

The identification and application of a method to test chloride ingress into concrete, sulphur-concrete and sulphur-cement coated concrete

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Abstract

Concrete is the main material used for the construction of civil structures in industry. Concrete is also used in the construction of nuclear power plant civil structures (e.g. the containment building).

Concrete ages but also degrades over time due to exposure to environmental conditions and therefore requires maintenance to ensure the safety of workers, the public and the environment. The durability of concrete can be improved by the addition of admixtures such as fly ash, and the application of polymers as surface coats.

The ability of a sulphur cement as a sealer for concrete was investigated with the view to providing increased durability under saltwater exposure conditions where chloride ingress in concrete and cement will cause increased deterioration of civil nuclear structures.

For this project, different concrete specimens were prepared, a surface coating was applied to some specimens for comparison purposes, and the chloride conductivity test was performed on the specimens. The literature review indicates that with the application of a surface coat, the durability of the specimen increases, but in this project it was not found to be the case. This may be attributed to the shortcomings of the testing equipment that was used, as well as the testing procedure.

Keywords: Concrete, Cement, Chloride, Corrosion, Sulphur, Permeability, Diffusion, Coat, Nuclear

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List of abbreviations

American Society for Testing and Materials (ASTM).....	5
calcium hydroxide [Ca(OH) ₂]	11
hydrochloric acid (HCl)	10
Ordinary Portland Cement (OPC).....	3
Pressurized Water Reactors (PWR).....	1
Rapid Chloride Permeability Test (RCPT).....	11
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List of symbols

A = area (m^2)

b = initial absorption

C = concentration

D_{eff} = effective diffusion coefficient

g = gravity (m/s^2)

Δh = change in hydraulic head

J = flux of ions

k = material permeability

Q = flow rate (m^3/s)

r = radius of capillary tube

R = Gas constant ($8.314 \text{ J}/(\text{molK})$)

S = sorptivity

t = time

T = absolute temperature (K)

v = velocity

γ = surface tension

θ = wetting angle

ρ = density (kg/m^3)

η = viscosity

CHAPTER 1 BACKGROUND

Introduction

The most commonly built nuclear reactors are Pressurized Water Reactors (PWR) such as the Koeberg nuclear power plant in South Africa. PWRs have containment structures which consist of concrete encasement bases with a reinforcement mat, vertical walls and a dome. The containment houses the steam generators, the reactor pressure vessel, the pressuriser, pumps, etc. The reinforced concrete encasement provides a platform for the containment internals and contributes to ensuring containment of potential radionuclide leakages.

Apart from the internals, spent and fresh fuel are also contained in the auxiliary building, usually in close proximity to the containment building. The spent fuel pools are made of reinforced concrete which contains large water volumes with the spent fuel elements.

Also, most nuclear power stations are located along the coast, and are therefore exposed to the coastal seawater spray which aggravates the corrosion of reinforced concrete structures. In the presence of chlorides, moisture and oxygen, a chemical reaction occurs within concrete which gives rise to corrosion that leads to the formation of cracks and lowering of the concrete's integrity.

Since the South African nuclear power plant fleet is planned to be built along the coast, potential chloride ingress into concrete is thought to be one of the main contributors to the possible deterioration of the reinforced concrete structures.

Problem Statement

The problem is the prevention/limitation of chloride ingress and corrosion of reinforced concrete used for nuclear plants built in salt spray environments.

Research Aims

The aim of this study is to review the mechanisms of concrete corrosion and chloride ingress:

- I. in an effort to find methods to inhibit such ingress, and
- II. to review concrete mineralogy and chloride ingress test methods and to identify and apply a feasible method of measuring chloride ingress.

Outline

This dissertation is organized as follow:

Chapter 1 provides an introduction, problem statement, research aims and the outline of this document.

In Chapter 2, a literature study is done which include an overview of cement mineralogy and chemistry of cement, the different types of cement, the concrete corrosion process, international concrete test methods, other test methods and lastly, ways of concrete protection is discussed.

Chapter 3 contains the experimental procedure of this dissertation, Chapter 4 contains the results and discussion, and lastly Chapter 5 contains the conclusions and recommendations.

CHAPTER 2 LITERATURE STUDY

2.1 Overview

This chapter discusses the following: concrete basics, different cement types, concrete corrosion process, the different concrete durability test methods and different concrete protection methods.

2.2 Mineralogy and Chemistry

Concrete consists of Ordinary Portland Cement (OPC), aggregates, and sand. Cement is the most important ingredient of concrete because it binds the different filler ingredients.

Concrete is weak in tension due to its low tensile strength and brittle nature. This weakness is overcome by adding reinforcement steel (rebar) to concrete. Concrete containing rebar is called reinforced concrete.

Cement as the binder in concrete is made up of different compounds. As stated by Neville (2011), the raw materials to produce cement are mainly lime, silica, and clay containing a high percentage of aluminium and iron oxide which are mixed and sintered to form OPC after crushing of formed clinkers.

The main phases in cement formed during sintering and contained in the powder of the crushed clinkers are tricalcium silicate $[(\text{CaO})_3\text{SiO}_2]$, dicalcium silicate $[(\text{CaO})_2\text{SiO}_2]$, tricalcium aluminate $[(\text{CaO})_3\text{Al}_2\text{O}_3]$, and tetracalcium aluminoferrite $[(\text{CaO})_4\text{Al}_2\text{Fe}_3]$, abbreviated as C_3S , C_2S , C_3A and C_4AF respectively.

The amount of C_3A in cement is small, but it performs an important function in cement. The main advantage of C_3A is its chloride binding ability. C_3A binds with any available chloride ions to form calcium chloroaluminate, thereby reducing the available chloride ions which may contribute to the steel corrosion process in reinforced concrete. It also contributes to the early strength (1 to 3 days) of cement/concrete. However when pure C_3A is added to water, the C_3A will rapidly harden. To delay this hardening process, gypsum is added to cement.

Taylor (1997) states that C_3S provides initial strength and C_2S provides strength to cement at a later stage (>28 days) of aging. C_4AF also provides strength to cement but to a lesser extent compared to other chemical compounds. It also provides cement with its characteristic colour.

The general compositional limits of Portland cement expressed as elemental oxides are presented in Table 1 below.

Table 1: Elemental composition of Ordinary Portland Cement (OPC) expressed as oxides

Oxide	Weight Percentage
SiO ₂	17-25%
Al ₂ O ₃	3-8%
Fe ₂ O ₃	0.5-6%
CaO	60-67%
MgO	0.5-4%
Na ₂ O (Alkalis)	0.3-1.2%
SO ₃	2-3.5%

The minor chemical oxides include magnesium oxide (MgO), titanium dioxide (TiO₂), manganese (III) oxide (Mn₂O₃), potassium oxide (K₂O), sulphur trioxide (SO₃) and sodium oxide (Na₂O).

Concrete obtains its strength from the chemical reaction between cement and water, and this process is called hydration. In the presence of water, cement reacts as follow (Penn State College of Engineering, n.d.);

- C₃A reacts with gypsum to produce ettringite and heat. Ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) is a hydrous calcium aluminium sulfate mineral, and it contributes to the initial setting/stiffening of the cement mixture
- C₃S produces calcium silicate hydrates, lime and heat. The short-networked fiber structure of the calcium silicate hydrates contributes significantly to the initial strength of the cement
- When all the gypsum has been consumed, ettringite reacts with the remaining C₃A and monosulphate aluminate hydrate crystals (C₄ASH₁₈) are formed
- C₂S in the presence of water, form calcium silicate hydrates and heat. These calcium silicate hydrates contributes to the long term strength of concrete.

¹ Silica/Silicon Dioxide

² Aluminium Oxide

³ Iron (III) Oxide

⁴ Calcium Oxide

2.3 Types of cement

According to the American Society for Testing and Materials (ASTM, 2007) there are different types of cement namely Type I, II, III, IV, and Type V;

- Type I is a general purpose cement used for normal construction where no special properties are required
- Type II is used where construction is exposed to moderate sulphate attack where a moderate heat of hydration is required and where the concrete will be in contact with soil and possibly with ground water
- Type III is used where an early high strength is needed. The 3 day compressive strength of this cement is equal to the 7 day strength obtained by Type I and II cements. After approximately 2 months, there is little difference in the long term strengths of these cements
- Type IV is used where low heat of hydration is needed. The strength development of this cement is slow, but after approximately 2 years its strength is higher than the above cements. It is used in large concrete structures such as dams
- Type V is used where high sulphate resistance is needed where the concrete is exposed to alkaline soil and ground water sulphates and have a lower early strength compared to that of Types I, II, III cement

The chemical compound compositions of the different cement types are presented in Table 2 below.

Table 2: Chemical compound compositions in Portland Cements

Cement Type	C₃S	C₂S	C₃A	C₄AF
Type I	50-65%	10-30%	6-14%	7-10%
Type II	45-65%	7-30%	2-8%	10-12%
Type III	55-65%	5-25%	5-12%	5-12%
Type IV	35-45%	28-35%	3-4%	11-18%
Type V	40-65%	15-30%	1-5%	10-17%

According to Naus (2007), Type II cement is used for the construction of nuclear power plant safety related concrete structures because of its high sulphate resistance and lower heat of hydration compared to Type I cement.

There are also fly ash cement and sulphur cement types available.

2.4 Concrete corrosion process

2.4.1 Concrete chloride ion transport mechanisms

Chlorides can enter concrete through permeation, absorption and diffusion. Bioubakhsh (2011) states that the diffusion of ions occurs in water saturated concrete. In order for diffusion to occur in concrete, there must be a chloride ion concentration gradient and the concrete must remain in a saturated phase. Diffusion will be the main chloride ion transport mechanism, if the concrete is fully saturated. The diffusion process can be described by Fick's Law;

$$J = -D_{eff} \frac{\partial C}{\partial x},$$

Where,

J = flux of ions

D_{eff} = effective diffusion coefficient

C = concentration

Absorption occurs due to the liquid being sucked into partially filled concrete pores by capillary action. Absorption will not occur if the pores are full (saturated). Absorption is the main chloride ion transport mechanism in unsaturated concrete. The absorption process is described by the following expression;

$$A = b + S\sqrt{t}$$

Where,

A = mass or volume of liquid absorbed per square unit

b = initial absorption

S = sorptivity

t = time (min)

The theory of capillarity or unsaturated flow can be explained by the relationship between absorption and the square root of time.

