rate up to 340 days, and then again a growing trend up to 361 days. The mass gain in concrete specimens was hypothesised to be due to the formation of ettringite which is expansive in nature. The microstructural analysis of these concrete specimens confirmed the formation of ettringite. Ettringite is found in concrete specimens by XRD analysis (Figures 4.7 to Figure 4.9). The reduction in mass gain rate may be due to the loss of ettringite structures from the surface through heating cycles. Whilst it is difficult to confirm the exact reason for the fluctuation of mass gain, the combined effect of sulphate and acid exposure has often provided similar observations in other reported work. The trend of mass gain is similar for all mix designs. The mass gain rates of Mix B and Mix C are provided in Figures 4.2 and 4.3 respectively.

Figure 4.4 illustrates the mass gain data for the concrete specimens from the three mixes immersed in 2% sodium sulphate solution by mass. The mass gain increases with the increase in the water-to-cement ratio of the specimens. Higher water-to-cement ratio means increased permeability, which provides more space for expansive volumetric reactions to take place. This observation is consistent with the observation of Khatri et al. (1997) where less permeable concrete showed less expansion in sulphate exposure conditions. According to Figure 4.4, the percentage mass gain
increased with time. Similar trends were also observed for specimens immersed in 4% and 5.5% sodium sulphate and are presented in Figures 4.5 and 4.6 respectively.

Figure 4.1: Expansion data for PC concrete under sodium sulphate exposure for Mix A

Figure 4.2: Expansion data for PC concrete under sodium sulphate exposure for Mix B
Figure 4.3: Expansion data for PC concrete under sodium sulphate exposure for Mix C

Figure 4.4: Effects of water cement ratio on expansion of PC concrete under 2% sodium sulphate exposure
Figure 4.5: Effects of water cement ratio on expansion of PC concrete under 4% sodium sulphate exposure

Figure 4.6: Effects of water cement ratio on expansion of PC concrete under 5.5% sodium sulphate exposure
Figure 4.7: XRD analysis of PC concrete under 2% sodium sulphate exposure for Mix A

Figure 4.8: XRD analysis of PC concrete under 4% sodium sulphate exposure for Mix A
4.4 Effect of Sodium Sulphate Exposure on Compressive Strength of Concrete

At the end of sodium sulphate exposure all the specimens were tested for compressive strength. Compressive strength results are presented in Table 4.1 and in Figures 4.10 to 4.15. The Figures 4.10 to 4.12 indicate the effects of sodium sulphate exposure on compressive strength of the three concrete mixes at the end of the exposure period. The results do not indicate that the sulphate exposure has a significant effect on strength of concrete. This may be a result of complex mass gain or expansion which applies a coupling pressure on concrete assisting in maintaining the strength. The compressive strengths of the concrete specimens exposed to sodium sulphate solutions are less than the compressive strength of controlled specimens with three exceptions. However, there is no definite pattern for the compressive strength reduction for different concentrations of the sodium sulphate solutions. Figure 4.13 to 4.15 represents a comparison of compressive strength results obtained for three
different mixes at different ages. It is clearly visible that there is a strength reduction in concrete specimens immersed in sodium sulphate solution at 361 days for all three mixes for three different concentrations. This is may be due to the formation of expansive ettringite for which there is a crystal growth pressure developed which creates cracks inside the concrete. Due to the formation of cracks concrete looses its strength.

**Table 4.1: Compressive strength of specimens exposed to sodium sulphate solutions for 361 days**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Mix Design</th>
<th>Stress at End (MPa)</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td>A</td>
<td>38.62</td>
<td>31.74</td>
<td>35.18</td>
<td></td>
</tr>
<tr>
<td>2%</td>
<td>B</td>
<td>35.83</td>
<td>35.49</td>
<td>35.66</td>
<td></td>
</tr>
<tr>
<td>2%</td>
<td>C</td>
<td>39.20</td>
<td>37.94</td>
<td>38.57</td>
<td></td>
</tr>
<tr>
<td>4%</td>
<td>A</td>
<td>38.36</td>
<td>49.17</td>
<td>43.76</td>
<td></td>
</tr>
<tr>
<td>4%</td>
<td>B</td>
<td>48.03</td>
<td>35.56</td>
<td>41.80</td>
<td></td>
</tr>
<tr>
<td>4%</td>
<td>C</td>
<td>35.66</td>
<td>32.31</td>
<td>33.99</td>
<td></td>
</tr>
<tr>
<td>5.5%</td>
<td>A</td>
<td>42.17</td>
<td>38.49</td>
<td>40.33</td>
<td></td>
</tr>
<tr>
<td>5.5%</td>
<td>B</td>
<td>37.69</td>
<td>33.30</td>
<td>35.50</td>
<td></td>
</tr>
<tr>
<td>5.5%</td>
<td>C</td>
<td>33.73</td>
<td>33.45</td>
<td>33.59</td>
<td></td>
</tr>
<tr>
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<td>A</td>
<td>44.14</td>
<td>51.22</td>
<td>47.68</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>B</td>
<td>41.14</td>
<td>37.79</td>
<td>39.47</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>C</td>
<td>39.87</td>
<td>41.26</td>
<td>40.56</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.10: Compressive strength of the concrete specimen from Mix A under sodium sulphate exposure for 361 days**
Figure 4.11: Compressive strength of the concrete specimen from Mix B under sodium sulphate exposure for 361 days

Figure 4.12: Compressive strength of the concrete specimen from Mix C under sodium sulphate exposure for 361 days
Figure 4.13: Comparison of compressive strength results at different ages for Mix A

Figure 4.14: Comparison of compressive strength results at different ages for Mix B
4.5 XRD Analysis

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. XRD powder diffraction is most widely used for the identification of unknown crystalline materials and/or characterization of crystalline materials. XRD powder diffraction was used for the microstructure analysis of all samples at the end of exposure to the solution.

Figure 4.7 presents the XRD results of the specimen exposed to 2% sodium sulphate solution from Mix A for 361 days. Using two theta scales, X-rays were produced from 5 to 60 degree angles and the results were recorded. From the figure it is clear that the concrete specimen consists of three major ingredients: ettringite, thaumasite and gypsum. The dominant ingredient is ettringite, followed by gypsum, and a small amount of thaumasite is also recorded. Other mix designs and exposure to different
concentrations of solutions reveals that ettringite is the major ingredient in the samples after 361 days of exposure (Figure 4.8 and Figure 4.9). For the specimens exposed to 2% sodium sulphate solution, Mix C contains more ettringite than any other, which is also true in the case of 4% sulphate exposure. For 5.5% sodium sulphate exposure, Mix A contains more ettringite than the other two mixes.

Therefore there is no direct relationship between amount of ettringite and the water-to-cement ratio of the specimens.

4.6 Microstructural Analysis Using SEM and EDX

The Scanning Electron Microscope (SEM) is one of the most versatile and widely used tools of modern science, as it allows the study of both morphology and composition of biological and physical materials. By scanning an electron probe across a specimen, high resolution images of the morphology or topography of a specimen can be obtained with great depth of field, at very low or very high magnifications from SEM analysis. Compositional analysis of a material may also be obtained by monitoring secondary X-rays produced by the electron-specimen interaction. This process is called Energy-dispersive X-ray spectroscopy (EDX), and is sometimes referred to as EDS or EDAX analysis. It is a technique used for identifying the elemental composition of specimens, or an area of interest thereof. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own without the latter. The output of an EDX analysis is an EDX spectrum. The EDX spectrum is simply a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which most X-rays have been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen.
A micrograph of concrete samples immersed in sodium sulphate solutions is presented in Figure 4.16 to Figure 4.19. Figure 4.16 and Figure 4.17 represent the microstructure of the outer surface of a concrete cylinder specimen after 361 days of exposure to 2% and 4% sodium sulphate solution. From these two figures it is clear that the surface of concrete specimens contains ettringite crystals. The needle-like crystal of ettringite dominates the concrete specimen's microstructure. There are some voids and microcracks visible at the surface of the specimen near ettringite structures, which may be due to the formation of expansive ettringite. Figure 4.18 and 4.19 represent the microstructure of the inner surface of concrete specimens exposed to 2% sodium sulphate solution. In the case of the inner surface, no ettringite was found in the specimen, which confirms that ettringite forms only in the exposed surface due to the reaction of sulphate with hydroxides of cement.

