Effects of Selected Media on Novel Portland Pozzolana Cement

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other University or for other award

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DEDICATION

To my beloved wife; Tabitha Wangarũ Njaũ, daughter; Joy Nyambaiyũ, mum; Margaret, Nyambaiyũ and daddy; Geoffrey Wachira. All this is to bring happiness and aspiration in our lives.

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LIST OF SYMBOLS AND ACRONYMS USED IN THIS WORK

Cement Chemical Nomenclature and Symbols

$A = Al_2O_3$, $C = CaO$, $C_3A = 3CaO.\ Al_2O_3$ (Tricalcium Aluminate),

$C_4A\bar{S}H_{12} = 3CaO.Al_2O_3.CaSO_4.12H_2O$,

$C_6A\bar{S}_3H_{32} = 3CaO.Al_2O_3.3CaSO_4.32H_2O$ (Ettringite), $C_2S = 2CaO.SiO_3$ (Dicalcium Silicate), $C_3S = 3CaO.SiO_2$ (Tricalcium Silicate), $CH = CaO.H_2O$ or $Ca(OH)_2$, $CO_2 = \check{C}$, $C\bar{S}H_2 = CaSO_4.2H_2O$, $H = H_2O$, $M = MgO$, $N = Na_2O$, $S = SiO_2$, $\bar{S} = SO_3$.

Acronyms Used

AAR = Alkali Aggregate Reactions

ALS = Acetylene Lime Sludge

ASTM = American Standard for Testing and Materials

BB = Reject or Broken Bricks

$\check{C}^A$ = Aggressive CO_2

CCR = Calcium Carbide Residue

Cement Mortar = mortar made from either OPC, PPC or PCDC

Cl1 or 2 = Chloride simulated solutions with chloride concentration equal to or twice the sea water respectively

Corrosive Media = seawater, 20,000 and 40, 000 ppm Cl^- ($MgCl_2$) solution, distilled water, 2342 and 4684 ppm SO_4^{2-} (Na_2SO_4) solution

$\check{C}^S$ = Stabilising CO_2

CSE = Copper-Copper Sulphate Reference Electrode

CSH = Calcium silicate Hydrate

DALS = Dried Acetylene Lime sludge

GGBS = Ground Granulated Blast Furnace Slag

HCL = Hollow Cathode Lamps

ISAB = Ionic Strength Adjustment Buffer

KEBS = Kenya Bureau of Standards

KS = Kenya Standard

LPR = Linear Polarisation Resistance

MSH = Magnesium Silicate Hydrate

OPC = Ordinary Portland Cement

OPC + PFA = OPC + 25 % Pulverised Fuel Ash

PCDC = a blend of 55 % OPC and 45 % Test Ash

PFA = Pulverised Fuel Ash

PPC = Portland Pozzolana Cement or Blended Cement

RH = Rice Husks

RHA = Rice Husks Ash

SBE = Spent Bleaching Earth

SCE = Saturated Calomel Electrode

SO 1 or 2 = Sulphate simulated solutions with sulphate concentration equal to or twice the sea water respectively

T_{Cal} = Calculated T- Value (From T – Test)

T_{Crit} = Critical T – Value (Reference values from T – Test Tables)