- Theory of capillarity:

$$P_c = \frac{2\gamma\cos\theta}{r}$$

Where,

P_c = capillary pressure

γ = surface tension

θ = wetting angle

r = radius of capillary tube

- Theory of unsaturated flow:

$$v = -K \frac{dh}{dx}$$

Where,

K = coefficient of permeability or hydraulic conductivity

Furthermore, chloride ingress (Bioubakhsh, 2011) into concrete also occurs by means of permeation and a pressure gradient is required for this process to occur. This transport mechanism occurs if a hydraulic head is applied on one side of a concrete structure. Areas where hydraulic heads are maintained are rare, therefore permeation can be regarded as a minor chloride transport mechanism. The permeability process can be described by Darcy's Law.

$$v = \frac{Q}{A} = \frac{k\rho g\Delta h}{\eta L}$$

Where,

v = velocity

Q = flow rate (m³/s)

A = area (m²)

ρ = density (kg/m³)

Δh = change in hydraulic head

L = thickness of specimen (m)

η = viscosity

g = gravity (m/s²)

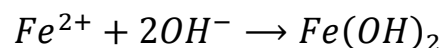
k = material permeability (m²)

Bioubakhsh (2011) further states that when concrete is exposed to wetting and drying cycles, the chlorides initially enter the concrete by means of absorption, which lead to a build-up of chloride ions close to concrete surface from which diffusion can occur. Diffusion occurs when there is adequate pore liquid in the concrete and absorption occurs when the pores are partially filled and the liquid is sucked into the concrete by means of capillary forces. Therefore, diffusion and absorption are the main transport mechanisms responsible for chloride ion ingress into concrete.

2.4.2 Reinforced concrete corrosion

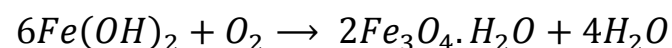
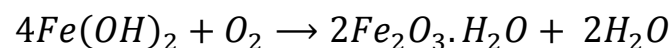
Broomfield (2007) states, when reinforced steel is exposed to air and water, corrosion of the steel will start. Concrete is naturally alkaline due to the high concentrations of soluble calcium, sodium and potassium oxides, and these oxides protect the embedded steel against corrosion.

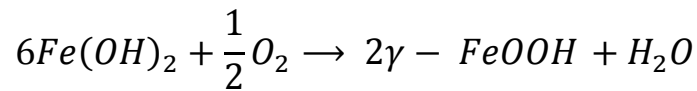
In the presence of water, the oxides form ferrous hydroxides which maintain the concrete pH of 12-13.



Ferrous hydroxide can be oxidized (Trejo et al, 2009) further to form hydrated ferric oxide (red rust) and hydrated magnetite ($Fe_3O_4 \cdot H_2O$), also called green rust.

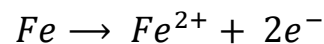
When the hydrated ferric oxide and the hydrated magnetite are dehydrated, ferric oxide (red) and magnetite (black) is formed. Due to the alkaline nature of concrete, ferrous hydroxide can oxidize into gamma ferric oxyhydroxide which forms an impermeable layer on the steel surface.





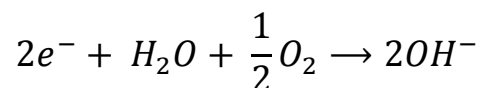
The above mentioned products form a passive film on the reinforced steel which protects it against corrosion. Unfortunately, this passive layer is not always maintained and can be damaged by carbonation or chloride attack, and corrosion starts.

The corrosion chemical reaction (Broomfield, 2007)) starts with steel releasing electrons in the presence of water;



This is called the anodic reaction.

The formation/release of these two electrons has to be balanced within the steel surface to ensure electrical neutrality. Therefore there has to be another chemical reaction which can use the electrons and this is called the cathodic reaction:



The anodic-cathodic chemical reaction is presented in

Figure 1

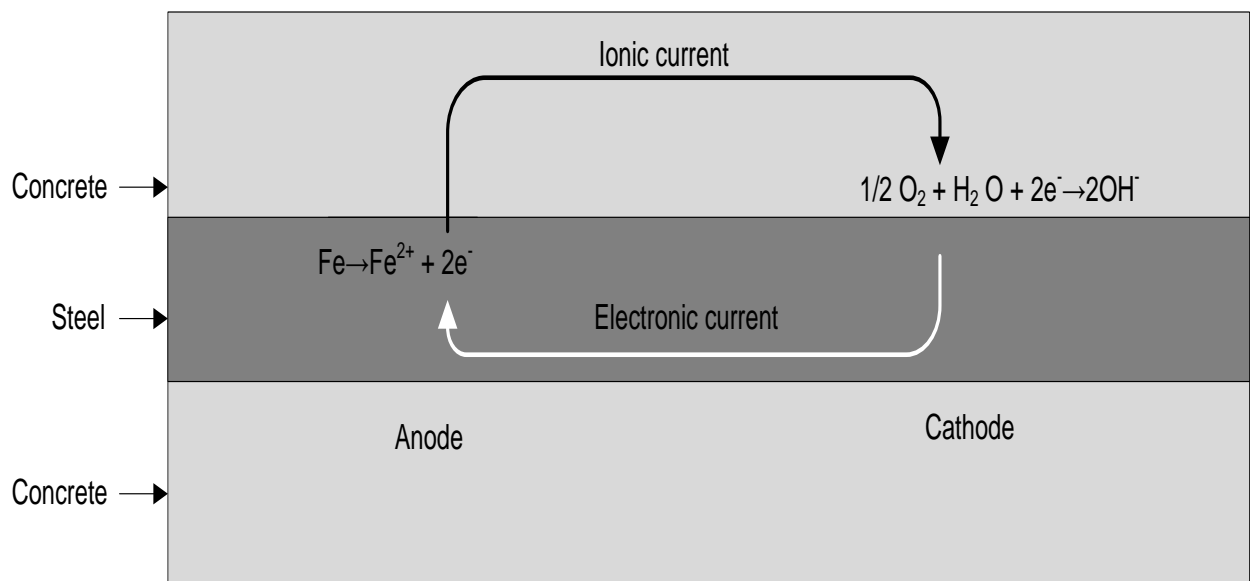
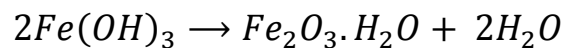
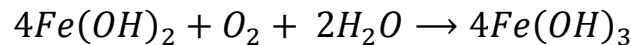
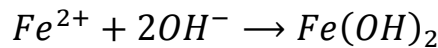


Figure 1: Schematic representation of the anodic-cathodic reaction

The hydroxyl ions released from the cathodic reaction increases the alkalinity and also strengthens/improves the passive layer in concrete.

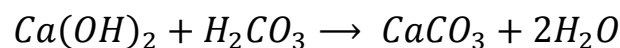
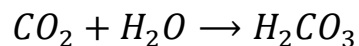
Following the anodic-cathodic reactions, the hydroxyl ions interact with ferrous ions which form ferrous hydroxide [$Fe(OH)_2$], which in the presence of oxygen and water is turned into ferric hydroxide [$4Fe(OH)_3$];



The volume of unhydrated ferric oxide (Fe_2O_3) is twice that of the steel it substitutes. When Fe_2O_3 becomes hydrated it increases 6 to 10 times in size. This makes the steel even more porous, which leads to cracking, peeling, flaking and delamination of the concrete.

The main causes of concrete corrosion are carbonation and chloride attack.

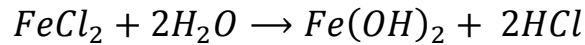
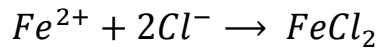
Carbonation occurs due to the interaction of carbon dioxide (CO_2) with concrete hydroxides. Firstly, the CO_2 dissolves in the concrete pore water to form carbonic acid [H_2CO_3], which in turn interacts with unreacted calcium hydroxide [$Ca(OH)_2$] in the cement to form calcium carbonate [$CaCO_3$];



Although there are large amounts of calcium hydroxide in concrete which maintains its alkaline pH, carbonation eventually lowers the pH to a level where corrosion of the steel starts.

Chlorides can be introduced into concrete by casting (the use of accelerators or the contamination of the concrete mix water with seawater) and/or they can enter by diffusion (sea salt spray or direct seawater wetting).

Bioubakhsh (2011) states that chlorides destroy the protective passive layer when chlorides reach a critical concentration level (0.4 to 1% per mass cement) in the concrete. The protective layer is destroyed as follows: iron interacts with the chlorides to form iron chloride, which in the presence of water is converted into iron hydroxide and hydrochloric acid (HCl). The HCl destroys the passive layer and the steel starts to corrode;



2.5 International Test Methods

Various test methods (Gardner, 2006) exist which are used to determine the chloride ingress into concrete. The methods include:

- The Bulk Diffusion Test,
- The Rapid Chloride Permeability Test (RCPT),
- The Rapid Migration Test, and
- The Chloride Conductivity Test.

2.5.1 Bulk Diffusion Test (NT⁵ Build 443, 1995)

The Nordtest (NT) brand was developed by the Nordic countries in 1973. Over the years, various Nordic test methods were developed, including the Bulk Diffusion Test.

For the Bulk Diffusion Test, at least 3 specimens are required. Concrete cube blocks are core drilled with a barrel saw (75mm Ø) and then cut with a diamond tipped saw into 100mm length specimens.

The specimens are soaked in saturated calcium hydroxide [Ca(OH)₂] for 28 days. Each specimen is removed from the solution, dried and weighed daily. When the mass of the specimens does not change more than 0.1 mass percentage, they are removed from the Ca(OH)₂ solution.

The specimens are covered with epoxy resin, except for the top of the specimen. After the epoxy has dried, the specimens are soaked in sodium chloride (NaCl) for approximately 35 days.

After the soaking period, profile grinding is done to determine the chloride ingress. The specimens are ground and the dust from different depths of the specimen is collected. The chloride concentration of the dust samples are chemically analysed and the concentration is plotted against depth.

⁵ The Nordic Test Methods

2.5.2 Rapid Chloride Permeability Test (ASTM C1202)

The Rapid Chloride Permeability Test (RCPT) was developed in 1981 (Whiting, 1981) and became the preferred chloride permeability test method due to its relative ease to use, and it is an inexpensive test.

The test set up consists of 2 cells which are connected to a voltage source (Figure 2 and Figure 3.)

Specimens are cut (100mm Ø and 50mm length) from concrete cubes, coated with epoxy and placed in the test device. The one cell is filled with 3% NaCl and the other cell is filled with 0.3M sodium hydroxide (NaOH). Each specimen is subjected to 60V DC current for 6 hours. The charge passing through the specimens are used to rate the concrete/cement. The permeability of each specimen is rated according to Table 3.

According to Stanish et al. (1997), the main disadvantage of this test is the temperature increase in the specimen when voltage is applied for 6 hours to the concrete specimen. This decreases the resistance of the concrete specimens and this will give lower quality concrete specimens a poorer result rating.