Corresponding EDX spectra of the concrete specimens of Figures 4.16 and 4.17 are presented in Figures 4.20 and 4.21 respectively. The EDX spectrum shows that the calcium dominates the surface of the specimen, followed by silicate and oxygen. Silicon, calcium and oxygen represent the ettringite structure as these three are the major components of ettringite.
Figure 4.16: SEM analysis of outer surface of PC concrete under 2% sodium sulphate exposure for Mix A

Figure 4.17: SEM analysis of outer surface of PC concrete under 4% sodium sulphate exposure for Mix A
Figure 4.18: SEM analysis of inner surface of PC concrete under 2% sodium sulphate exposure for Mix A

Figure 4.19: SEM analysis of inner surface of PC concrete under 4% sodium sulphate exposure for Mix A
Figure 4.20: EDX analysis of PC concrete under 2% sodium sulphate exposure for Mix A

Figure 4.21: EDX analysis of PC concrete under 4% sodium sulphate exposure for Mix A
4.7 Discussion

The two primary reactions involved in early stage sodium sulphate attack on PC concretes result in the formation of gypsum and ettringite. According to Santhanam (2001) a considerable quantity of ettringite forms before any expansion of the mortar occurs under sodium sulphate exposure and expansion begins with the formation of gypsum. Santhanam (2001) found that the quantity of ettringite increases when the increase in expansion is registered and concludes that it is possible that the mortar system initially can accommodate the products formed by the sulphate attack reactions, and when the quantity of attack products reaches a certain level, expansion occurs. In the present experiment a mass gain in all concrete specimens immersed in sodium sulphate solution was observed. The XRD, SEM and EDX analysis confirms that the mass gain in the concrete is due to the formation of ettringite. The volume of the ettringite is higher than the reactant components, and hence it occupies more space in the resultant structure and allows expansion of the concrete.

Two main hypotheses have been proposed to explain the mechanism of expansion. One view is that expansion is caused by the growth of the relatively large crystals that form at aggregate interfaces and elsewhere (Diamond, 1996, Yang et al., 1999a, Yang et al., 1999b). The other is that it is caused, or at least begins with the growth of the much smaller crystals formed within the paste (Johansen; et al., 1993).

Compressive strength of concrete was not significantly affected by the exposure to sulphate environment.
Chapter 5

Deterioration of Concrete under Exposure to Sulphuric Acid

5.1 Introduction

Degradation of concrete infrastructure exposed to sewage can be caused by the aggressive sulphuric acid formed by biogenic methods. According to published research, acid attack is more detrimental than sulphate attack. By understanding the behaviour of concrete specimens exposed to sulphuric acid solutions under accelerated conditions, an understanding of the deterioration mechanism can be developed.

This chapter presents the results of mass change, length change and SEM, XRD analysis of concrete specimens exposed to sulphuric acid over a period of one year. Results are considered in comparison with the findings of other researchers to unravel the exact mechanism which underpins the observed mass loss and length change.

5.2 Previous Work

The primary reaction product manifested on the concrete surface due to exposure to sulphuric acid is gypsum associated with volume expansion (factor of 2.2 compared to the volume of reactants), which can induce tensile stresses in concrete, resulting in cracking and spalling (Monteny et al., 2001). If not washed out, the accumulation of
gypsum on the surface of concrete may slow down the corrosion rate due to surface sealing (Rendell and Jauberthie, 1999). Further reaction of gypsum with calcium aluminate phases in the cementitious matrix can form ettringite, which has a greater volume increase (up to a factor of 7) than that of gypsum, thus leading to more micro- and macro-cracking. In addition, sulphuric acid decomposes the cementitious matrix by decalcifying calcium silicate hydrate (C–S–H), thus contributing to strength loss. Several researchers have studied the effect of cement type, cement content, water-to-cementitious materials ratio (w/cm), supplementary cementitious materials (SCMs), and polymeric materials on improving the resistance of mortar or concrete to sulphuric acid attack (Ehrich et al., 1999, Fattuhi and Hughes, 1988b, Torii and Kawamura, 1994b, Roy et al., 2001).

In a series of chemical tests with different sulphuric acid concentrations of 1–3%, Fattuhi and Hughes (Fattuhi and Hughes, 1988b) showed that sulphate-resistant Portland cement (SRPC) did not offer marked improvement compared to ordinary Portland cement (OPC) in reducing the mass loss of mortar or concrete specimens. Also, they indicated that for high (greater than 1%) sulphuric acid concentrations, minimizing the cementitious material content in concrete can effectively reduce the rate of acid attack expressed by mass loss. Because acid specifically attacks cementitious constituents, concretes with a low water/cement ratio and a high cementitious volume fraction are more vulnerable to greater mass loss. The effect of reducing the water/cement ratio on improving the resistance of concrete to sulphuric acid attack was only significant at lower acid concentrations (1%) (Fattuhi and Hughes, 1988a). The researchers found that the deterioration of the specimens measured by means of weight loss increased with a corresponding increase in cement content. Depending on the acid concentration, increasing the volume fraction of cement from 10% to 17% caused an increase in weight loss with a factor of 2 in a 1% sulfuric acid solution, and an increase in weight loss with a factor of almost 3 in a 3% sulphuric acid solution.
They also found a decrease in weight loss due to a decrease in water/cement ratio. When the water/cement ratio was reduced from 0.4 to 0.3, in the case of the 1% sulfuric acid solution, the loss in weight was nearly 20%. The reduction of the water/cement ratio did not cause any decrease in weight loss in the case of the 3% sulfuric acid solution. In fact, often a combination of two opposite effects took place. Due to a lower water/cement ratio, porosity decreases and corrosion should be lower. Moreover, the relative amount of cement increases and this implicates higher corrosion. Fattuhi and Hughes (1988a) stated that brushing had a strong influence on the results. At the beginning of the deterioration, an increase in weight is accompanied by volume expansion of the specimens, and often less difference between several concrete types can be found. Due to brushing of the specimens, a large part of the gypsum formed on the surfaces can be removed. Therefore a loss in weight can be measured and a difference between the several concrete types can be found.

Over the past 20 years, the use of supplementary cementitious materials (SCM) in concrete has become very common due to their technological, economical, and environmental benefits. The use of SCMs such as silica fume and fly ash in concretes has been found to improve the resistance of concrete to sulphuric acid attack because of the reduced presence of calcium hydroxide, which is most vulnerable to acid attack (Durning and Hicks, 1991). Using silica fume in binary cement systems as a partial replacement for ordinary Portland cement was found to be effective in the reduction of acid attack (Durning and Hicks, 1991, Mehta, 1985). Some other research (Mehta, 1985, Caballero et al., 2000) has shown remarkable improvement in the acid resistance of concrete using fly ash. It has also been reported that the use of a ternary cement consisting of 10% silica fume and up to 60% fly ash has a better performance than other SCM concretes, despite weight loss of the concrete samples of up to 25% after 56 days immersion in 1% sulphuric acid solution (Tamimi, 1997).
Durning and Hicks (1991) used a 1% and a 5% sulphuric acid solution to subject concrete specimens to 7-day attack cycles. After every cycle, the specimens were brushed and weighed. They investigated the effect of silica fume addition on resistance to sulphuric acid. It was found that, as the amount of silica fume increased (from 0% to 30% by mass of cement), the resistance of the specimens also increased. When a 30% replacement was used, the number of cycles to failure of the specimens in the 1% sulfuric acid solution was already doubled. Yet, in the more concentrated acid solution, there was a noticeably slower increase in the resistance. It took only 1 or 2 cycles more until failure of the specimens was obtained. Durning and Hicks (1991) attributed this difference to the decomposition of calcium silicate hydrate in the more concentrated liquid in addition to the reaction with the free calcium hydroxide. In contrast, Yamoto et al. (1989) found that the addition of 30% silica fume almost doubled the time to failure of the specimens in a sulfuric acid solution of even 5%. They attributed the increase of resistance for the specimens with silica fume to the decrease of permeability. It must be noted that these researchers did not brush their specimens. Thus, brushing of specimens, or not, may have an important influence on the results obtained.