Test Ash = A blend of DALS and a calcined mix of RH, SBE, ground BB

w/c = Water to Cement Ratio

ABSTRACT

Cement is subject to degradation by aggressive media found in the environment. Durability tests are therefore necessary for any cementitious material in a given environment. The work reported in this thesis involved the study of the effects of selected aggressive media on a cement, made from inter-mixing Ordinary Portland Cement (OPC), dried acetylene lime sludge (DALS) and an incinerated mix of reject bricks (BB), spent bleaching earth (SBE) and rice husks. The cement was labelled Portland Combined DALS Cement (PCDC). Initial tests showed that PCDC met the Kenya Standard requirements for Portland Pozzolana cement (PPC). PCDC was subjected to various media which included sea water, distilled water, chloride and sulphate solutions in a laboratory set-up. The experiments were carried alongside OPC, 25 % Pulverised Fuel Ash substituted OPC (OPC + PFA) and commercial PPC. The study was carried out in two phases; cement mortar moulded into 100 mm cubes subjected to the media and reinforced mortar cubes subjected to a wet and dry alternate environment of 3.5 % sodium chloride solution. PCDC exhibited continued compressive strength gain in all media except in chloride solutions. PCDC exhibited comparable gain in compressive strength and selected ions intake/leach to PPC in sulphate solutions and distilled water. PCDC exhibited higher strength gain than OPC in distilled water. Except in chloride solutions, PPC exhibited higher strength gain than OPC. In Corrosion tests, the PCDC mortar rebars showed early attainment of active corrosion coupled with higher corrosion rates over a short period of time than OPC as w/c ratio was increased. The PCDC showed a decreased chloride penetration than OPC as w/c and depth of cover increased. PCDC showed the lowest apparent chloride diffusion coefficients. The resistivity of PCDC in the aggressive media suggested that it required greater depths of cover, where reinforcement was to be used, and long term curing to improve on its resistivity. The tests showed that PCDC can be used for general construction work in the tested media in a similar manner to PPC.

CHAPTER ONE

INTRODUCTION

1.1 Background

Cement is generally defined as a substance that can hold together pieces of aggregates, coarse and/or fine, together to form a solid mass (Lea, 1956). There are hydraulic cements that set and harden in presence of water, for example, Portland cements. On the other hand, non-hydraulic cements such as lime harden on exposure to air (Lea, 1970). Typical examples of Portland cement include rapid hardening, quick setting, white, waterproofed, low heat, sulphate resisting, iron ore, non-shrinking, air-entraining and Ferrari cement (Lea, 1956). Others include Asphalt Cements which are bituminous and are mainly applied to surface layer in flexible pavement surfaces (Young, *et al.*, 1998). Specific types of Portland cements are given in ASTM C 150 (ASTM, 2005a). Blended cements are a mixture of mainly pozzolana and Portland cements. They have varied specifications (ASTM, 2008).

In the production of Portland cement, argillaceous and calcareous material are inter-ground, either in a wet or dry form and clinkerized in a rotary furnace at a temperature in excess of 1300 °C, fuelled by petroleum oil or coal. The resultant clinkers are inter-ground with about 5 percent gypsum ($CaSO_4.2H_2O$) to give Portland cement (Lea, 1956). The process is quite expensive, especially due to the high energy demand (García, *et al.*, 2007) for fuel during clinkerisation process and grinding. The resultant Portland cement is therefore expensive and unaffordable to many, especially in developing countries. In addition, there is enormous amount of CO_2 emitted during the production of the cement;

For every tonne of cement manufacture, a tonne of CO_2 gas is emitted (García, *et al.*, 2007; Mohammed, *et al.*, 2008). CO_2 is the chief green house gas responsible for global warming.

Portland cement, on its own is prone to attack by aggressive media, for example sulphates, chlorides or a combination of the two among and many others. Hydrated Ordinary Portland cement (OPC) has a resultant high $Ca(OH)_2$, about 20 percent by weight, that makes it susceptible to attack especially by the acids and sulphates. In Kenyatta University, the students' hostels, namely Nyayo hostels, had started showing signs of deterioration due to aggressive sewerage waste. This had manifested itself through white marshy substances on the outside surface of the walls where toilets are located. Although painting has occasionally been done to mask the effect, circumstances are that the walls' concrete is still under attack.

Blending OPC with pozzolana materials makes it less permeable, thus reducing the ingress of aggressive media. The pozzolana react with the resultant $Ca(OH)_2$ producing more cementious material. The reaction between pozzolana and $Ca(OH)_2$ makes blended Portland cement gain overall higher strength but after a longer period as compared to OPC. The pozzolana hence improves on cement quality and reduces the $Ca(OH)_2$ content, the most susceptible component. Natural pozzolana mainly require grinding and are thus less costly in terms of preparation (Blanks and Kennedy, 1955). The resultant cement is relatively low costing. In Kenya, naturally found tuff is used as pozzolana.