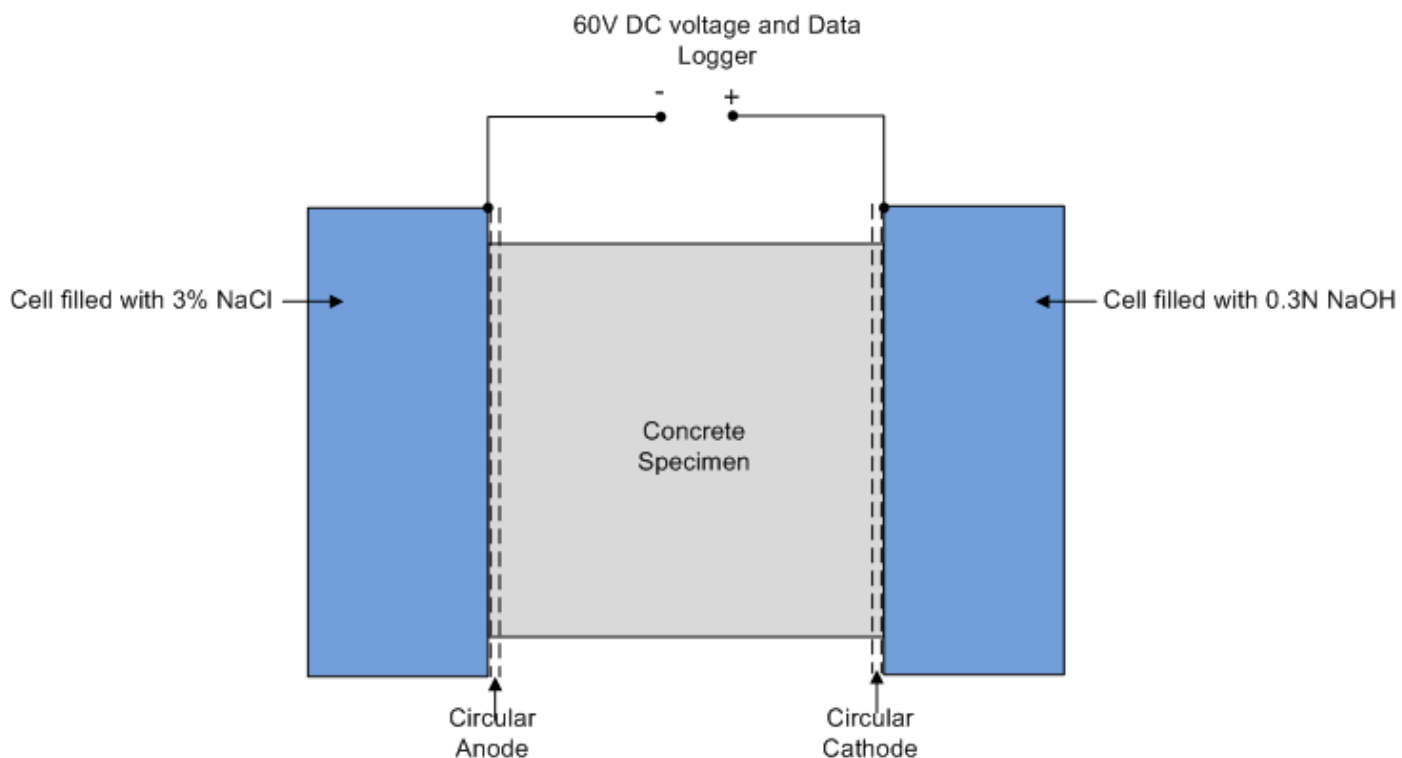


Figure 2: Schematic diagram of ASTM C1202 Test

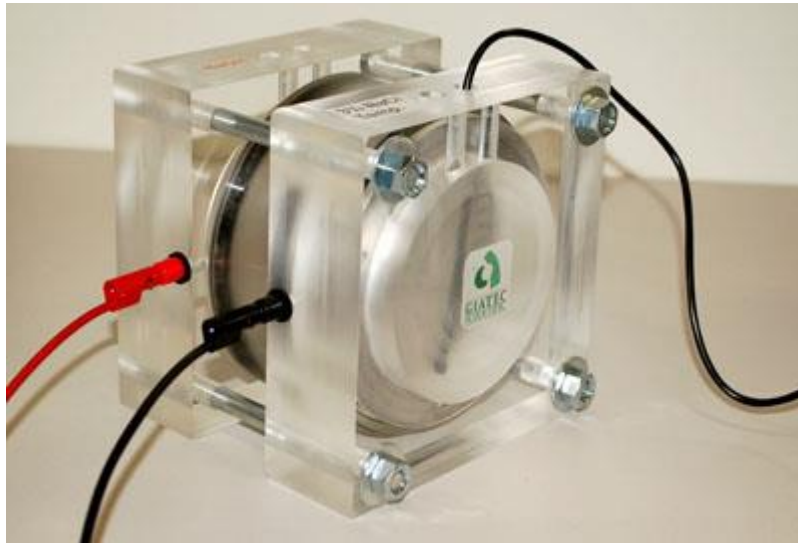


Figure 3: A picture of the ASTM C1202 Test setup (www.giatecscientific.com)

Table 3: RCPT ratings as per ASTM C1202

Charge (Coulombs)	Chloride Ion Permeability
>4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very Low
<100	Negligible

Gardner (2006) states that concretes containing fly ash should not be tested after 28 days in the RCPT. Testing should rather take place at 56 or 90 days in the case of concretes containing fly ash because fly ash is a slow reacting modifier.

2.5.3 Rapid Migration Test (NT BUILD⁶ 492)

This Rapid Migration Test (RMT) test was accepted in 1999 as the Nordic test standard for the determination of the concrete chloride content.

⁶ The Nordic Test Methods

The RMT set up consists of a plastic container, a rubber sleeve and a power source (Figure 3). Cylindrical specimens are core drilled with a barrel saw (75mm Ø) from the cube concrete blocks and cut into 100mm length pieces with a diamond tipped saw.

Before placing the specimens in the apparatus, each is subjected to a vacuum process. The vacuum process is carried out as follows:

Towel dry the specimens and place in a vacuum container. Reduce the pressure in the container to 1-5kPa and maintain the vacuum for 3 hours. After the 3 hours have passed, fill the container with saturated calcium hydroxide $[\text{Ca}(\text{OH})_2]$ solution until all the specimens are covered. Saturated $\text{Ca}(\text{OH})_2$ is obtained by dissolving excess $\text{Ca}(\text{OH})_2$ in distilled or de-ionised water. Maintain the vacuum for 1 more hour, and keep the specimens in the solution for 16 to 20 hours.

Following the vacuum process, the test is carried out as follows:

Fill the reservoir with 10% NaCl solution. Fit the rubber sleeve onto the specimen and secure it with two clamps (Figure 3). Fill the sleeve above with 0.3M NaOH. Apply a voltage of 30V to the specimen, record the current and record the temperature using a thermocouple. After 18 hours, rinse the specimens with tap water and towel dry each. Split each specimen axially and spray 0.1N silver nitrate onto the freshly split section. If chlorides are present in the specimen, white silver chloride precipitation will be visible on the specimen. If no chlorides are present in the specimen, the solution turns brown and silver oxide $[\text{Ag}(\text{OH})_2]$ is formed. Finally, measure the chloride depth penetration, and record the readings.

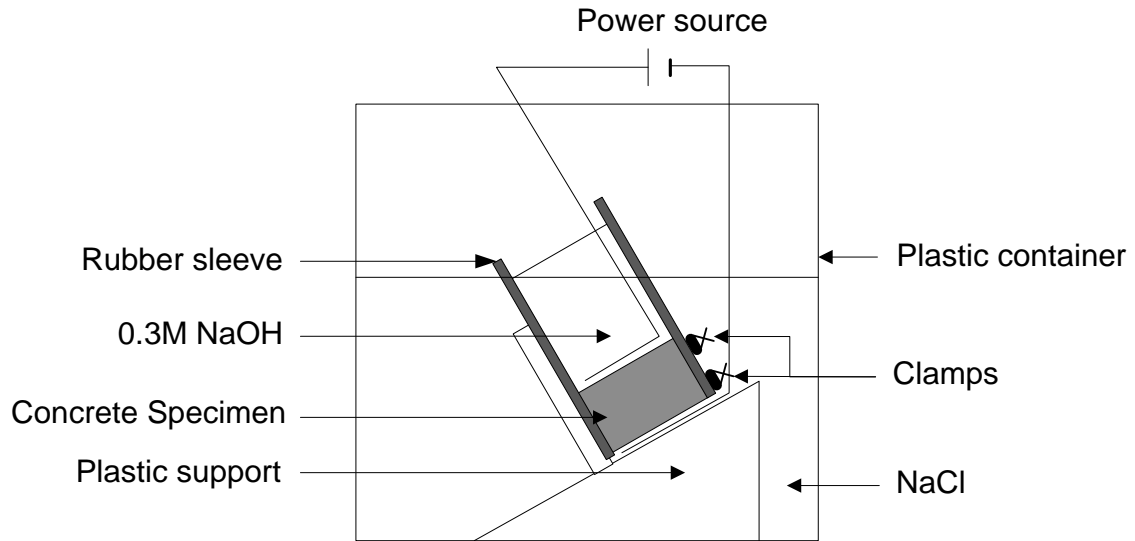


Figure 3: Schematic representation of the Rapid Migration Test set-up (NT BUILD, 492, 1999)

The chloride penetration depth is used to determine the diffusion coefficient (D);

$$D = \frac{zFE}{RT} \cdot \frac{x_f}{t}$$

With x_f = penetration depth

z = ion valence for chloride, $z=1$

F = Faraday's constant (9.648×10^4 J/(Vmol))

E = applied electrical voltage (V)

R = Gas constant (8.314 J/(molK))

T = absolute temperature (K)

t = time of voltage application

Gardner (2006) states that the electrical field adds energy to the ions which increases the diffusion process. The effect the electrical field has on the transport and binding of chloride ions have not been adequately researched.

2.5.4 Chloride Conductivity Test (CCT)

Internationally, various concrete test methods have been developed with the South African CCT method, which is based on the basics of these methods.

The CCT set-up consists of different plastic cylinders which fit into each other. The centre/middle portion contains the specimen, and on either side is the anode and cathode (

Figure 5). The schematic representation of the test set-up is presented in Figure 4.

The specimens are cut into cylindrical discs from the concrete cubes. A diamond tipped core barrel is used to drill the cylinders and a diamond tipped saw is used to cut the discs. The size of each cylindrical disc is 70+/-2mm in diameter and 30+/-2mm in thickness.

Before testing the specimens, they are oven dried for 7 days and then saturated with 5M NaCl. The 5M NaCl solution is prepared by adding 2.9kg NaCl to 10 liters of water and stirring the mixture until all the salt has dissolved. After the vacuum process (Section 3.4) and soaking of specimens, a direct current voltage of 10V is applied across each specimen and the current and voltage is recorded.

The Chloride Conductivity Test has a longer specimen preparation time compared to the RCPT and the Rapid Migration Test which is due to the 7 day specimen drying time.

Gardner (2006) investigated various uncertainties with regard to the chloride conductivity test; i.e. specimen damage during drying, specimen size, and the specimen saturation:

- Specimen drying – no conclusive results were obtained and more investigation is required in this regard.
- Specimen size – the results indicate a higher conductivity in thicker specimens. This may be due to lesser microcracking in the thinner specimens.
- Specimen saturation – the results indicate that specimens are adequately saturated between 7 and 18 days.