Chang et al. (2005b) found after 168 days immersion in sulphuric acid solutions, that cylinders of concretes with slag and silica fume and concrete with limestone aggregate, silica fume and fly ash had 1.1% and 1.5% mass gain respectively, while the concretes OPC, OPC with slag and OPC with silica fume lost mass by 2.8% to 6.8% respectively. In contrast, the reference concrete using Portland cement had the greatest mass loss of 10.6%.

5.3 Physical Properties

Figures 5.1 to 5.3 present a comparison of mass loss data of control specimens with specimens immersed in sulphuric acid solutions for 361 days from the three mix designs. The mass loss in the specimens exposed to sulphuric acid increases with
time, and for control specimens it increases up to 100 days followed by a reduction up to the end. It is clear that the increase in acidity (reduction in pH) leads to greater reduction in mass. The actual mass loss data of the concrete is shown graphically in Figure 5.2 for Mix A. The mass loss of specimens immersed in sulphuric acid solution shows a similar trend for all three different concrete mixes (Figures 5.1-5.3). The control specimens also lost mass with respect to time, possibly due to the heating cycles of 105 °C for 24 hours. Due to this heating cycle, the concrete specimens may demonstrate faster dehydration of the CSH gel and increase in porosity which is related to mass loss. Castellote et al. (2004) also observed a similar result.

Figures 5.4 and 5.5 represent the effect of water-to-cement ratio on mass loss of concrete specimens under sulphuric acid exposure. Mass loss is not directly related to the water-to-cement ratio. The observation made by other researchers that increase in water-to-cement ratio led to a larger mass loss was not clearly observed here.
Figure 5.2: Mass loss of PC concrete under sulphuric acid exposure for Mix B

Figure 5.3: Mass loss of PC concrete under sulphuric acid exposure for Mix C
Figure 5.4: Effects of water cement ratio on mass loss of PC concrete under sulphuric acid exposure of pH 3.0

Figure 5.5: Effects of water cement ratio on mass loss of PC concrete under sulphuric acid exposure of pH 4.0
5.4 XRD Analysis

XRD analysis was carried out on concrete samples at the end of exposure to different solutions for 361 days. Based on visual comparison of the relative intensities of the peaks for a particular phase in one sample with the same peaks in another sample, some conclusions are made which are not absolute quantitative determinations. Also some qualitative analysis of the samples was conducted using a Bruker 'Search and Match” routine of the background subtracted diffraction patterns against the International Centre for Diffraction Data (ICDD) database.

Figures 5.6 and 5.7 present the XRD results of the specimen exposed to sulphuric acid solution from Mix A for 361 days. Using two theta scales, X-rays were produced from 5 to 60 degree angles and the results were recorded. From the figure it is apparent that the concrete specimen consists of three major ingredients; ettringite, thaumasite and gypsum. The dominant ingredient is ettringite, followed by gypsum and a small amount of thaumasite is also recorded. The results of other mixes and exposures to different concentration solutions also reveal the same conclusion that the ettringite is the major ingredient in the samples after 361 days of exposure (Figures A-34 to A-39).
Figure 5.6: XRD analysis of PC concrete under sulphuric acid exposure of pH 3.0 from Mix A

Figure 5.7: XRD analysis of PC concrete under sulphuric acid exposure of pH 4.0 from Mix A
5.5 SEM and EDX Analysis

Micrographs of concrete samples immersed in sulphuric acid solutions of different pH and from different mixes are presented in Figures 5.8 to 5.10. Figure 5.8 represents the microstructure of concrete specimens immersed in sulphuric acid solutions of pH 3.0 for 361 days in Mix A. From these figures it is clear that the surface of concrete specimens contains gypsum and there is a void which is filled by ettringite crystals. Figure 5.9, a micrograph of a specimen immersed in acid solution of pH 4.0 in Mix A shows a similar microstructure: a mixture of gypsum and ettringite on the surface of the specimens. Figure 5.10 shows a high density ettringite structure on the surface of a Mix C specimen immersed in acid solution of pH 4.0.

Corresponding EDX spectra of the concrete specimens of Figures 5.8 and 5.10 are presented in Figures 5.11 and 5.13 respectively. The EDX spectrum shows that calcium dominates the surface of the specimen followed by silicate and oxygen. As silicon is the primary content of cement EDX shows a silicon peak. The peak of calcium and oxygen represents the ettringite structure. EDX analysis was carried out on concrete surface and the elements spectra are collected from “Point Analysis”. The peaks are identified using “Auto Peak” function. Sometimes identifying the peaks automatically can give wrong information about the elemental composition of the specimen and hence required to correct them by doing manual identification of peaks. Choosing auto function allows only to identify the dominant peaks and it does not focus on the other small peaks. Hence it may be possible that the presence of sulphur is not listed in some EDX spectrum.
Figure 5.8: SEM analysis of PC concrete under sulphuric acid exposure of pH 3.0 for Mix A

Figure 5.9: SEM analysis of PC concrete under sulphuric acid exposure of pH 4.0 for Mix A
Figure 5.10: SEM analysis of PC concrete under sulphuric acid exposure of pH 4.0 for Mix C

Figure 5.11: EDX analysis of PC concrete under sulphuric acid exposure of pH 3.0 for Mix A
Figure 5.12: EDX analysis of PC concrete under sulphuric acid exposure of pH 4.0 for Mix A

Figure 5.13: EDX analysis of PC concrete under sulphuric acid exposure of pH 4.0 for Mix C
5.6 Acid Penetration Depth

In order to identify the severity of acid exposure, at the end of exposure the acid penetration depth was measured using different acid-base indicators. The concrete specimens were cut in the middle and then acid-base indicator solution has been sprayed onto the sample to see whether it reacts or not. All the laboratory specimens showed reaction with only Phenolphthalein. When Phenolphthalein sprayed on the specimen, this indicator shows colourless surface if the surface has a pH of 9 or less. It, however shows a distinct pink colour if the pH is higher than 9. In this experiment the Phenolphthalein reacts in the whole surface area of concrete indicating a 100% penetration. The sample collected from the field is also examined similarly for measuring acid penetration depth. The field sample of concrete septic tank also exhibits a 100% penetration of acid. The XRD, EDX and acid penetration depth results obtained from both laboratory and field specimens provide an inkling that a similar mechanism is applicable for both the above stated cases. Figure 5.14 and Figure 5.15 shows the concrete specimens after acid penetration tests where they showed distinct pink colour.

Figure 5.14: Acid penetration of concrete specimens exposed to sulphuric acid solution
5.7 Effect of Acid Exposure on Compressive Strength of Concrete

The compressive strength of concrete specimens exposed to sulphuric acid solutions are presented in Table 5.1 and in Figure 5.16 to 5.21. From the results shown in Figure 5.16 to 5.18 it is clear that the strength of concrete reduces with the strength of the acidity in the exposed environment. The effect is more pronounced in mixes with high cement content. The effect was also observed by Fattuhi and Hughes (Fattuhi and Hughes, 1988b).
Table 5.1: Compressive strength of concrete specimen exposed to sulphuric acid solution after 361 days

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Stress at End (MPa)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>Average</td>
<td></td>
</tr>
<tr>
<td>Acid_3_A</td>
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<td>15.27</td>
<td>16.85</td>
<td></td>
</tr>
<tr>
<td>Acid_3_B</td>
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<td>32.37</td>
<td></td>
</tr>
<tr>
<td>Acid_3_C</td>
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<td>34.58</td>
<td>38.29</td>
<td></td>
</tr>
<tr>
<td>Acid_4_A</td>
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<td>19.70</td>
<td>26.59</td>
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</tr>
<tr>
<td>Acid_4_B</td>
<td>-</td>
<td>27.40</td>
<td>27.40</td>
<td></td>
</tr>
<tr>
<td>Acid_4_C</td>
<td>22.85</td>
<td>-</td>
<td>22.85</td>
<td></td>
</tr>
<tr>
<td>Control A</td>
<td>44.14</td>
<td>51.22</td>
<td>47.68</td>
<td></td>
</tr>
<tr>
<td>Control B</td>
<td>41.14</td>
<td>37.79</td>
<td>39.47</td>
<td></td>
</tr>
<tr>
<td>Control C</td>
<td>39.87</td>
<td>41.26</td>
<td>40.56</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.16: Compressive strength of concrete specimen exposed to sulphuric acid solution for 361 days from Mix A
Figure 5.17: Compressive strength of concrete specimen exposed to sulphuric acid solution for 361 days from Mix B