Mainly due to cost and improving the properties of OPC, the most commonly used cement, several researchers have endeavoured to search for high quality and relatively low cost alternative cementious materials. Lime-pozzolana cements and Pozzolana blended Portland cements are common examples. Lime has historically been used as a construction material. Although OPC and other cementious materials have found more use, it is still difficult to entirely substitute lime. This is because lime is less rigid thus allowing for slight movement of the building; porous, thus allowing for evaporation of water that may contain aggressive media; and has less thermo-expansion coefficient than cement. It is for these reasons that a majority of researchers are finding relevance in substituting cement with lime and neat limes (Callebaut, *et al.*, 2001; Duffy, *et al.*, 1991; Mosquera, *et al.*, 2006; O'Brien, *et al.*, 1995). Lime, although reluctantly in some places, has been replaced with Portland cements or its blend, for example, in situation necessitating high mechanical strength, low porosity and rigidity but these properties have found limitation in use to conserve the historic buildings (Elert, 2002). Lime-pozzolana cements are finding increasing interest for social construction in developing countries (Villar-Cociña, *et al.*, 2003).

The test cement in this study is essentially a blended Portland Cement, which was prepared by a process described by Muthengia, (2003). The cement was labelled PCDC for the purpose of this research. PCDC is a blend of dried acetylene lime sludge (DALS), OPC and a calcined mix of spent bleaching earth (SBE), rice husks (RH) and ground reject bricks (BB).

In his research, Muthengia (2003) determined and evaluated the compressive strength of the resultant ash from incinerating the RH, SBE and BB in mix with DALS, laboratory $Ca(OH)_2$ and/or OPC. The worker (Muthengia, 2003) determined pozzolanic activity of the incinerated RH/SBE/BB-mix ash when in blend with OPC (Muthakia, *et al.*, 2005;

Muthengia, *et al.*, 2005; wa-Thiong'o, *et al.*, 2005). He (Muthengia, 2003) reported that the PCDC met the Kenya Standard specification (KEBS, 1993) for Portland Pozzolana cement up to a 45 percent replacement of OPC. The test pozzolana of the incinerated mix of RH/SBE/BB with DALS was also reported to meet the standard specifications for Fly Ash and other pozzolana for use with lime (ASTM, 1991) mainly in terms of compressive strength requirements. It was therefore apparent that durability tests on the test cement be carried out to validate a recommendation for its application.

Housing and construction in Kenya is expensive and therefore unaffordable to a majority of low income earners. This is due to the escalating prices of cement mainly in tandem with energy cost. The result is mushrooming of poor housing and construction designs best exemplified by the slums of Kibera, Mukuru kwa Njenga and Mathare Estates in the Nairobi city of Kenya. A recent move by the government of Kenya is the bid to reducing the construction cost by use of locally available materials in construction. This will take the dimension of mostly using locally made bricks as the main construction material (Vincent, 2006). The use of a blend of the affordable cementious materials, such as one in this study would lead to further reduction in the cost. This is because in most housing projects, high strength binders are not a necessity.

The corrosive media used in the study were of high concentration. They were designed to give accelerated test results in a laboratory set-up mocking performance in the natural environment. The solutions included sea water, distilled water and solutions of magnesium chloride and sodium sulphate. Commercial OPC, PPC and PCDC were used as cement for making cement mortar. Unless otherwise stated, the term 'cement mortar' shall be used in reference to cement mortar made from either of the above cements.

1.2 Justification of the Study

Muthengia's (2003) work reported a cementious material that could offer a more affordable cement. The cement could lead to better housing facilities for a low income Kenyan and people in other developing countries. The environments where the cement would be used have lots of corrosive agents. In Kibera for example, waste waters of industrial and domestic origins, run through any available sloppy channel on the ground and would be in contact with built structures from the cement. Although the tests carried out by Muthengia (2003) are the basic and necessary ones for determining a potential cementious material, durability tests require to be done for a promising material. A major concern and the point of reference in this study revolves around assessing the durability of the PCDC in selected simulated salty environments of sulphates, chlorides and seawater. This was to give an accelerated test for the performance of the cement in the environment.

Investigation on the durability of the PCDC cement is necessary for making decisions in conditions under which the cement is applicable. In assessing its durability vis a vis OPC and PPC, the study was aimed at establishing whether the test material could be used in the normal and harsh environmental conditions. The study was expected to suggest suitability or otherwise of the test cement.

The results of this study were expected to give an insight on the durability of the test cement. Knowledge of the corrosive resistivity will lead to research on possible ways of improving the test cement. The study was thus engineered at establishing the robustness of the test cement vis a vis the commercial OPC and PPC.