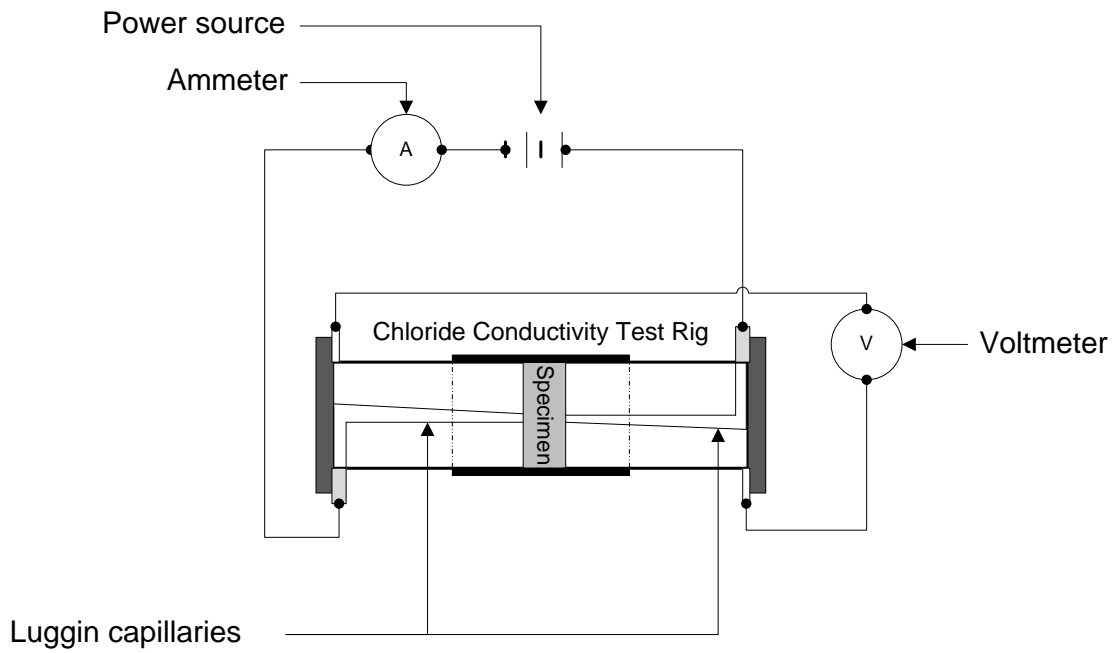


Figure 4: Schematic representation of the Chloride Conductivity test setup

Figure 5 relates to the components in Figure 6.

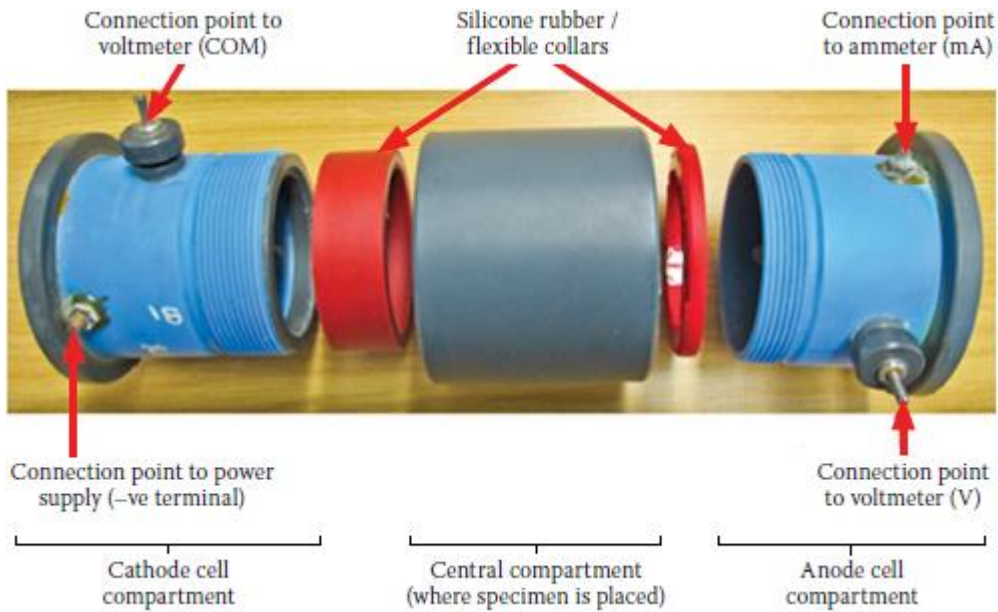


Figure 5: The chloride conductivity test set-up (modified after Otieno and Alexander, 2015)

2.6 Other concrete test methods

Beushausen and Alexander (2008) investigated the South African durability index test methods and they compared these tests with internationally accepted methods. The oxygen permeability test, Cembureau⁷ test and water penetration tests will be briefly discussed below.

2.6.1 Oxygen permeability index test (OPI test)

This South African test measures the decrease in pressure when oxygen passes through a concrete specimen ($\varnothing = 68\text{mm}$ and thickness = 25mm). Before testing start, the specimens are oven dried for 7 days at 50°C. During testing, the decrease in pressure is monitored for a specific time period which gives an indication of the permeability of the specimen.

2.6.2 Cembureau permeability test

This international test measures the gas flow through a concrete specimen ($\varnothing = 150\text{mm}$ and thickness = 50mm) under constant pressure. Beushausen and Alexander (2008) states that the gas flow in both tests (OPI test and Cembureau test) depends on the pressure difference across the specimen, the specimen area, thickness and porosity and the viscosity of the gas used. This test measures the permeability of concrete specimens.

2.6.3 Water penetration tests

Both tests (South African water sorptivity test and the RILEM test) measure the unidirectional movement of water into a concrete specimen. These tests measure the change in specimen mass over time. This provides the amount of water absorbed into the concrete specimens.

Beushausen and Alexander (2008) found the South African water sorptivity index test does not conform to international standards. They state the South African chloride conductivity test and the oxygen permeability test conform with international standards and can be compared against international test results.

⁷ The European Cement Association

2.7 Concrete Protection

The inherent porosity of concrete makes it easy for chloride ions to enter it which lead to concrete corrosion. Limiting the diffusion, permeation and absorption processes will automatically decrease the ingress of chloride ions into concrete. This can be achieved by the application of surface sealers onto concrete, and/or the usage of materials (e.g. fly ash) which increases the durability of cement/concrete.

A literature study was carried out on different ways/methods whereby chloride ingress into concretes is decreased.

Almusallam et al. (2003) investigated the chloride permeability of different surface coats. The RCPT method was used to determine the chloride permeability of specimens. They investigated the performance of commercially available surface coatings, namely acrylic coats, polymer emulsion coats, epoxy resin coats, polyurethane coats and chlorinated rubber coats. The permeability of coated and uncoated concrete samples were compared. Type V cement (cement content = 370kg/m^3 and water/cement ratio = 0.45) was used to prepare the concrete samples.

Different surface coatings were applied to the ends of the samples and rapid set epoxy coat was applied to the curved surfaces to make them impermeable. Both surface coats were applied to the specimens as per the manufacturer's specifications. The results (Almusallam 2003:476) indicate polyurethane and epoxy coats provide the best resistance to chloride ions, compared to the other coats.

Sivasankar et al. (2013) investigated how surface coatings affect the chloride and moisture permeability of reinforced concrete. The RCPT method was used to determine the permeability of specimens coated with different sealers. The sealers that they used included a water proofing admixture (Type 1) added to concrete, an aqueous silane siloxane based coating (Type 2), and a thixotropic silane and siloxane water repellent coating (Type 3). After curing the concrete specimens for 28 days, the specimens were dried for 7 days at room temperature. Type 1 sealer was added during preparation of the specimens, and Type 2 and 3 were applied with brushes. Two coats (Type 2 and 3) were applied to the specimens within a 24 hour period. The thixotropic silane and siloxane water repellent coating (Sivasankar et al. 2013; 619) was found to be the most effective sealer.

Zulu and Allopi (2014) investigated the performance of concrete mixed with fly ash against normal concrete. Current specifications for fly ash usage in cement are limited to 30% and they investigated the performance of higher percentages of fly ash in cement. They state that the durability of concrete depends on its permeability and diffusivity. The permeability and diffusivity of concrete is related to concrete pore structure. Therefore, concrete with low permeability will also have low diffusivity. The investigation confirms that the inclusion of fly ash in concrete decreases the concrete pores and also improve the concrete durability.

They subsequently investigated the compressive strength, oxygen permeability index, water sorptivity test and chloride conductivity of concrete specimens containing different fly ash percentages (30, 40, 50 and 60 percent). The water-cement ratio of the mixes was the same (0.5), but the OPC cement content differed. Detailed mix compositions are presented in the Zulu and Allopi (2014:155) report. After 28 days the following results were obtained:

Concrete containing 50% and 60% fly ash had a lower chloride conductivity compared to concrete containing 30% and 40% fly ash. The lower the conductivity of the concrete, the better is the concrete quality. The concrete chloride conductivity classification criteria are presented in Table 4.

Table 4: Chloride conductivity classification criteria (Alexander et. al. 1999)

Chloride Conductivity (mS/cm)	Concrete Quality
< 0.75	Very good
0.75 – 1.5	Good
1.5 – 2.5	Poor
> 2.5	Very poor

Table 4 provides the acceptance limits for the chloride conductivity of concrete specimens. From these results, Zulu and Allopi (op. cit.) concluded that using increased (higher than the specification limit) percentages of fly ash in concrete gives results which falls within acceptable acceptance limits (Table 4), however more research is required in this regard to remove the uncertainty of using higher fly ash percentages in the concrete industry. Oh et al. (2002) investigated resistance of different high performance concrete (HPC) types to chloride absorption. The RCPT tests were performed on different HPC mixes.

The admixtures used with OPC were silica fume, fly ash and blast furnace slag. Results indicate that concrete with silica fume showed the best resistance to chloride penetration (Oh et al. 2002:228). They claim that silica fume concrete showed the best results because it makes the concrete structure denser. Although there was a decrease in chloride penetration, it could not be completely blocked from the different concrete mixtures.

Hola and Ksiazek (2009) investigated ways to protect rebar (reinforced steel) in concrete against corrosion by the application of a sulphur composite layer on the steel consisting of 63% weight sulphur (binder), 33% weight quartz (filler), and 4% weight carbon black as an additive. Different coating thicknesses were applied to the steel to find the ideal thickness. The ideal coat thickness was 1.5mm. The results (Hola and Ksiazek, 2009; 56) indicate that the corrosion rate of uncoated steel was 3 orders of a magnitude higher than the sulphur cement coated steel.

Fontana et al. (1998) released a guide for the mixing and placing of sulphur concrete on behalf of the American Concrete Institute (ACI). They used modified sulphur, however if unmodified sulphur is used it will lead to the following:

- Upon cooling to 114°C, crystallization occurs and monoclinic sulphur (S_{β}) is formed with a 7% volume decrease.
- Further cooling to 96°C, the S_{β} transform to orthorhombic sulphur (S_{α}) which is more stable at room temperature.
- Since S_{α} is more dense than S_{β} , the induced stress can cause premature failure of the concrete due to cracking of the sulphur.