Figure 5.18: Compressive strength of concrete specimen exposed to sulphuric acid solution for 361 days from Mix C
Figure 5.19: Comparison of compressive strength results at different ages for Mix A exposed to sulphuric acid solution

Figure 5.20: Comparison of compressive strength results at different ages for Mix B exposed to sulphuric acid solution
Figure 5.21: Comparison of compressive strength results at different ages for Mix C exposed to sulphuric acid solution

5.8 Comparison of Sulphate Exposure and Sulphuric Acid Exposure

Ettringite and gypsum are the primary products of the chemical reaction between a sulphate-bearing solution and cement hydration products. Failure by expansion as a result of sulphate attack has traditionally been attributed to the formation of ettringite (Santhanam et al., 2001a, Mehta, 1983c, Cohen, 1983c, Odler and Gasser, 1988b).

The proposed mechanism for attack by sodium sulphate solution is shown in the schematic diagram in Fig. 5.22. Step 1 depicts the initial stage of the process. The mortar specimen has just been introduced into the Na$_2$SO$_4$ solution that has a pH of 6–8. The pH of the surrounding solution changes to 11–12 a few minutes after the specimen is introduced. If the water surrounding the mortar is stagnant, as is the case in a laboratory test, the pH will remain in the range of 11–12. However, in the case of a flowing sulphate solution, such as that in groundwater, the pH may stay at a low level.
However, the rate of expansion after this initiation, i.e., during Stage 2, is not significantly different when the pH of the solution is low. Thus, it can be assumed that the attack will proceed in a manner described by this model. In Step 2, gypsum and ettringite start forming in the regions close to the surface. The surface zone of the mortar, where expansive gypsum and ettringite have formed, behaves like a skin that is trying to expand. However, the bulk of the mortar underneath, which is chemically unaltered, tries to resist this expansion. Thus, as described in Step 3, a resultant compressive force is generated in the surface region, while the bulk of the mortar is subjected to tensile forces. This causes cracks to appear in the interior of the mortar, as shown in Step 4. Over time, the surface zone deteriorates due to continued penetration of the solution. When the solution is able to reach the cracked interior zones, it reacts with the hydration products and leads to deposition of attack products inside the cracks, as well as in the paste. Gypsum primarily deposits in the cracks and in voids, because these provide the best sites for nucleation. Hence, as shown in Step 5, a new region inside the mortar becomes the zone of deposition. This region then tries to expand, causing resultant tensile forces in the interior of the mortar. New cracks then appear in the interior zones. At this stage (Step 6), there are three distinct zones within the mortar—the disintegrated surface, the zone of deposition of attack products, and the interior cracked zone that is chemically unaltered. The disintegrated surface zone is also prone to the formation of thaumasite, because the sulphate solution has direct access to the decalcified C-S-H and ettringite in this region. The attack thus progresses at a steady rate until complete disintegration of the specimen occurs.

Sulfuric acid is a very aggressive acid that reacts with the free lime Ca(OH)$_2$, in cement paste forming gypsum (CaSO$_4$.2H$_2$O). An even more destructive action is the reaction between calcium aluminate present in cement paste and gypsum crystals. These two products form the less soluble reaction product, ettringite (3CaO.Al$_2$O$_3$.3CaSO$_4$.32H$_2$O). These very expansive compounds cause internal
pressure in the concrete, which leads to the formation of cracks. The reacted surface becomes soft and white. In general, the mass change results appear to indicate that the dissolution caused by hydrogen ions lags behind the action caused by sulphate ions in the early stages of immersion in acid. The former action would mainly cause dissolution and mass loss, however, the latter could initially lead to mass gain and finally result in mass loss due to excessive expansion and cracking. The combined actions of dissolution and expansion gradually cause the surface layer of cement mortar to fail, which brings about significant mass reduction of the cylinders (Chang et al., 2005).

5.9 Length Change

Figure 5.23 represents the length change data of PC concrete under sulphuric acid exposure for 230 days. It shows contraction in all specimens with a small expansion from 110 to 130 days. Control specimens show maximum contraction followed by the specimen from less acidic solution. With the increase in acidity, the specimen's contraction reduces which indicates that the acidity increases the expansion of the concrete specimens.
Figure 5.22: Proposed mechanism of sodium sulphate attack

**Step 1**
- Na$_2$SO$_4$ solution;
- pH = 6 – 8
- Expanding, Resultant compression

**Step 2**
- Na$_2$SO$_4$ solution;
- pH = 11 - 12
- Gypsum and ettringite deposition

**Step 3**
- Resisting, Resultant tension

**Step 4**
- Cracked interior

**Step 5**
- Disintegrated surface
- Cracked zones and pores filled with gypsum

**Step 6**
- Deposition zone
- New cracked zone
Figure 5.23: Length change of PC concrete under sulphuric acid exposure

5.10 Summary and Conclusions

The dominant reaction that takes place in the presence of sulfuric acid is the conversion of calcite to gypsum according to Equation 5.1.

\[
CaCO_3 + H_2SO_4 + H_2O = CaSO_4 \cdot 2H_2O + CO_2
\]

..................................................5.1

\[
4CaOAl_2O_3\cdot SO_3\cdot 12H_2O + CaSO_4\cdot 2H_2O + 16H_2O = (CaO)_4\cdot Al_2O_3\cdot (CaSO_4)_3\cdot 32H_2O
\]

..................................................5.2

This gypsum may react further with monosulphate to form ettringite which is expansive in nature. The secondary effect of sulphuric acid is the decalcification of calcium-silicate-hydrate gel (CSH) thus loosening the cementitious structure (Hill et al., 2003, Santhanam, 2001).

Compressive strength is significantly affected by acid exposure with changes as high as 20% for specimens made of concrete having a high cementitious content. This
confirms the observation of Fattuhi and Hughes (1988b) that concrete with low w/c are more vulnerable to acid exposure.

It may be concluded that low w/c ratio concrete mixes whilst having a low porosity could still be vulnerable to acid attack due to high cement content.

The length change data indicates that the mass loss/gain is not clearly represented in measurements of length change. Since the trends are difficult to analyse and not clear, further analysis utilised the mass loss/gain and not the length change.
Chapter 6

Predicting Deterioration

6.1 Introduction

Work presented in previous chapters attempted to understand the expected deterioration regime of concrete septic tanks under sulphate and acid attack. Since it is impossible to create the exact field conditions in the laboratory for a prolonged period, an attempt was made to create a suitable accelerated deterioration test which will assist researchers to establish a predictive model which then can be calibrated with field measurements to ascertain the possible levels of deterioration in the field. This chapter presents the development of deterioration from laboratory measurements and validation with field measurements.

6.2 Nature of Accelerated Tests

Creating field conditions inside the laboratory is problematic and it is often difficult to eliminate conflicting effects with field simulations. The scale of testing and the need for results within a short time period also make field simulation in the laboratory quite impractical. However, it is often possible to design adequate accelerated tests without altering the deterioration mechanism, which can mimic the behaviour in the field to a certain degree. The definition of accelerated tests is found in ASTM E 632-82 (Standard Practice for Developing Accelerated Tests to Aid Prediction of Service Life of Building Components and Materials) which states that accelerated tests are those in which the degradation of building materials is intentionally accelerated over that
expected in service. However, accelerated tests should meet the basic assumption that
the mechanism of action is identical in the laboratory and in the field. Deterioration of
concrete in sulphate environments depends on numerous factors such as the service
environment which includes the concentration of sulphate solution, temperature and
humidity variations. Thus in order to predict concrete performance in situations such as
sulphate attack, it is essential to incorporate these effects into any model that is
developed for prediction purposes.