1.3 Statement of the Problem

Cements and cementious materials are subject to being degraded by aggressive environments when used in construction works. The cement under study has materials that have not been well documented in terms of their durability in aggressive media such as salty environments. The blending materials, DALS and the mix of incineration of RH, BB and SBE can either help to improve resistance of OPC or be point of attack from corrosive salty environments.

1.4 Objectives

1.4.1 General Objective

To investigate and compare the durability of PCDC cement with commercial PPC and OPC in salty media of solutions of $MgCl_2$, NaCl, Sea water and Na_2SO_4.

1.4.2 Specific Objectives

i. To investigate the pH change and exchange of selected ions between the cement mortar and the corrosive media.

ii. To determine the corrosion rates and corrosion potentials versus time of rebars in simulated reinforced cement mortar at varied water to cement ratio.

iii. To investigate the change in compressive strength of the cement mortar cubes subjected to the corrosive media.

iv. To investigate the chloride absorption profile of the cement mortar at varied water to cement ratio.

CHAPTER TWO

LITERATURE SURVEY

2.1 Pozzolana, Limes and Pozzolana-Lime cementious Materials

Pozzolana is defined as a siliceous and/or aluminous material that in itself possesses no cementious properties, but when finely ground, it reacts with lime in presence of water to form cementious products at room temperature. The major reaction can be summarised as given by equation 2.11 (Takemoto and Uchikawa, 1980)

$$SiO_2 + nCa(OH)_2 \xrightarrow{\qquad} nCaO.SiO_2.nH_2O \qquad 2.11$$

The silicate and aluminium hydrates resulting from pozzolana – calcium hydroxide reactions have similar properties as Portland cement's hydrates (Young, *et al.*, 1998).

Pozzolana can be found naturally or made artificially. Natural pozzolanas include volcanic ash, Zeolite rocks (Modernite and Clinoptilolite in Greece) (Fragoulis, 1997; Nai-qian, 1988), Montimorillonite and Opaline materials (for example Cherts) (Blanks and Kennedy, 1955). Kenyan Tuff, a volcanic rock, is generally blended with OPC to make commercial Portland Pozzolana Cements (PPC) (Muthengia, 2003). The naturally-occurring pozzolanic materials owe their pozzolanicity to volcanic glass as opposed to crystalline silica. This results from the hydro-heating effects during volcano eruptions (Fragoulis, 1997).

Pozzolanic rice husks ash, results from carefully incinerated rice husks at controlled temperatures under conditions of aeration. Rice husk ash (RHA) has been reported to be pozzolanic when in blend with OPC (Agarwal, 2006; Deepa, *et al.*, 2006; Nehdi, *et al.*, 2003; Qingge, *et al.*, 2004) as well as DALS (Jaturapitakkul and Roongreung, 2002). Pozzolanic rice husk ash-lime has been widely used as a building material in India and other parts of the world. A large amount of rice husks is burnt in open fields in Kenya and the resultant ash applied in rice fields to improve on soil productivity because it enhances the plant defence mechanism (Bélanger, *et al.*, 2003). The silica in this ash is in an unreactive and non absorbable form thus of less value to the soil. In Egypt, the scourge of seeing rice husks being burnt in open air has initiated research to burn it in a Torbed reactor that forms a cementious material. This results in a useful product and tackles disposal problems (Nehdi, *et al.*, 2003).

Several authors have reported on modes of incinerating rice husks to give pozzolanic ash. Mehta (Mehta, 1979) states that pozzolanic RHA can be produced at 500 °C at prolonged period, as well as at 680 °C but within less than a minute. Ochung'o (1993) describes production of pozzolanic ash in a fixed bed kiln at temperatures lower than 600 °C for about 24 hours. Nehdi *et al.* (2003) used Torbed reactors for production of pozzolanic ash at temperatures of between 750 and 830 °C. Feng, *et al.* (2004) pre-treated samples of RH with HCl then washed and compared them with untreated RH (Feng, *et al.*, 2004). The treated RH showed relatively high pozzolanicity after being incinerated up to about 950 °C. The treated RH exhibited minimal change in pozzolanicity, as measured from conductivity measurement, with combustion times of between 4 to 12 hours at 950 °C. The untreated RH, however, showed a decrease in pozzolanicity beyond 750 °C and significant drop in pozzolanicity as incineration period increased from 4 to 12 hours. They attributed the pre-treatment of the RH with HCl to washing off of impurities of alkali and alkali metal ions as well as halides and thus a higher silica residual content.