Fontana et al. (1998) state that, similar to other authors, sulphur has to be modified for increased stability and durability and to reduce expansion and contraction during thermal cycles. Two methods to modify sulphur are described in their guide (Fontana et al. 1998):

- In Method 1, the polymeric sulphur product is modified with equal parts of cyclopentadiene oligomer and dicyclopentadiene. The composition of materials are as follow: sulphur 95%, carbon 5%, hydrogen 0.5%, specific gravity at 25°C is 1.9 and the viscosity at 135°C is 25 to 100.
- In Method 2, the modified sulphur is obtained by using olefinic hydrocarbon polymers (Escopol) as modifier. The composition of materials was as follows; sulphur 80%, carbon 18%, and hydrogen 2%.

Wrzesinski and McBee (1988) compared the permeability of sulphur concrete to Ordinary Portland Cement (OPC) based concrete. They used the RCPT to determine the chloride permeability of concretes. The OPC concrete contained 278 kg/m³ cement and a water cement ratio of 0.5. The sulphur concrete mixture contained 19% modified sulphur cement and 81% aggregate. The results (Wrzesinski and McBee 1988:7) indicate that the lowest chloride permeability was found in sulphur concrete when compared with OPC based concrete.

Various studies were performed to improve the properties of sulphur concrete. Adeh et al. (2008) investigated how different mixtures of aggregates and reaction time influence the strength of sulphur concrete. The sulphur cement used consisted of 58% sand and 10% fines (silica fume = 2% and stone powder = 8%). The fine aggregates (sand) used had a particle size of 150µm to 4.75mm and fines used, such as silica fume had a particle size of less than 150µm. They investigated the modification of sulphur (using a native additive) under 3 different conditions:

- Sulphur was melted in an oil bath and olefinic admixture added at 130-140°C. This temperature was maintained for 3 hours during the mixing process;
- Olefinic admixture was added at 150-160°C and this temperature was maintained for 3 hours;
- Olefinic admixture was added at 130-140°C, and the mixture was heated for 0.5, 1.2, and 3 hours. The 3 hour mixture obtained the highest compressive strength.

The use of fillers such as silica flour, as claimed by Adeh et al. (2008), increases the viscosity of the mix which assists in placing the sulphur cement on slopes. The aggregates were preheated before it was added to the molten sulphur. It is claimed that this prevents solidification when the different materials come into contact with molten modified sulphur (32%) and ensures a homogenous mix is obtained. From the sulphur mix 50mm cubic samples were made and demoulded after 24 hours. Various tests were performed on the samples after 75 hours. Sulphur concrete prepared at 140°C for 3 hours had the best compressive strength (20MPa).

Pouya et al. (2010) investigated the repair ability of different concrete types (silica fume concrete, polymer modified silica fume concrete and sulphur concrete) in corrosive environments. The silica fume concrete that they worked with contained 7% silica fume and the modified silica fume concrete

contained 7% silica fume and 30% styrene butadiene rubber latex. For the preparation of sulphur concrete, dicyclopentadiene was used to modify sulphur. Aggregates of various sizes (maximum size 16mm) were used to ensure a homogenous mix was obtained. Approximately 2% silica fume was included in the sulphur concrete mix.

Pouya et al. (2010) investigated the permeability and strength of the different concrete specimens and obtained the following results:

- The sulphur concrete had the highest flexural strength compared to the other concrete types (OPC⁸, silica fume concrete and polymer modified silica fume concrete).
- The sulphur concrete had the lowest water permeability compared to the other concrete types (OPC, silica fume concrete and polymer modified silica fume concrete).

From the above results, Pouya et al. (2010) state that sulphur concrete can be used as structural repair concrete instead of OPC concrete, for the repair of deteriorated concrete structures.

In conclusion, it was found that corrosion can occur due to diffusion, permeation and absorption of corrosive ions (e.g. chloride ions) into reinforced concrete. The literature review indicates that the corrosion process can be prevented (or considerably slowed down) by the application of surface sealers onto concrete, addition of fly ash to cement, and by using modified sulphur cement.

This study investigated the application of a modified sulphur cement coating on concrete [OPC = CEM II/A-M (V-L)] and the use of sulphur concrete, to verify their protection behaviour against chloride intrusion. The chloride conductivity test method was applied to determine the degree of chloride permeability, if any. Tests were carried out on the concrete specimens in order to determine the effectiveness of the sulphur cement coating.

⁸ OPC concrete = Control mix

CHAPTER 3 EXPERIMENTAL PROCEDURE

In an effort to test and apply the findings of the literature study, the reviewed South African CCT was selected as a test procedure. This test procedure was performed on prepared specimens to determine the feasibility of the method and to determine the chloride intrusion resistance of the subjected specimens. In addition, to OPC based concrete specimens, sulphur concrete specimens and a sulphur based sealer/coat applied to the OPC concrete were prepared and tested. The results of these tests were evaluated against the chloride resistance and durability of OPC based concrete.

For this investigation CEM II/A-M (V-L) 42.5MPa cement was used for the preparation of the OPC concrete.

The CEM II/A-M (V-L) nomenclature has the following meaning;

- CEM II – Portland cement with fly ash;
- A-M – Portland cement from 80-94% clinker;
- V-L – Fly ash and Limestone 6-20%;
- 42.5 – Relative cement strength.

The sulphur concrete specimens did not contain any cement for binding purposes.

3.1 Specimen Composition and Preparation

The following concrete specimens were used in the investigation: OPC CEM II/A-M (V-L) concrete (control), concrete with a sulphur based surface coat and sulphur concrete:

- The concrete control specimens (OPC based) consisted of the following: OPC cement, aggregates and sand (Appendix 1). This was thoroughly mixed and cast into standard cubes (15cm x 15cm). After 24 hours the cubes were demoulded and allowed to cure for 28 days according to standard curing procedures. After the curing period, specimens were cored and cut into discs (Figure 6) from the prepared samples for the CCT tests.



Figure 6: Concrete cylinders and discs

- The concrete with the surface coat had the same composition as the concrete referred to above but the cored specimens were coated with a sulphur cement coating. The surface coating consisted of sulphur (52%), fly ash (45%) and a plasticizer modifier (3%). The thickness of sulphur cement surface coat layer was approximately 1mm.
- The sulphur concrete consisted of sulphur, aggregates and a plasticizer modifier. The sulphur concrete was mixed and cast into standard cubes (15cm x 15cm). This concrete was allowed to cure for 1 day. After curing, cylindrical specimens were cored-drilled from the cubes, cut into discs and finally the CCT was performed on each specimen.

The chloride conductivity tests were carried out on each sample at Afrisam's main laboratories in Johannesburg. All the specimens for this test were oven dried for 7 days, followed by NaCl saturation (Section 3.4).

The specimens for the tests were cut from the following positions from the concrete cubes:

- OPC based concrete cube – outer specimens used (Figure 7),
- OPC based concrete cube with surface coat – outer (Figure 7) specimens used and

- Sulphur concrete cube – random position of specimens (Figure 8).

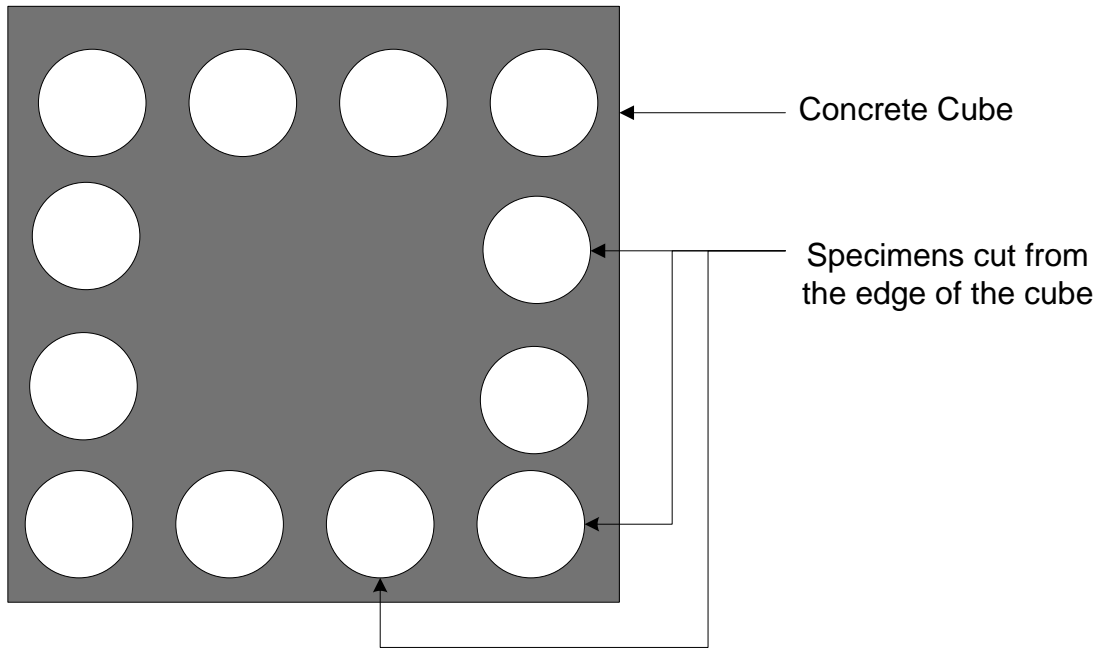


Figure 7: Specimens Drill Template (cut from the edge of the concrete cubes)

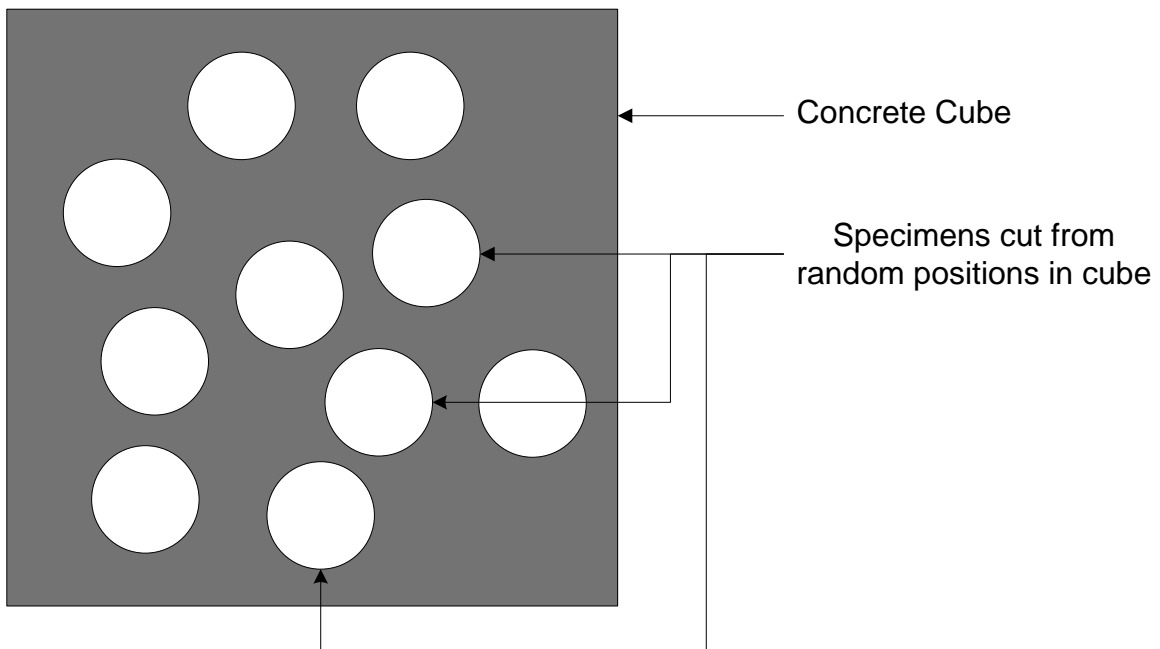


Figure 8: Specimen Drill Template (random positioning)

Four specimens were used per concrete type for the performance of the chloride conductivity test. Four additional specimens were similarly treated in order to confirm the results obtained.