6.3 Predictive Models

Researchers use various indicators to describe the damage caused by sulphate attack
such as expansion, compressive strength, mass change, hardness etc. The
mechanisms or set of reactions causing the variations in these physical properties are
sometimes quite different, and this causes difficulties in the interpretation of the results.
Thus it is essential to identify the parameter or set of parameters that can most reliably
express deterioration. Most traditional studies of sulphate attack have considered two
important factors related to the chemistry: the C₃A content and the water-to-cement
ratio. However, the importance of other factors, such as the C₃S content and the type
of sulphate solution is also recognised by researchers.

Engineers have also tried to develop various approaches to estimate the long-term
durability of concrete structures subjected to sulphate attack. Early attempts to predict
the remaining service life of concrete were relatively simple and mainly consisted of
linear extrapolations based on a given set of experimental data (Kalousek et al., 1972,

Following these initial efforts, many authors have later tried to elaborate more
sophisticated ways to predict the durability of concrete. Most of these early service-life
models essentially consist of empirical equations. All have been developed using the
same approach. An equation linking the behaviour of the material to its microstructural properties is deduced from a certain number of experimental data. In most cases, the mathematical relationship is derived from a (more or less refined) statistical analysis of the experimental results.

More recently, researchers have tried to develop a new generation of more sophisticated models to predict the service life of concrete exposed to sulphate environments. These mechanistic (or phenomenological) models can be distinguished from the purely empirical equations by the fact that they are generally based on a better understanding of the mechanisms involved in the degradation process.

Santhanam (Santhanam, 2001) uses expansion, dynamic modulus of elasticity, mass change, and compressive strength as the physical parameters to build the predictive model. However he explains that compressive strength and dynamic modulus are not appropriate parameters for the investigation of sulphate attack. According to him, micro-cracks generated by expansion during sulphate attack may have a tendency to close during the application of a compressive stress which may lead to incorrect interpretations regarding the level of damage. Moreover, in the case of dynamic modulus, the results are often inconsistent owing to localized zones of failure within the specimens.

6.4 Previous Work

Since there has been little work published on septic tanks, the author of the present study was guided by previous work published on the deterioration of sewerage pipes. The rate of corrosion of concrete pipes depends on the strength and density of concrete, the degree of acid penetration, the acid value and the circulation of hydrogen sulphide in the atmosphere. Non-accelerated laboratory testing was started by the U.S. Bureau of Reclamation (USBR) to establish the influence of concrete-mix parameters
on sulphate resistance over 50 years ago. Concrete specimens were monitored at regular intervals with field exposure conditions of sulphate concentrations. Kurtis et al. (Kurtis, 2002) conducted statistical analysis of a portion of the data to predict the expansion of the concrete as a function of time, w/c ratio, and C_3A content. Jambor (1998) is among the first researchers to develop an empirical equation describing the rate of “corrosion” of hydrated cement systems exposed to sulphate solutions. The equation is derived from the analysis of a large body of experimental data obtained over a fifteen-year period. The objective of the comprehensive research program was to investigate the behaviour of 0.6 water–binder ratio mortar mixtures totally immersed in sodium sulphate (Na_2SO_4) solutions. Based on the analysis of the results obtained during the first four years of the test program, Jambor (1998) proposed the following equation to predict the degree of sulphate-induced corrosion (DC):

\[ DC = [0.11 S^{0.45}] [0.143 t^{0.33}] [0.204 e^{0.145 C_3A}] \] ........................................6.1

Where

S = SO_4 concentration of the test solution (expressed in mg/l),
t = Immersion period (expressed in days) and
C_3A = Percentage in tricalcium aluminate of the Portland cement (calculated according to Bogue’s equations).

Jambor (1998) also proposed to multiply equation (6.1) by a correcting term (\( \eta_a \)) to account for the presence of supplementary cementing materials (such as slag and the volcanic tuff):

\[ \eta_a = e^{-0.016 A} \] ........................................................................................................6.2

Where A represents the level of replacement of the Portland cement by the supplementary cementing material (expressed as a percentage of the total mass of binder).
As can be seen, the degree of corrosion predicted by Jambor’s model (Equations (6.1) and (6.2)) is directly affected by the sulphate concentration of the test solution and the $C_3A$ content of the cement used in the preparation of the mixture. In that respect, the model is useful to investigate the influence of various parameters such as cement composition on the behaviour of laboratory samples. It is, however, difficult to predict the service-life of concrete structures solely on the basis of Jambor’s model. The author does not provide any information on the critical degree of corrosion beyond which the service-life of a structure is compromised.

According to Pomeroy (Pomeroy, 1977), the theoretical corrosion rate prediction equation is given by,

$$CR = 11.4 \times k \times \varphi_{sw} \times (1/a)$$

Where

$CR =$ average rate of corrosion of concrete by acid (mm per year)

$k =$ coefficient for acid reaction, accounting for estimated fraction of acid remaining on wall

- 0.8 for $S$ (increase of sulphide concentration) $\leq 1.0$
- 0.7 for $1.0 \leq S \leq 5.0$
- 0.6 for $S > 5.0$

$\varphi_{sw} =$ flux of hydrogen sulphide to pipe wall (g/m² * h)

$a =$ coefficient for alkalinity of concrete, normally 0.16.

The rate of corrosion of concrete pipes has been expressed by Thistlethwayte (Thistlethwayte, 1972) using the theoretical equation
\[
CR = 19.9 \times 10^5 \times \frac{K_{sa} \times P_{H2S} \times A_{sa}}{z \times \rho \times A_{aw}}
\]

Where

\( K_{sa} \) = rate of absorption of \( H_2S \) on pipe wall (kg/m² * h)

\( P_{H2S} \) = partial pressure of \( H_2S \) (ppm)

\( A_{sa} \) = ratio of surface width of waste stream to exposed perimeter of pipe wall above water surface (m²/m)

\( z \) = of cement content of concrete (kg/m³)

\( \rho \) = density of concrete (kg/m³)

\( A_{aw} \) = exposed perimeter of pipe wall above water surface (m²/m).

Both expressions indicate that the corrosion rate is usually measured as mm/year and that it is a function of the acid concentration, coefficient of alkalinity of concrete (or the cement content), exposed area of pipe above sewerage and the pressure of \( H_2S \).

6.5 Details of the Model

The following are the details of the statistical models developed using Microsoft Excel and SPSS®. A nonlinear regression analysis has been conducted to develop these models. Separate nonlinear-regression based models were developed for sodium sulphate and sulphuric acid solution exposure. Data for these models were collected from the results of all concrete mixes stored in the different concentration solutions for 361 days.

The dependent variable chosen for the model was the mass loss of the specimen measured per 500 gm. The independent or explanatory variables were the following:

- Cement (C)
- Acid concentration (pH)
- Sodium sulphate concentration (K)
- Time (T)

Initial regression analysis of data have shown that the best fit curve for the prediction of
mass loss as a function of time is a mass loss vs. time. Subsequently, optimization
using multiple regression has shown that the best fit equation for the observed mass
loss data of specimens exposed to H₂SO₄ solution is:

\[ ML = \frac{(pH)^{-1.795} \times 0.0172 \times C^{-0.579}}{(2 \times 10^{-4} + T^{-1.9134})} \]

Where

ML = Mass loss of the concrete specimen (per 500 gm)

pH = pH of the surrounding acid solution or the environment

C = Amount of cement used in the mix design (expressed in kg/m³)

T = Time of exposure (expressed in days)

A similar expression has been derived to evaluate the mass gain of concrete under
exposure to sodium sulphate solutions:

\[ MG = \frac{K^{1.0064} \times (1 + C^{0.00068})}{(2.04 \times 10^{-84} + T^{-1.8175})} \]

Where

MG = Mass gain of the concrete specimen (per 500 gm)

K = Concentration of sodium sulphate solution (expressed as percentage)

C = Amount of cement used in the mix design (expressed in kg/m³)

T = Time of exposure (expressed in days)
6.6 Calibration of the Model

6.6.1 Analysis of the Model Using Laboratory Data

6.6.1.1 95% Probability Plot

A statistical analysis of mass loss and mass gain for different conditions was carried out to determine the efficacy of the model. Statistical analysis is an integral part of any research based on concrete as it is an unpredictable element. Different statistical methods can be used to understand the characteristics of data collected from concrete exposure to different aggressive environments. The 95% probability plot was carried out to see the relationship between predicted and actual mass loss and mass gain for different exposure conditions.