Spent bleaching earth (SBE) is the resultant clay obtained after the earth has been used in bleaching petroleum or edible oils. The naturally mined bleaching earths, mainly bentonite and Montimorillonite, are normally activated traditionally by hydrochloric or sulphuric acids. The resultant bleaching earths remove impurities that impart colour such as β–carotenoids, chlorophyll, residual soaps, fatty acids, phosphatides and trace metals. Activated carbon is sometimes added to the bleaching earth to remove traces of polynuclear aromatic hydrocarbons (PAH) (Norris, 1982; Patterson, 1976). The resultant clay, SBE, has oil contents in excess of 20 percent by weight (Mana, *et al.*, 2007; Muthakia, *et al.*, 2005; Muthengia, 2003; Pizarro and Park, 2003; Pollard, *et al.*, 1993). The residual oils are dangerous to the environment as they are combustible and thus can easily cause fires. They are also a hazard to water bodies and aquatic life as they may depict the same problems as oil spills in waters. In more developed countries than Kenya, the production of SBE is enormous. In Algeria, for example, it exceeds 8000 tonnes per year (Mana, *et al.*, 2007). Alternative uses of SBE has been an issue of exploration for over half a century (Pollard, *et al.*, 1993). Pollard, *et al.* (1993) explored the re-use of re-activated SBE in bleaching edible oil. The researchers (Pollard, *et al.*, 1993) found the re-activated SBE to have limited removal of chlorophyll derivatives and negligible uptake of β–carotenoids and phosphorus. SBE has been used as an additive in animal feeds and in manufacture of soaps (Tsai, *et al.*, 2002). It has also been impregnated with normal sodium hydroxide solution and thermally activated at 100 °C for absorption of dyes from textile industry (Mana, *et al.*, 2007). Other alternative re-use of the SBE includes utilisation in brick industries, addition to bitumen and burning (Tsai, *et al.*, 2002). The waste when produced in large quantities may not find immediate use. In Kenya, the material is relocated and dumped in prescribed places (Muthengia, 2003). This is hazardous to health and safety.

Bleaching clays have high silica and alumina contents. Thermal analysis of the clays shows dehydration peaks at temperature ranges of 500-700 °C (Dodd and Tonge, 1987; Mackenzie, 1957). At these ranges, the clays should possess pozzolanic activities (Cook, 1986). Muthengia (2003) reported that SBE made pozzolanic material at 550 °C. The material requires external source of energy for production of a pozzolanic product. En-masse combustion of the material in a furnace produced non-pozzolanic material (Muthakia, *et al.*, 2005). Thus production of large amounts of pozzolanic material, for example in a commercial scale, from SBE would require a conservative form of external energy for the process to be economically viable. Muthengia (2003) clearly outlines how this can be done using the energy from rice husks and the SBE itself.

Broken bricks result from improperly burnt bricks or broken finished clay products. Clay products are processed from silica and/or alumina-rich clays at temperature of up to 900 °C, the temperature at which a majority of clays become pozzolanic (Cook, 1986). Therefore, resultant reject bricks (BB) may possess pozzolanic activity (Muthakia, *et al.*, 2005). Research by Muthakia *et al.* (2005) showed that thermal activation of BB at 550 °C improved on its pozzolanicity. BB have been used as pozzolana materials in most countries including India (Cook, 1986). Khatib (2005) compared the performance of concrete with and without BB as replacement of fine aggregates. The concrete with BB as fine aggregate showed a higher compressive strength after 28th day of curing showing that the aggregates reacted to form additional cementious material. A major setback was that the BB affected expansion and shrinkage of the resultant concrete (Khatib, 2005). O'Farrel *et al.* (2000) observed that partial replacement of high C_3A cements with ground bricks increased resistance to expansion and reduced strength loss when the cement mortar was subjected to sea water (O'Farrel, *et al.*, 2000). BB have also been used as aggregates in hydraulic lime mortars for the restoration of historic masonry in Crete, Greece (Maravelaki-Kalaitzaki, 2005). Heikal (2000) observed that addition of BB in OPC improved its heat resistance at least to some extent (Heikal, 2000). In Kenya, BBs are sold cheaply mainly for paving walkways or landfills which become dusty with time (Muthakia, *et al.*, 2005).