3.2 Sulphur Coating Preparation

A heat source (Figure 9) was used to melt the sulphur. The temperature of the heat source was monitored with the aid of a thermocouple (Figure 10) and a modifier was added to the molten sulphur which modifies the sulphur to have thermoplastic properties. The mixing procedure of the sulphur cement coat is described below.



Figure 9: Heat source

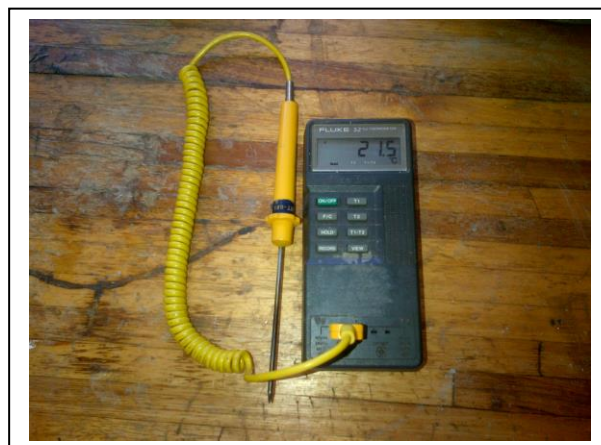


Figure 10: Thermocouple with digital display

The following mixing procedure was followed for the sulphur coating cement:

- Fifty two grams sulphur, 45 grams fly ash and 3 grams of liquid modifier were used for the sulphur cement coating;
- A melting pot (Figure 9) was pre-heated to approximately 120°C
- The sulphur was added to the pot and allowed to melt;
- The modifier was added and mixed with the molten sulphur. The modifier and sulphur were allowed to react for 30 minutes;
- The temperature of the mixture was regularly checked with the aid of the thermocouple provided with a numeric readout;
- Finally, fly ash was added to the molten sulphur (whilst the temperature was gradually increased to 130°C), whilst being thoroughly stirred. On completion of proper mixing, the hot mix was painted onto the flat faces of the cored concrete disc specimens with the aid of a brush.

3.3 Concrete Preparation

The concrete mixing procedure was as follows as applied by Wearne Concrete: 19mm aggregates (44%), OPC cement (17%), and 33% sand (crusher dust and plaster sand) was thoroughly mixed before water was added. After mixing, the concrete mix was poured into moulds. The samples were demoulded the following day and allowed to cure (under water at room temperature) for 28 days before coring, cutting and testing of the specimens.

3.4 The Chloride Conductivity Test

The drying and vacuum process, current and voltage measurements and the calculations required to perform the chloride conductivity test (Alexander et al, 1999) are discussed below:

- Drying and vacuum processing of specimens

After cutting the specimens, each was oven dried for 7 days at 50°C, and then stored in a desiccator.

The thickness, diameter and mass of each sample were measured.

The specimens were placed in the vacuum tank (Figure 11) and arranged such that the maximum surface area of each specimen was exposed.

A vacuum of 75 to 85kPa was created in the tank and this vacuum was maintained for 3 hours +/-15 minutes. .

After 3 hours have passed, a salt solution (5M NaCl) was allowed to enter the tank until the specimens were covered to a depth of approximately 40mm. The vacuum in the tank was reset to 75 to 85kPa and maintained for an additional 1 hour +/- 15 minutes.

After the hour passed the vacuum was released and the specimens were soaked in the salt solution for 18 hours +/- 1 hour.

After the 18 hours have passed each specimen was towel dried.

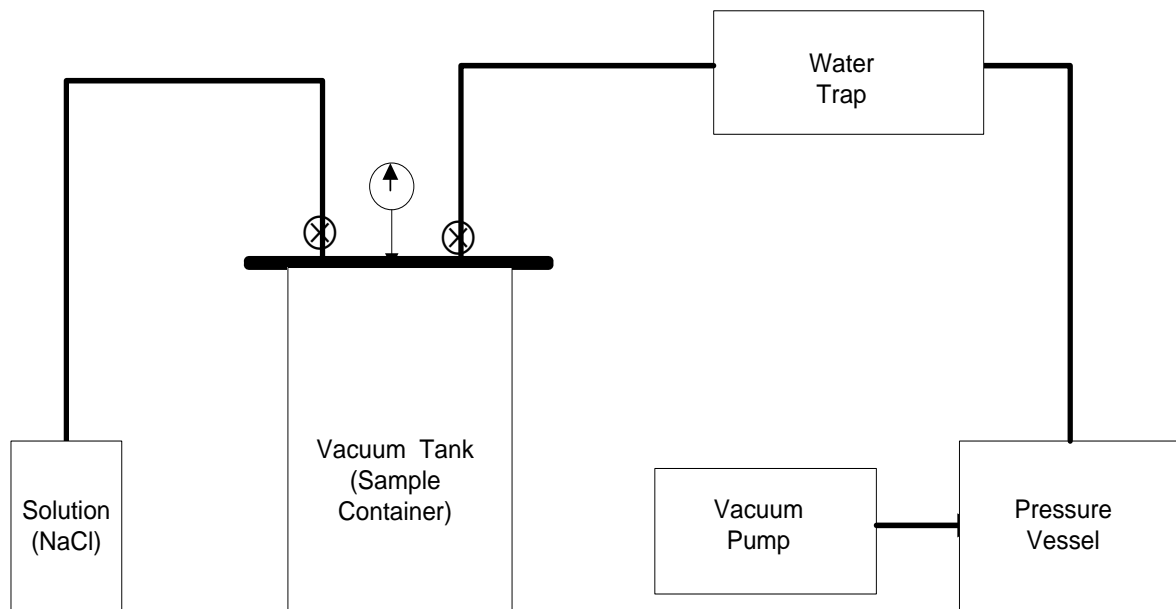


Figure 11: Schematic representation of the vacuum tank set up

The specimens prepared in the manner described above were used to determine the CCT measurements. Each specimen was placed in the test rig

(Figure 4) and the current was obtained at 10V potential difference. The data obtained is presented in Table 5.

- Current and Voltage measurement

The measurement was carried out at room temperature (23°C) and a voltage of 10V was applied across the specimen.

Both cells of the apparatus were filled with 5M NaCl and the specimens were placed in position. The current and voltage were recorded.

To find the conductivity of each specimen the following steps were followed;

The diameter was measured at 2 points and the average calculated,
The thickness was measured at 3 points and the average calculated,
The area of each specimen was then calculated, and
Finally current and voltage of each specimen were measured before the conductivity was calculated.

The conductivities of the specimens were calculated with the data presented in Table 5, by using the following equation;

$$\sigma = \frac{It}{VA}$$

with:

σ = Specimen conductivity(mS/cm)

I = Electric current (mA)

V = Voltage (V)

t = Specimen thickness (cm)

A = Specimen cross – sectional area (cm²)

Table 5: Test data and results

	Concrete (Control) CEM II /A-M (V-L)					Concrete with surface layer					Sulphur concrete			
	Sample 1	Sample 2	Sample 3	Sample 4		Sample 1	Sample 2	Sample 3	Sample 4		Sample 1	Sample 2	Sample 3	Sample 4
Diameter	68.09	68.11	68.13	68.15	Diameter	68.01	68.00	68.03	68.01	Diameter	68.11	68.10	68.04	68.07
Diameter	68.10	68.12	68.10	68.14	Diameter	68.00	68.02	68.01	68.00	Diameter	68.17	68.10	68.07	68.09
Average diameter	68.10	68.12	68.12	68.15	Average diameter	68.01	68.01	68.02	68.01	Average diameter	68.14	68.10	68.06	68.08
Thickness (mm)	28.77	30.35	28.74	29.68	Thickness (mm)	32.59	33.75	31.80	33.30	Thickness (mm)	30.14	29.81	30.27	29.98
Thickness (mm)	29.84	29.95	29.18	30.18	Thickness (mm)	33.15	33.65	32.45	33.02	Thickness (mm)	29.17	29.80	29.97	30.11
Thickness (mm)	29.38	30.45	28.78	30.21	Thickness (mm)	32.55	33.23	32.51	33.10	Thickness (mm)	30.39	29.81	29.46	30.42
Thickness (mm)	29.63	30.16	30.21	29.99	Thickness (mm)	29.63	33.45	32.41	34.10	Thickness (mm)	29.65	30.24	29.91	30.30
Ave Thickness (mm)	29.41	30.23	29.23	30.02	Ave Thickness (mm)	31.98	33.52	32.29	33.38	Ave Thickness (mm)	29.84	29.92	29.90	30.20
Area	36.41	36.43	36.41	36.45	Area	36.30	36.32	36.31	36.30	Area	36.48	36.41	36.37	36.39
Voltage	7.06	7.14	6.98	7.25	Voltage	7.20	5.51	7.36	7.23	Voltage	5.08	7.34	7.40	7.43
Amps	13.60	9.20	11.20	10.60	Amps	10.30	9.90	8.90	13.20	Amps	16.20	11.30	8.31	10.80
Conductivity	0.16	0.11	0.13	0.12	Conductivity	0.13	0.17	0.11	0.17	Conductivity	0.26	0.13	0.09	0.12
Average conductivity	0.13 mS/cm				Average conductivity	0.14 mS/cm				Average conductivity	0.15 mS/cm			
Surface coat =	Suplhur = 52%, fly ash = 45% and modifier = 3%													
Concrete =	CEM II/A-M (V-L)													
Concrete with surface layer	CEM II/A-M (V-L) + Sulphur cement layer													
Sulphur concrete														

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Laboratory Results

Table 6 provides the chloride conductivity test results of each concrete⁹ specimen and the average conductivity of each concrete type. Figure 12 provides the average chloride conductivity of the different concrete types and Figure 13 provides a comparison of the chloride conductivity results of this investigation with other research results, with the same cement composition.

Table 6: Chloride conductivity results of concrete, concrete with sulphur cement layer¹⁰ and sulphur concrete

Chloride Conductivity (mS/cm)					
Sample	<u>Control Concrete</u>	Series I	Series II	Series I	Series II
		<u>Concrete + Sulphur Cement Coating¹¹</u> (mS/cm)		<u>Sulphur Concrete</u> (mS/cm)	
1	0.16	0.13	0.08	0.26	0.18
2	0.11	0.17	0.18	0.13	0.17
3	0.13	0.11	-	0.09	-
4	0.12	0.17	-	0.12	-
Average	0.13	0.15	0.13	0.15	0.18

The laboratory worksheets for sulphur concrete, concrete, and concrete with sulphur cement layer, including the Series II concrete is presented in Appendix 2, Appendix 3, Appendix 4, and Appendix 5 respectively.