Figures 6.1 and 6.2 depict the 95% probability curve for sulphuric acid and sodium sulphate attack respectively. The $R^2$ value obtained for the 95% probability plot is 0.9286 when the actual mass loss was compared with the predicted mass loss for sulphuric acid exposure (Figure 6.1). In addition, it was observed that there were very few outliers outside the +95% and −95% line, which indicates that the developed equation is compatible with the result obtained from the experiment. Moreover, while analysing the 95% probability curve in the case of sodium sulphate exposure, it was observed that the $R^2$ value was 0.787 (Figure 6.2). One of the reasons for obtaining a low $R^2$ value may be the presence of more outliers in comparison with the earlier figure (Figure 6.1). However an $R^2$ value of more than 75% can be considered as substantial, considering the fact that predicted mass gains were observed for different concentrations of sodium sulphate exposure.

6.6.1.2 45 Degree Line

Further, it was decided to carry out an analysis in order to identify the resemblance between actual and predicted data. Figures 6.3 and 6.4 depict the relationship between
the actual and predicted data for sulphuric acid and sodium sulphate exposure respectively. It can be observed from the figures that a 45 degree line (1:1 line) and +50% and -50% (parallel to 1:1 line) were plotted to carry out the analysis. Figure 6.3 illustrates that in most cases the mass loss data were in the 50% range with a few exceptions (from 3 to 6 gm per 500 gm of actual and predicted data) for sulphuric acid exposure. This indicates the efficacy of the developed equation which will be used to predict the mass loss of concrete specimens. Furthermore, Figure 6.4 shows that there are many outliers in comparison with the sulphuric acid exposure conditions. This indicates that in the case of sodium sulphate exposure there is a widespread presence of scattered points and hence the equation developed may not be entirely applicable to predict mass gain effectively.

![Figure 6.1: 95 percent probability plot for actual and predicted data obtained from sulphuric acid solution](image)

Figure 6.1: 95 percent probability plot for actual and predicted data obtained from sulphuric acid solution
Figure 6.2: 95 percent probability plot for actual and predicted data obtained from sodium sulphate solution

Figure 6.3: Comparison between the mass loss obtained from actual and predicted from sulphuric acid solution
6.6.1.3 Percentage Error

To gain confidence in the developed regression model, it was decided to obtain the percentage error between the actual mass loss and predicted mass loss. The percentage error was calculated by using Equation 6.1.

\[
\% \text{ error} = \left( \frac{M_a - M_p}{M_a} \right) \times 100
\]

where,

\( M_a \) = Actual mass loss or gain

\( M_p \) = Predicted mass loss or gain

Tables 6.1 and 6.2 illustrate the percentage error of the actual and predicted mass loss or gain due to sulphuric acid and sodium sulphate exposure of 361 days respectively. Table 6.1 shows that the maximum percentage error is 20.57% for Mix B with pH 4.0 and a minimum of 0.11% for Mix C with pH 4.0, and the rest are within tolerable limits.
This indicates that the model developed to predict mass loss due to sulphuric acid exposure can be effectively used.

Table 6.1: Comparison of actual and predicted mass loss of concrete specimen for different mix designs and different pH for 361 days of sulphuric acid exposure

<table>
<thead>
<tr>
<th>Mix Design</th>
<th>pH</th>
<th>Mass Loss</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Actual</td>
<td>Predicted</td>
</tr>
<tr>
<td>A</td>
<td>3</td>
<td>11.00</td>
<td>9.58</td>
</tr>
<tr>
<td>A</td>
<td>4</td>
<td>5.02</td>
<td>5.72</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>10.59</td>
<td>9.69</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>4.80</td>
<td>5.78</td>
</tr>
<tr>
<td>C</td>
<td>3</td>
<td>10.10</td>
<td>9.66</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>5.77</td>
<td>5.76</td>
</tr>
</tbody>
</table>

Table 6.2: Comparison of actual and predicted mass gain of concrete specimens for different mix designs and different concentrations for 361 days of sodium sulphate exposure

<table>
<thead>
<tr>
<th>Mix Design</th>
<th>Concentration in percent</th>
<th>Mass Gain</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Actual</td>
<td>Predicted</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>4.95</td>
<td>3.87</td>
</tr>
<tr>
<td>A</td>
<td>4</td>
<td>7.50</td>
<td>7.77</td>
</tr>
<tr>
<td>A</td>
<td>5.5</td>
<td>10.24</td>
<td>10.71</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>5.48</td>
<td>3.77</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>8.45</td>
<td>7.56</td>
</tr>
<tr>
<td>B</td>
<td>5.5</td>
<td>10.75</td>
<td>10.42</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>4.66</td>
<td>3.80</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>7.78</td>
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<tr>
<td>C</td>
<td>5.5</td>
<td>9.63</td>
<td>10.52</td>
</tr>
</tbody>
</table>
6.6.1.4 Verification of Developed Model

Using a predictive model, the actual and predicted data points are plotted in Figures 6.5 to 6.10 to check whether the model is capable of producing actual data. Figures 6.5 to 6.7 represent the mass loss of concrete specimens exposed to sulphuric acid solution. The predicted line represents the values calculated using the model, and this was found to present a reasonable fit to the data points. Figures 6.8 to 6.10 represent the mass gain of concrete specimens exposed to sodium sulphate solution. Here the actual data points are not exactly on the predicted line, but they are at or near the line, which means that the model developed is quite reasonable for predicting the mass gain of concrete specimens.

6.6.2 Analysis of the Model Using Field Data

A field sample of concrete septic tank was collected from the suburb of Doncaster in Manningham City Council and was examined for loss of thickness as well as microanalysed. The micrograph of the concrete is presented in Figure 6.11. The concrete septic tank sample is 18 years old and the thickness loss was found to be 2.5 mm. The tank is 1 m in diameter and 2 m in length. The pH of the tank inside was found to be 6.0. Using the derived model, the mass loss per 500 gm of the sample is 3.22 gm. Assuming concrete density to be 2400 kg/m$^3$, the weight of the tank is 544.005 kg. Hence the total actual mass loss of the septic tank is 3502.2 gm. When sulphate attack occurs in concrete, the outer or the contact surface of the concrete expands and hence loses its density to a lower value. Only the cementitious materials are washed out from the concrete surface or affected. Hence we can assume the mass loss in the septic tank is mainly the loss of cementitious materials and the density of the outer cementitious mortar surface is around 750 kg/m$^3$. Assuming the cementitious-to-aggregate ratio in the concrete is 0.3, the volume loss of the sample can be derived from Equation 6.8.
$\Delta V = \frac{\Delta M}{\rho_m}$  .................................................................6.8

Where

$\Delta V =$ Volume loss in m$^3$

$\Delta M =$ Mass loss in Kg

$\rho_m =$ Density of outer mortar surface in Kg/m$^3$

Using Equation 6.8 the volume loss of the concrete septic tanks is 0.00467 m$^3$. The corrosion of the tank was calculated using Equation 6.9.