Acetylene lime sludge (ALS), sometimes referred to as calcium carbide residue (CCR), is the resultant sludge from the manufacture of acetylene gas. The process involves the reaction of calcium carbide with water as per the equation 2.12 (John, 1993)

$$CaC_2 + 2H_2O \xrightarrow{\qquad} C_2H_2 + \underset{(ALS)}{Ca(OH)_2} \qquad 2.12$$

In developing countries, ALS finds use although not to its exhaustion. In Thailand, for example, the material is disposed off in destined dumping sites after it has been sun-dried in open fields since it is produced in large amounts due to the demand for acetylene gas (Jaturapitakkul and Roongreung, 2002). In Kenya, the material is mainly sold to constructors for liming roads. When dried at appropriate temperatures, for example, at 110 °C (Muthengia, 2003), the material can be used as lime for production of lime-pozzolana cements with activated SBE, BB, RHA and an incinerated mix of RH/BB/SBE. Similar observations were made by Jaturapitakkul and Roongreung (2002) although in use with RHA.

SBE has been reported to have a substantive amount of oil and a calorific value of about 15 kJ/kg (Muthengia, 2003), a comparable value to that of RH. In light of this, Muthengia (2003) used a combination of RH and SBE to thermally activate RH, SBE and BB to make pozzolanic materials. The resultant pozzolanic material when in blend with DALS and OPC made a cementing material that met the Kenyan standard specification for Portland pozzolana cements class IV requirements in terms of compressive strength.

PCDC contains $Ca(OH)_2$ of about 15 percent by mass (Muthengia, 2003). This is in addition to the by product of hydrating Portland cement of about 20 percent by weight (Rasheeduzzafar Al-Saadoun, *et al.*, 1990). This gives a total of calcium hydroxide of about 26 percent by weight of binder (PCDC) through a conservative estimate at 45 percent by weight replacement of OPC by the test ash. This thus posses serious concern as $Ca(OH)_2$ has been mentioned severally to be a major focal point of attack by aggressive media. In addition to the vulnerability of the $Ca(OH)_2$ phase, the blending of OPC with lime increases its porosity, water permeability and vapour diffusivity (Mosquera, *et al.*, 2006) which in turn affect the durability of concrete or mortar (Baroghel, 2007).

Pulverised fuel ash (PFA) is the ash separated from the flue gas of a power station burning coal. The chemical and phase component of PFA is dependent on the burning condition and the constituent mineral associated with the burnt coal. Bituminous coal gives rise to glassy phase rich in SiO_2, Al_2O_3 and Fe_2O_3 and low in CaO while sub-bituminous coal or Lignites give ashes that are rich in CaO and mainly of crystalline phases (Taylor, 1997). PFA is a pozzolanic material that has been studied widely to improve or affect the properties of OPC in one way or the other. The main properties include workability, resistance to chemical attack, mechanical properties among them flexural or compressive strength, setting times, porosity et cetera (Ampadu and Torii, 2002; Bai, *et al.*, 2003; Camilleri, *et al.*, 2006; Poon, *et al.*, 2003; Thomas and Matthews, 2004). Camilleri *et al.* (2006) observed that utilisation of PFA in concrete reduced its radioactivity that was otherwise associated with it when damped in landfills in Malta. The effect of the PFA on the above properties is dependent on the chemical as well as physical property of the PFA (Ampadu and Torii, 2002; Poon, *et al.*, 2003). American Standard of Testing and Materials (ASTM, 2005b) C 618 broadly categorises the PFA in to two groups of class F and C based on their chemical composition, limiting their particle size and loss on ignition. But due to numerous sources of PFA from different power plants, other countries, for example Japan have developed or are developing their own standards to cover up for the gap (Ampadu and Torii, 2002).