⁹ Wearne Concrete Potchefstroom

¹⁰ Sulphur = 52%, fly ash = 45% and modifier = 3%

¹¹ CEM II/A-M (V-L) + Sulphur cement layer

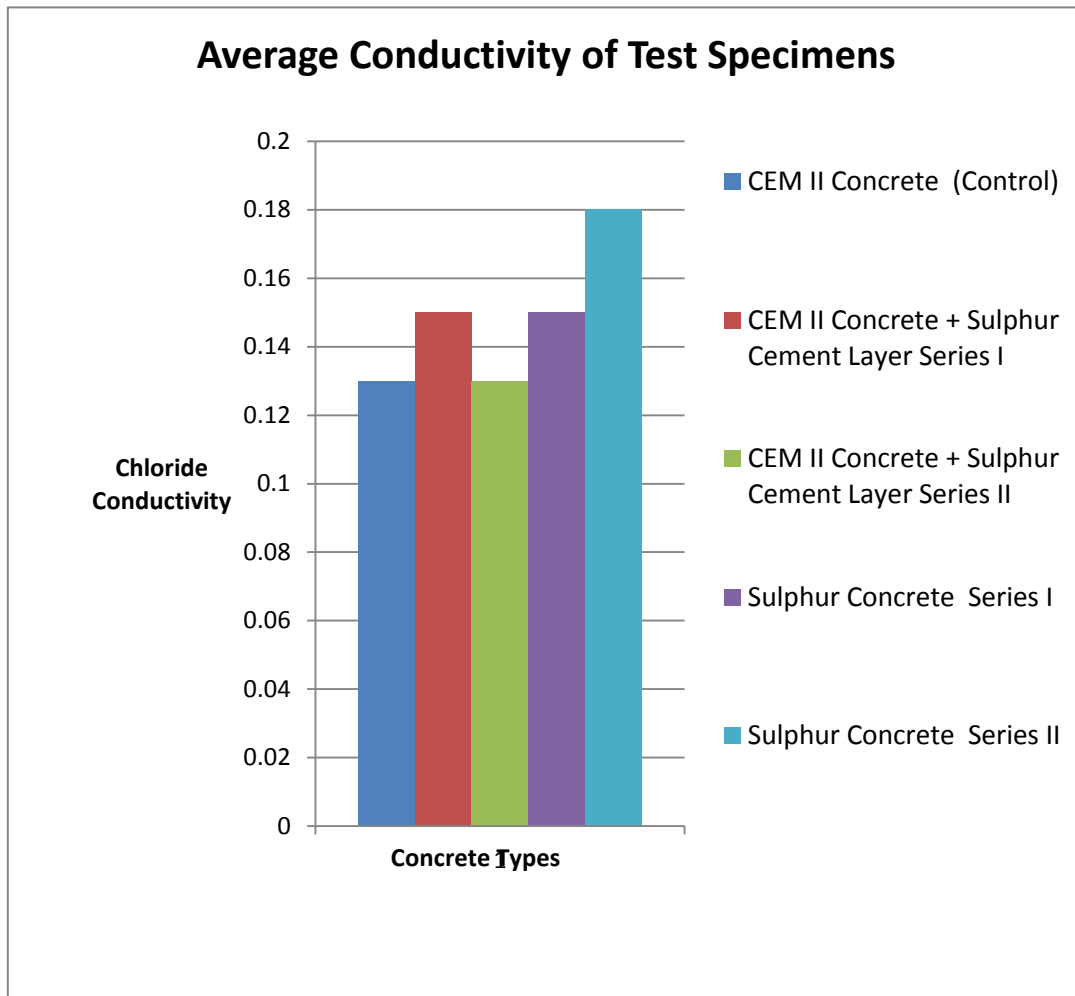


Figure 12: Average Chloride Conductivity of Test Specimens

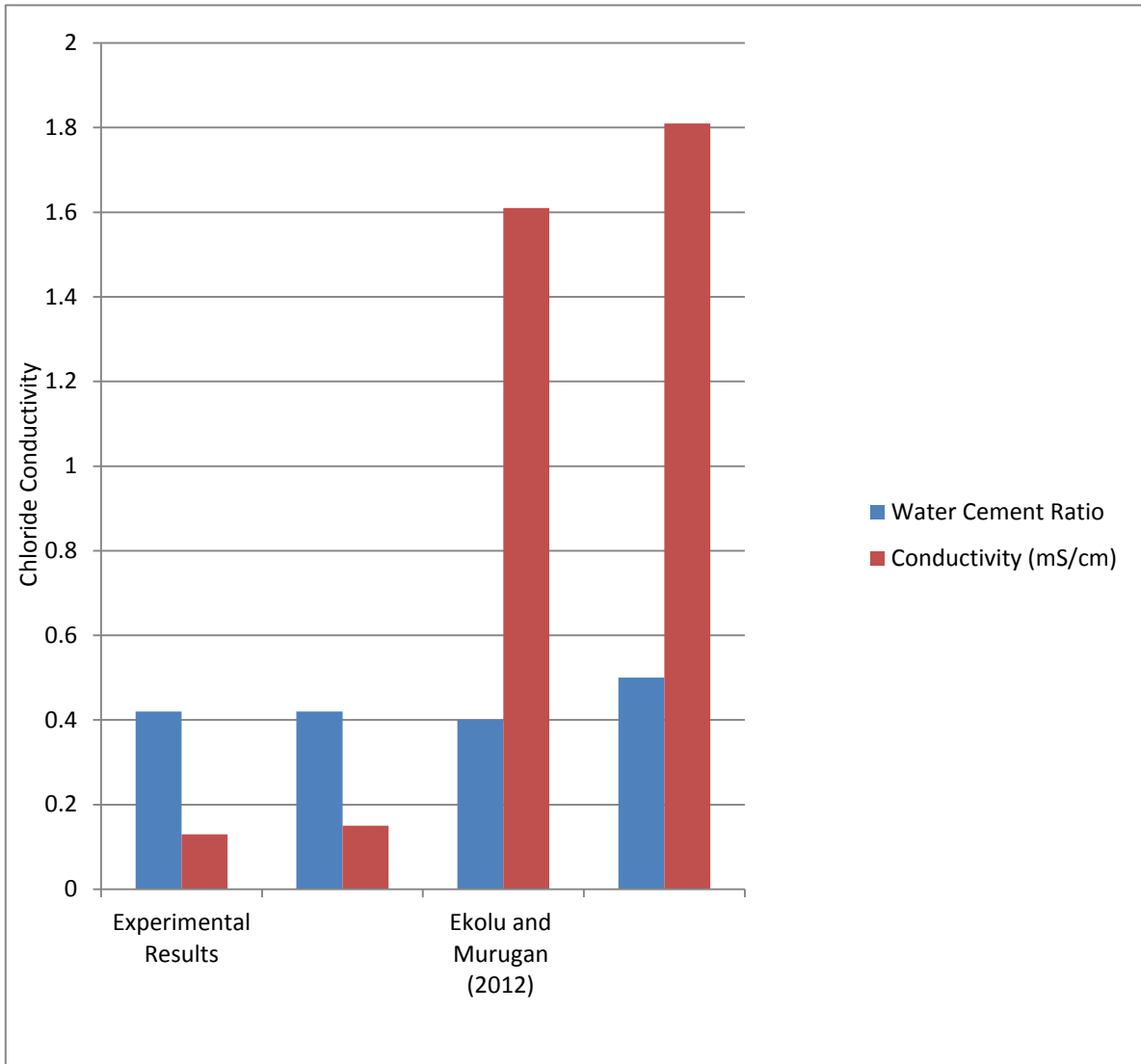


Figure 13: Comparison of concrete Experimental results vs Ekolu and Murugan (2012) concrete results

4.2 Discussion

The chloride conductivity of different concrete types was tested to see whether the application of a surface coat and using sulphur concrete, would change the permeability of the concretes. Four specimens of each concrete type were tested in Series I and in Series II; only 2 specimens were used to verify (retest) the results of Series I.

The conductivity results of all the different concrete types (Table 6) are less than 0.75mS/cm, which indicate that all the concretes have good resistance to chloride ingress, based on the chloride conductivity classification criteria in Table 4. The conductivity of specimens 2, 3, and 4 of the control specimens

are very similar (0.11mS/cm, 0.13mS/cm and 0.12mS/cm). Specimen 1 has a conductivity of 0.16mS/cm. This higher conductivity when compared to the other 3 specimens can be attributed to improper/poor fitting of the specimen into the perimeter of the apparatus. This poor fitting leads to increased NaCl flow/leakage between the anode and cathode compartments, which will thus give a higher conductivity result.

The results of the coated concrete specimens are very similar to the control specimen results. Two specimens have lower conductivity and 2 have higher conductivity which is similar to the chloride conductivity of specimen 1 of the control specimen. The reason for the higher conductivity of the coated specimens is thought to be due to the imperfections on the specimens (Figure 14).

The same can be argued for the sulphur concrete results as was done for the concrete coated results above.



Figure 14: Photo of CEM II concrete with sulphur based coating, illustrating the variation in coating thickness

Furthermore the coated specimens testing method followed in this chloride testing measurement procedure have short comings. In hindsight, separate specimens of the coat should have been made to test the conductivity of the coating only/separately, and not the conductivity of approximately 4mm coating and 25mm concrete as what have been done in this investigation.

The average chloride conductivity (Series I) of the concrete (Control Concrete specimens), concrete with surface coat (Concrete + Sulphur Cement Layer) and sulphur concrete were 0.13mS/cm, 0.15mS/cm and 0.15mS/cm respectively. These chloride conductivity results are very good according to the chloride conductivity classification criteria as presented in Table 4. The chloride conductivity of the control specimens were lower than the chloride conductivity observed for the surface coated and sulphur concrete specimens (Figure 12). This result was not expected as the literature survey indicated the sulphur concrete and surface coated specimens results should have been lower than the control specimen. Additional specimens (Series II) that were subjected to this test, were used to verify/refute the Series I results (Table 6). The average conductivity results of Concrete + sulphur layer and the Sulphur Concrete were 0.13 and 0.18 respectively. The Series II specimens confirms the results (Series I) obtained as presented in Table 6.

The experimental results of this investigation were compared against research results carried out by Ekolu and Murugan (2012) (Table 7). They investigated the chloride conductivity of different cement types, including CEM II/A-M (V-L) as was used in this investigation. No surface coat was applied to the concrete specimens used by Ekolu and Murugan (2012).

Table 7: Comparison of experimental results versus Ekolu and Murugan (2012) results

	Results			
	This study		Ekolu and Murugan (2012)	
Specimen	Control	Surface coated	No surface coat on specimens	
Cement Type	CEM II/A-M (V-L) 42.5			
Conductivity (mS/cm)	0.13	0.15	1.61	1.81

The chloride conductivity results of this investigation are much lower than the conductivity results of Ekolu and Murugan (2012). The classification criteria indicates this investigation results are very good when compared to the results of Ekulo and Murugan (2012). This may be due to better preparation of the mixes and the improved density due to the sand aggregate interaction.