$CR = \frac{\Delta V}{\lambda \times A_s}$,  .................................................................6.9

Where

$CR =$ Corrosion in mm

$A_s =$ Surface area in m$^2$

$\lambda =$ Cement to aggregate ratio in concrete surface (assumed 0.3)

The corrosion of the tank was found to be 1.983 mm using Equation 6.9. The actual corrosion of the septic tank wall is 2.5 mm. The percentage error of the predicted thickness loss is 20.7%. The difference may be due to not considering other factors which affect deterioration in field conditions.
Figure 6.5: Predicted mass loss of the concrete specimen of Mix A in sulphuric acid solution

Figure 6.6: Predicted mass loss of the concrete specimen of Mix B in sulphuric acid solution
Figure 6.7: Predicted mass loss of the concrete specimen of Mix C in sulphuric acid solution

Figure 6.8: Predicted mass gain of the concrete specimen of Mix A in sodium sulphate exposure
Figure 6.9: Predicted mass gain of the concrete specimen of Mix B in sodium sulphate exposure

Figure 6.10: Predicted mass gain of the concrete specimen of Mix C in sodium sulphate exposure
6.7 Summary

Available models were discussed to gain understanding of the deterioration mechanism of concrete when exposed to sulphate and sulphuric acid environments. The effect of accelerated tests on the deterioration mechanism has been discussed and the assumptions of achieving similar degradations were explained. Using statistical analysis of the experimental results, two predictive models have been proposed to evaluate the deterioration of concrete when exposed to sulphate and acid attack. These models can be used to predict thickness and mass change of septic tanks investigated in the thesis.

\[
ML = \frac{(pH)^{-1.795} \times 0.0172 \times C^{-0.579}}{(2 \times 10^{-4} + T^{-1.9134})}
\]

\[
MG = K^{1.0064 \times (1 + C^{0.000068})} \frac{1}{(2.04 \times 10^{-04} + T^{-1.8175})}
\]
Application of the equation to predict field deterioration has shown that the predictive power of the models is quite reasonable.
Chapter 7

Conclusions and Recommendations

7.1 Introduction

Corrosion of concrete by sulphate and biogenic sulphuric acid attack is a well known and documented problem in waste water collection and treatment systems throughout the world. The research work presented an experimental study aimed at predicting the life expectancy of concrete septic tanks used in country Victoria. The results in the preceding chapters have shown that there are inherent differences in the mechanism of attack between sodium sulphate and sulphuric acid solution. The major stages of the study can be summarized as follows:

a) Chapter Two presented a review of previous work on sulphate and acid attack. The review allowed the identification of the major mechanisms of deterioration of concrete when exposed to sulphate and sulphuric acid. A summary of the mechanisms and the required underlying conditions was provided in the review.

b) An accelerated test was developed to ascertain the deterioration of concrete under acid and sulphate exposure. The test method was shown to offer similar deterioration products as observed in the field.

c) Chapters Four and Five presented the findings of the deterioration of concrete when exposed to sulphate and acid attack.

d) A predictive model has been developed for predicting deterioration of laboratory specimens and presented in Chapter Six.
Further details follow.

### 7.2 Conclusions Drawn from the Review of Previous Work

The review of previous work identified that there are a number of different mechanisms of deterioration which can lead to the destruction of concrete when exposed to sulphate and acid attack. These can be summarised as:

- a) Ettringite formation
- b) Gypsum formation
- c) Physical deterioration
- d) Delayed ettringite formation
- e) Thaumasite attack

### 7.3 Findings from the Accelerated Tests

An experimental methodology developed by the author was based on the findings of the previous work as well as initial field measurements. In summary, three physical measurements: length change, mass change and compressive strength change were adopted, as well as three microstructural measurements: SEM with EDX and XRD. Materials used in the preparation of specimens were similar to those in concrete used in septic tanks. It was hypothesised that the length change and mass change measurements would capture any expansion or corrosion of the concrete, and microstructure examination would reveal the products of deteriorations to identify the mechanism. Analysis of field samples indicated that the deterioration products formed were identical in both the field and laboratory samples. This observation confirmed that the adopted accelerated testing method will be suitable for understanding deterioration in the field.
7.4 Deterioration of Concrete when Exposed to Sulphate

In this experiment a mass gain in all concrete specimens immersed in sodium sulphate solution was observed. The XRD, SEM and EDX analysis confirmed that the mass gain in the concrete is due to the formation of ettringite. The volume of ettringite is higher than the reactant components and hence it occupies more space in the resultant structure and allows expansion of the concrete.

Two main hypotheses have been proposed to explain the mechanism of expansion. One view is that expansion is caused by the growth of the relatively large crystals that form at aggregate interfaces and elsewhere (Diamond, 1996, Yang et al., 1999a, Yang et al., 1999b). The other is that it is caused (Johansen; et al., 1993), or at least begins with the growth of the much smaller crystals formed within the paste.

7.5 Deterioration of Concrete when Exposed to Acid Attack

The dominant reaction that takes place in the presence of sulfuric acid is the conversion of calcite to gypsum. The gypsum may react further with monosulphate to form ettringite, which is expansive in nature. The secondary effect of sulphuric acid is the decalcification of carbon-silicon-hydrate gel (CSH), thus loosening the cementitious structure (Hill et al., 2003, Santhanam, 2001). This has led to mass loss.

7.6 Effects of Exposure on Compressive Strength of Concrete

The compressive strength of concrete specimens were significantly reduced due to the exposure to sulphuric acid solutions. This may be a result of formation of expansive materials like ettringite which creates crystal growth pressure and hence formation of cracks inside the concrete. The reduction in strength could be due to corrosion which is depicted by mass loss.
7.7 A Model for Prediction of Deterioration of Concrete when Exposed to Sulphate and Acid Attack

Available models were studied to gain an understanding of the deterioration mechanism of concrete when exposed to sulphate and sulphuric acid environments. This allowed identification of major variables. Using the experimental results, two statistical models have been developed to predict mass loss or gain of concrete specimens when exposed to sulphuric acid and sulphate attack. The equations developed are:

\[
ML = \frac{(pH)^{-1.795} \times 0.0172 \times C^{-0.579}}{(2 \times 10^{-4} + T^{-1.9134})}
\]

\[
MG = \frac{K^{1.0064} \times (1 + C^{0.00068})}{(2.04 \times 10^{-04} + T^{-1.8175})}
\]

7.8 Predicting Corrosion of Septic Tanks

In order to validate the proposed model, field concrete samples were collected from a decommissioned septic tank. The pH value of the effluent was established from a similar tank located in the same locality and of the same age. Corrosion predicted using the model developed was observed to be reasonably consistent with the corrosion observed in the field samples.

7.9 Recommendation for Future Work

Some areas for future investigations are as follows,

- A major problem facing researchers in this field is that there is no standard test method or specifications for measuring resistance to sulphate and sulphuric acid attack. Accordingly, extensive research is needed to standardize methods
and test procedures related to the resistance of concrete to $\text{H}_2\text{SO}_4$ and sulphate attack.

- Biogenic sulphuric acid generation was not considered in this study. This may be an important factor in the deterioration of concrete when exposed to such environments, and in future studies biogenic acid production should be considered.

- In the work presented here, a constant level of acid was used for accelerated tests. If the nature of biogenic acid production is known, the tests could simulate the variation in acidity.

- In the present study only sodium sulphate was considered for sulphate attack from surrounding soil. Future research should consider different cations for sulphate exposure.