Other potential and studied pozzolana include sugar cane baggase ash (Villar-Cociña, *et al.*, 2003), natural pozzolana as opaline rock (Luxán, *et al.*, 1989), Kenya volcanic tuff (Muthengia, 2003), diatomaceous earth (Kastis, *et al.*, 2006), ground granulated blast furnace slag (GGBS) (Barnett, *et al.*, 2006; Chang, *et al.*, 2005; Guo, *et al.*, 2007), calcined metakaolin clays are also well documented pozzolanic materials. A more recent study in Kenya, showed that a selected Kaoline-rich clays, from specified Kenyan regions, are potential pozzolana (Gathua, 2005).

Workers who recently worked on similar pozzolanic materials to the test-ash under investigation in this study are Villa-Cocinña *et al.* (2003). The workers moulded a wet combination of milled sugar cane fibres, crushed rice husks and clay material (mica-montimorillonite) (Villar-Cociña, *et al.*, 2003). To make pozolanic material, the workers heated the mixture in an electric furnace at temperature ranges of 800 to 1000 °C as compared to Muthengia (2003) who uses a self combusting system at a temperature of below 700 °C. It is therefore apparent that the test-ash might prove to be economically viable to produce as it uses no external source of energy. More so, it provides a means of waste disposal. It is therefore important to carry out test on its durability.

2.2 Portland Cement

Portland cement is made by clinkerisation of calcareous and argillaceous material at temperatures in excess of 1300 °C (Taylor, 1997). Table 2.1 summarises the general chemical composition of Portland cement (Blanks and Kennedy, 1955). The proportion may vary with the type of Portland cement manufactured.

Table 2.1: Approximate Chemical Composition of OPC

Oxide	Percent (%) w/w
CaO	60-67
SiO_2	18-26
Al_2O_3	2.5-8
Fe_2O_3	1.5-6.0
MgO	0.6-4
$Na_2O + K_2O$	0.2-1.3
SO_3	1-3

A typical Portland cement is constituted of four main phases namely tricalcium silicate (C_3S), dicalcium silicae (C_2S) [mainly present as β-polymorph], tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). The approximate composition percentage by mass of these phases is shown in table 2.2 below (Blanks and Kennedy, 1955).

Table 2.2: Approximate Phase Composition of OPC

Phase	Percent (%) w/w
C_3S	20-57
β-C_2S	20-52
C_3A	4.5-12
C_4AF	7-16

During grinding of clinker, about 5 percent gypsum ($CaSO_4.2H_2O$) by weight of cement is added to control instant hardening of cement during hydration.

Portland cement gains its strength upon hydration (Lea, 1956). Equations 2.13 – 2.15 give a summary of the hydration reactions of the main constituents of Portland cement (Czernin, 1962; Taylor, 1997)

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH \tag{2.13}$$

$$2C_2S + 4H \longrightarrow C_3S_2H_3 + CH \tag{2.14}$$

$$C_3A + 6H \longrightarrow C_3AH_6 \tag{2.15}$$

$$C_4AF + 4CH + 22H \longrightarrow C_4AH_{13} + C_4FH_{13} \tag{2.16}$$

Reaction 2.15 proceeds very rapidly besides being highly exothermic and hence cement can undergo flash set. The reaction may cause concrete crack or inhibit mass construction due to excessive heat generation. The added gypsum, $C\bar{S}H_2$, reacts with C_3A at the initial stages of cement hydration to produce ettringite, $C_6A\bar{S}_3H_{32}$, as given by equation 2.17 (Taylor, 1997)

$$3C\bar{S}H_2 + C_3A + 26H \longrightarrow C_6A\bar{S}_3H_{32} \tag{2.17}$$

The ettringite is crystallized and precipitated on the tricalcium aluminate preventing further reaction between it and water. This controls the flash set. With time, due to pressure build up, the crystal breaks exposing more C_3A and the sequence continues. After all $C\bar{S}H_2$ has been exhausted or out of contact with C_3A, the remaining C_3A reacts with $C_6A\bar{S}_3H_{32}$ and/or CH as given by equations 2.18 and 2.19 (Taylor, 1997)

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \longrightarrow 3C_4A\bar{S}H_{12} \tag{2.18}$$

and

$$C_3A + CH + 12H \longrightarrow C_4AH_{13} \tag{2.19}$$

The hydration products of C_3A and C_4AF are of no strength significance to hydrating cement.. The oxide constituents of aluminium and iron that in turn lead to formation of the C_3A and C_4AF are, however important in forming a liquid phase during clinkerisation. It is through this liquid phase (flux) that silica and lime dissolve and react at relatively lower temperatures to form the C_3S and C_2S phases. The temperature required for such a reaction without the flux would otherwise be extremely high and hence the production of Portland cement would be more expensive (Czernin, 1962).