Furthermore, the difference in the outcome of this investigation research results compared to the literature research results can be attributed to various reasons/factors:

- The control concrete specimen had no surface coat and therefore had a smooth contact point with the CCT apparatus luggin capillaries. The rest of the specimens had a surface coat applied to each and this lead to a rough/uneven apparatus contact point. The poor contact point of the luggin capillaries with the surface coated specimens may have resulted in unsatisfactory outcome of the results when compared with the literature study results.
- During the course of this investigation, the CCT apparatus was revamped (Otieno and Alexander, 2015) to improve on its durability and reliability. During their investigations, they found a difference between the old and new CCT apparatus test results, and they also investigated the reason for these differences. In their study they found the old apparatus provided lower values than that of the new apparatus. The reason for this difference was the incomplete filling of the anode and cathode compartments with salt solution. The incomplete filling of the apparatus compartments resulted in increased resistance in the specimen due to the smaller specimen area, and this lead to lower current flow through the specimen. Since the old CCT apparatus was used during this investigation, the possibility of incomplete filling of the cathode and anode compartments could have resulted in the lower values obtained in the tests. The old CCT apparatus can be modified (Otieno and Alexander, 2015) to ensure complete filling of the apparatus compartments.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Based on the results obtained from the experimental investigation, the following conclusions were reached:

- The test (chloride conductivity test) used in the experimental investigation is not suitable for specimens where a surface coat has been applied. The surface coat forms small imperfections and uneven surfaces on the specimens which will or can lead to poor contact between the apparatus and the specimens which may result in inaccurate readings.
- The investigation could not confirm results as the literature survey suggests, however, when comparing the results (of the same cement type) with other research results, the results of these determinations displayed a much better quality than the other research results.
- The old CCT apparatus set-up procedure leads to incomplete filling of the compartments at times. This may lead to inaccurate result readings, and this may be the reason for the low conductivity results obtained in this investigation. The old CCT apparatus should be upgraded to ensure proper filling of the compartments.
- The CCT results of the specimens are very low, i.e. good quality concrete, and the three concrete types have almost the same conductivity, that is, if compared to the required standard (Table 4). The resolution of the CCT apparatus is not high/good enough to clearly distinguish between the different cement types used in this investigation.

5.2 RECOMMENDATIONS

The following recommendations are made:

- More investigations are required in this specific field. The updated South African chloride conductivity test and the international rapid test should both be used in future research investigations.
- A thorough study is required to determine the proper use and calibration of the equipment to ensure that reliable results can be obtained.
- The new CCT apparatus should be used, or the old CCT apparatus can be used when modified, to ensure complete filling of the cathode and anode compartments.

- The application of the surface coat increases the thickness of the coated specimens when compared against uncoated specimens, and this may influence the conductivity results of the specimens. In order to deal with this uncertainty, increase the diameter of the uncoated specimens to ensure more or less similar diameters between the coated and uncoated specimens.
- Use CEM I cement without any addition of cement hardeners as this will give a better indication of the permeability of normal concrete compared to e.g. high performance concrete (as used in this experimental investigation). Also use different chloride test methods with good resolution quality to ensure the correct result/output is obtained. This will assist to differentiate between the different concrete types used in the experiments.

References

- Adeh N.B., Haghghi M.M. and Hosseini N.M. 2008, Preparation of sulphur mortar from modified sulphur.
- Alexander M.G., Ballim Y, and Mackechnie J.R. 1999, Concrete durability index testing manual, Research monograph no. 4.
- Almusallam A.A., Khan F.M, Dulaijan S.U., Al-Amoudi O.S.B. 2003, Effectiveness of surface coatings in improving concrete durability.
- ASTM C150 2007, Standard Specification for Portland Cement.
- Beushausen H and Alexander M.G. 2008, The South African durability index tests in an international comparison.
- Bioubakhsh S. 2011, The penetration of chloride in concrete subject to wetting and drying measurement and modelling.
- Broomfield J.P. 2007, Corrosion of steel in concrete, second edition: Taylor and Francis.
- Do M.J. and Chokie A.D. 1994, Aging Degradation of Concrete Structures in Nuclear Power Plants.
- Dunham C.W. 1985, The theory and practice of reinforced concrete.
- Ekolu S.O. and Murugan S. 2012, Durability Index Performance of High Strength Concretes Made Based on Different Standard Portland Cements.
- Fontana J.J, Farrell L.J., and Yuan R.L 1998, Guide for Mixing and Placing Sulphur Concrete in Construction.
- French Nuclear Energy (CEA), A Nuclear Energy Division Monograph 2010, 'Corrosion and Alteration of Nuclear Materials': Nuclear Energy Department.
- Gardner T.J. 2006, Chloride transport through concrete and implications for rapid chloride testing.
- Hola J., Ksiazek M. 2009, Research on usability of sulphur polymer composite for corrosion protection of reinforcing steel in concrete.
- Janz M., Byfors K. and Johansson L. 2008, Surface treatments, strategy and maintenance of concrete structures.

Neville A.M., 2011, Properties of concrete, fifth edition: Pearson Education Limited

Naus D.J., 2007, Primer on durability of nuclear power plant reinforced concrete structures.

Oh B.H., Cha S.W., Jang B.S., Jang S.Y. 2002, Development of high-performance concrete having high resistance to chloride penetration.

Otieno M, and Alexander M. 2015, Chloride conductivity testing of concrete – past and recent developments.

Penn State College of Engineering, n.d. Available from: <http://www.engr.psu.edu/ce/courses/ce584/concrete/library/construction/curing/Hydration.htm>.

Pouya H.S., Ganjian E., Parhizkar T., and Zamani A. 2010, Properties of polymer modified and sulphur repair mortars in aggressive environments.

Sivasankar A, Stango S.A.X., and Vedalakshmi R. 2013, Quantitative estimation on delaying of onset of corrosion of rebar in surface treated concrete using sealers.

Stanish K.D., Hooton R.D. and Thomas M.D.A. 1997, Testing the chloride penetration resistance of concrete: A Literature Review.

Taylor H.F.W. 1997, Cement chemistry, second edition: Thomas Telford Publishing.

Trejo D., Halmen C. and Reinschmidt K. 2009, Corrosion performance tests for reinforcing steel in concrete.

Whiting D. 1981, Rapid Determination of the Chloride Permeability of Concrete.

Wrzesinski W.R. and McBee W.C. 1998, Permeability and Corrosion Resistance of Reinforced Sulphur Concrete.

Zulu S. and Allopi D. 2014, Influence of high content fly ash on concrete durability.

Appendixes

Appendix 1 Concrete Mix Design

<u>Material Description</u>	<u>Percentage</u>
19mm Aggregate	43.9
Crusher Dust	22.9
Plaster Sand	9.6
OPC (Afrisam HSC CEM II/A-M (V-L)) 42.5MPa	16.5
Additive (BASF Glenium)	0.1
Water	7.0

Appendix 2 Sulphur Concrete Control Worksheet

AfriSam

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Materials

SF42 Chloride conductivity

Date: 26-08-2014

Carried out by: Linda

Sample No.	0875-4-MUZ-5		0875-4-MUZ-6		0875-4-MUZ-7		0875-4-MUZ-8	
Size, mm	Thickness	Diameter	Thickness	Diameter	Thickness	Diameter	Thickness	Diameter
	30.14		29.81		30.27		29.98	
	29.17	68.11	29.80	68.10	29.97	68.04	30.11	68.07
	30.39	68.13	29.81	68.10	29.46	68.07	30.42	68.09
	29.65		30.24		29.91		30.30	
Oven-dry mass, g	259.56		274.91		275.60		275.78	
Saturated mass, g	267.35		279.00		278.46		279.51	
Voltage, V	5.08		7.34		7.40		7.43	
Current, A	16.2		11.3		8.31		10.8	
Current, mA (X1000)								
Conductivity, mS/cm								
	Chipset		Honeycomb				Chipset	
Average Chloride conductivity, mS/cm								
.....								
Porosity, %								
	Average Porosity, %							
.....								

Appendix 3 Concrete Control Worksheet

AfriSam

Centre of Product Excellence	Materials
SF42 Chloride conductivity	

Date: 03-09-2014

Carried out by: LINDA

Sample No.	0895-14-5		0895-14-6		0895-14-7		0895-14-8	
Size, mm	Thickness	Diameter	Thickness	Diameter	Thickness	Diameter	Thickness	Diameter
	28,77	68,09	29,81	68,10	30,27	68,04	29,98	68,07
	29,84		29,80		29,97		30,11	
	29,38	68,10	29,81	68,10	29,46	68,07	30,42	68,09
	29,63		30,24		29,91		30,30	
Oven-dry mass, g								
Saturated mass, g								
Voltage, V	5,08		7,34		7,40		7,43	
Current, A	16,20		11,30		8,31		10,80	
Current, mA (X1000)								

Appendix 4 Concrete with sulphur cement surface coat Worksheet

AfriSam

Centre of Product Excellence SF42 Chloride conductivity	Materials
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Date: 09-09-2014

Carried out by: LINDA

Sample No.	0595-14-5		0595-14-6		0595-14-7		0595-14-8	
Size, mm	Thickness	Diameter	Thickness	Diameter	Thickness	Diameter	Thickness	Diameter
	32,88	68,01	33,75	68,00	31,80	68,03	33,30	68,01
	33,59		33,65		32,45		33,02	
	33,15	68,00	33,23	68,00	32,51	68,01	33,10	68,00
	32,55		33,45		32,41		34,10	
Oven-dry mass, g	278,47		272,32		273,46		277,52	
Saturated mass, g	291,60		285,57		284,65		288,84	
Voltage, V	7,2		5,51		7,36		7,23	
Current, A	10,3		9,9		8,9		13,2	
Current, mA (X1000)								
Conductivity, mS/cm								
	Average Chloride conductivity, mS/cm							
							

Appendix 5 Concrete and Sulphur concrete with sulphur surface coating
Worksheet

AfriSam

Centre of Product Excellence	Materials
SF42 Chloride conductivity	

Date: 25-09-2014

Carried out by: Linda

Sample No.	0895-14-5		0895-14-6		0895-14-7		0895-14-8	
Size, mm	Thickness	Diameter	Thickness	Diameter	Thickness	Diameter	Thickness	Diameter
	26.86		28.88		30.59		35.85	
	26.65	68.17	28.60	68.06	30.89	68.16	34.15	68.26
	25.90	68.12	28.86	68.09	30.45	68.19	36.98	68.29
26.11	28.06		30.89		36.74			
Oven-dry mass, g	228.04		245.00		297.83		311.72	
Saturated mass, g	237.54		255.90		301.57		321.01	
Voltage, V	6.86		6.02		7.40		6.11	
Current, A	8.0		13.5		14.8		10.8	
Current, mA (X1000)								
Conductivity, mS/cm								
	Average Chloride conductivity, mS/cm							