- To improve the resistance of concrete exposed to sulphate and sulphuric acid the use of pozzolanic additives which will reduce $\text{Ca(OH)}_2$ in concrete thus reducing the ingredients needed for deterioration can be explored.
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Appendix A

Figure A-1: Expansion data for PC concrete under Sodium Sulphate exposure for Mix B

Figure A-2: Expansion data for PC concrete under Sodium Sulphate exposure for Mix C
Figure A-3: Effects of water cement ratio on expansion of PC concrete under 4% Sodium Sulphate exposure

Figure A-4: Effects of water cement ratio on expansion of PC concrete under 5.5% Sodium Sulphate exposure
Figure A-5: XRD analysis of PC concrete under 2% Sodium Sulphate exposure for mix design B

Figure A-6: XRD analysis of PC concrete under 2% Sodium Sulphate exposure for mix design C
Comparison of SO4_2_A, _B, _C

Figure A-7: XRD analysis of PC concrete under 2% Sodium Sulphate exposure for different mix design

Figure A-8: XRD analysis of PC concrete under 4% Sodium Sulphate exposure for mix design A
Figure A-9: XRD analysis of PC concrete under 4% Sodium Sulphate exposure for mix design B

Figure A-10: XRD analysis of PC concrete under 4% Sodium Sulphate exposure for mix design C
Comparison of SO4_4_A, _B, _C

Figure A-11: XRD analysis of PC concrete under 4% Sodium Sulphate exposure for different mix design

SO4_5_A

Figure A-12: XRD analysis of PC concrete under 5.5% Sodium Sulphate exposure for mix design A
Figure A-13: XRD analysis of PC concrete under 5.5% Sodium Sulphate exposure for mix design B

Figure A-14: XRD analysis of PC concrete under 5.5% Sodium Sulphate exposure for mix design C
Comparison of SO4_5_A, _B, _C

Figure A-15: XRD analysis of PC concrete under 5.5% Sodium Sulphate exposure for different mix design

Figure A-16: SEM analysis of PC concrete under 2% Sodium Sulphate exposure for mix design C
Figure A-17: SEM analysis of PC concrete under 4% Sodium Sulphate exposure for mix design B

Figure A-18: SEM analysis of PC concrete under 4% Sodium Sulphate exposure for mix design C
Figure A-19: SEM analysis of PC concrete under 5.5% Sodium Sulphate exposure for mix design A

Figure A-20: SEM analysis of PC concrete under 5.5% Sodium Sulphate exposure for mix design B
Figure A-21: SEM analysis of PC concrete under 5.5% Sodium Sulphate exposure for mix design C

Figure A-22: EDAX analysis of PC concrete under 2% Sodium Sulphate exposure for mix design C
Figure A-23: EDAX analysis of PC concrete under 4% Sodium Sulphate exposure for mix design A

Figure A-24: EDAX analysis of PC concrete under 4% Sodium Sulphate exposure for mix design B
Figure A-25: EDAX analysis of PC concrete under 4% Sodium Sulphate exposure for mix design C

Figure A-26: EDAX analysis of PC concrete under 5.5% Sodium Sulphate exposure for mix design A
Figure A-27: EDAX analysis of PC concrete under 5.5% Sodium Sulphate exposure for mix design B

Figure A-28: EDAX analysis of PC concrete under 5.5% Sodium Sulphate exposure for mix design C
Figure A-29: Mass loss of PC concrete under Sulphuric acid exposure for Mix B

Figure A-30: Mass loss of PC concrete under Sulphuric acid exposure for Mix C
Figure A-31: Actual and predicted mass loss of PC concrete under sulphuric acid exposure for Mix B

Figure A-32: Actual and predicted mass loss of PC concrete under sulphuric acid exposure for Mix C
Figure A-33: XRD analysis of PC concrete under sulphuric acid exposure of pH 3.0 for mix design B

Figure A-34: XRD analysis of PC concrete under sulphuric acid exposure of pH 3.0 for mix design C
Comparison of Acid_1_A, B, C

Figure A-35: Comparison of XRD results of PC concrete under sulphuric acid exposure of pH 3.0 of different mix design

Acid_2_B

Figure A-36: XRD analysis of PC concrete under sulphuric acid exposure of pH 4.0 for mix design B
Acid_2_C

Comparison of Acid_2_A, _B, _C

Figure A-37: XRD analysis of PC concrete under sulphuric acid exposure of pH 4.0 for mix design C

Figure A-38: Comparison of XRD results of PC concrete under sulphuric acid exposure of pH 4.0 of different mix design
Figure A-39: SEM analysis of PC concrete under sulphuric acid exposure of pH 3.0 for mix design B

Figure A-40: SEM analysis of PC concrete under sulphuric acid exposure of pH 3.0 for mix design C
Figure A-41: SEM analysis of PC concrete under sulphuric acid exposure of pH 4.0 for mix design B

Figure A-42: EDAX analysis of PC concrete under sulphuric acid exposure of pH 3.0 for mix design B
Figure A-43: EDAX analysis of PC concrete under sulphuric acid exposure of pH 3.0 for mix design C

Figure A-44: EDAX analysis of PC concrete under sulphuric acid exposure of pH 4.0 for mix design B
Figure A-45: EDAX analysis of PC concrete under sulphuric acid exposure of pH 4.0 for mix design C
Appendix B

Table B-1: Weight of the concrete specimens in different concentration of sodium sulphate solutions from mix design A.

<table>
<thead>
<tr>
<th>Days</th>
<th>Weight (gm)</th>
<th>2% Na₂SO₄</th>
<th>4% Na₂SO₄</th>
<th>5.5% Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.0</td>
<td>1796.9 1817.7</td>
<td>1793.6 1773.4</td>
<td>1066.3 1820.0</td>
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</tr>
<tr>
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<td>1794.1 1816.6</td>
<td>1797.1 1777.5</td>
<td>1069.0 1825.2</td>
<td>936.1 1794.5</td>
</tr>
<tr>
<td>56.0</td>
<td>1794.6 1818.3</td>
<td>1797.2 1777.3</td>
<td>1072.2 1829.2</td>
<td>938.5 1798.4</td>
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<td>1074.9 1837.3</td>
<td>942.3 1807.9</td>
</tr>
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<td>1800.6 1780.4</td>
<td>1073.2 1836.4</td>
<td>942.1 1806.8</td>
</tr>
<tr>
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<td>946.9 1815.7</td>
</tr>
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<td>1809.9 1787.3</td>
<td>1075.7 1839.8</td>
<td>946.4 1812.5</td>
</tr>
<tr>
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<td>1802.6 1783.7</td>
<td>1076.5 1842.3</td>
<td>946.6 1812.2</td>
</tr>
<tr>
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</tr>
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<td>1080.2 1845.8</td>
<td>950.7 1818.3</td>
</tr>
<tr>
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<td>1818.6 1796.6</td>
<td>1085.5 1853.8</td>
<td>954.1 1824.8</td>
</tr>
</tbody>
</table>

Table B-2: Weight of the concrete specimens in different concentration of sodium sulphate solutions from mix design B.

<table>
<thead>
<tr>
<th>Days</th>
<th>Weight (gm)</th>
<th>2% Na₂SO₄</th>
<th>4% Na₂SO₄</th>
<th>5.5% Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.0</td>
<td>1794.5 1775.2</td>
<td>1801.0 1796.0</td>
<td>891.0 1768.4</td>
<td>769.8 1761.9</td>
</tr>
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<td>1803.9 1802.8</td>
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<td>773.7 1768.4</td>
</tr>
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<td>898.3 1785.0</td>
<td>778.4 1779.5</td>
</tr>
<tr>
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<td>1806.0 1805.8</td>
<td>896.6 1785.0</td>
<td>777.9 1779.2</td>
</tr>
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<td>779.7 1782.9</td>
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<td>1833.4 1823.9</td>
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<td>787.9 1797.1</td>
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</table>
Table B-3: Weight of the concrete specimens in different concentration of sodium sulphate solutions from mix design C.

<table>
<thead>
<tr>
<th>Days</th>
<th>Weight (gm)</th>
<th>2% Na₂SO₄</th>
<th>4% Na₂SO₄</th>
<th>5.5% Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1773.7</td>
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<tr>
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<td>1744.6</td>
<td>1767.0</td>
<td>812.6</td>
<td>1779.6</td>
</tr>
<tr>
<td>70.0</td>
<td>1745.6</td>
<td>1768.9</td>
<td>813.1</td>
<td>1784.3</td>
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<td>1781.9</td>
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<td>1785.6</td>
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Table B-4: Weight of the concrete specimens in different concentration of sulphuric acid solution from mix design A.

<table>
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<tr>
<th>Days</th>
<th>Weight (gm)</th>
<th>pH 2.5 to 3.5</th>
<th>pH 3.5 to 4.5</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<tr>
<td>70.0</td>
<td>1754.1</td>
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Table B-5: Weight of the concrete specimens in different concentration of sulphuric acid solution from mix design B.

<table>
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<th>Days</th>
<th>pH 2.5 to 3.5</th>
<th>pH 3.5 to 4.5</th>
<th>Control</th>
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<tbody>
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Table B-6: Weight of the concrete specimens in different concentration of sulphuric acid solution from mix design C.

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<th>Control</th>
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