C_3A is of great importance as a Cl^- sink when hydrated cement gets in contact with Cl^- environments. The products formed upon reaction with water are $C_3A.CaCl_2.10H_2O$, either β- or α-polymorphs depending on reaction temperature. At high temperatures, the β- polymorph dominates while the α- is preferentially formed at low temperatures. In sulphate solutions, $C_6A_2.C\overline{S}.CaCl_2.24H_2O$ exists, in which inter-layers containing Cl^- alternate with ones containing SO_4^{2-} (Taylor, 1997).

2.3 Portland Pozzolana Cement

Portland cement is blended with pozzolana mainly to improve its quality, reduce cost and manage waste. RH (Nehdi, *et al.*, 2003), a waste from rice mills, PFA from burning of coal for fuel, GGBS (Bai, 2003; Dhir, 1996), red mud from aluminium industry that is rich in iron (Pera, 1997) are all wastes that necessitate disposal. The cement industry can use such wastes including tyres and tire beads (Papakonstantinou and Tobolski, 2006). A majority of artificial pozzolana are waste products resulting from agricultural and industrial activities. The wastes preferentially have a higher proportion by mass of silica, alumina and iron which are essential components of pozzolana. Other trace constituents are alkali and alkali earth metal oxides and sulphates.

The desire to improve on the quality of Portland cement is the main reason for blending it with pozzolana. Pozzolana reacts with the resultant $Ca(OH)_2$ from cement hydration. This decreases the most prone substance, $Ca(OH)_2$, to aggressive agents like sulphates and acids (Blanks and Kennedy, 1955). $Ca(OH)_2$ is responsible for the high pH of concrete at initial stages of curing. The high pH maintains the passivity of the reinforcing steel (rebar). At later stages, the alkali oxides are responsible for the pH (Diamond, 1975) with the $Ca(OH)_2$ offering buffering action. $Ca(OH)_2$ is a phase that reacts with sulphates, carbon dioxide and magnesium-containing agents to give rise to expansive products, lowering concrete pH and hence affect the passivity of the rebar among other deleterious reactions.

The reaction of the resultant $Ca(OH)_2$ with pozzolana leads to production of more cementious material which makes the concrete less permeable, hence less prone to ingress of corrosive media. Addition of pozzolana has been shown to improve concrete resistance to sulphate attacks (Taylor, 1999) as well as chlorides permeation. This is achieved through reducing the permeability of concrete and the $Ca(OH)_2$ content. The finer particles of pozzolana park between the aggregates and cement grains thereby improving on the densification of the resultant concrete (Ampadu and Torii, 2002). By lowering chloride diffusivity, the blended cements increase the long term corrosion resistance of the mortars (Hossain and Lachemi, 2004; Page, *et al.*, 1986).

Pozzolana increases chlorides binding capacity (Dhir, 1996) and hence lowering the chances of rebar corrosion (Page, *et al.*, 1986; Thomas, 1996). The binding ability of chloride is via the pozzolana's Al_2O_3 content. The phase (Al_2O_3) has to be considered carefully if sulphate environment are to be encountered (Taylor, 1999) for they are a focal point of attack by the sulphates. Hossain and Lachemi (2004) observed that a higher level of Friedel's salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$) was formed in volcanic blended cements when compared to OPC. This in turn gave a better performance of the resultant blend in terms of reduced diffusivity, chloride ingress and passivation period of rebar (Hossain and Lachemi, 2004).

Pozzolana blended Portland cement is also known to exhibit a comparatively higher compressive strength although it is attained at a later stage of curing compared to neat OPC. This is attributed, again, to the reaction between the resultant $Ca(OH)_2$ from cement hydration and the pozzolana giving rise to additional CSH. Blended cement will show progressive increase in strength due to the slow reactivity of the pozzolana. Fly Ash has been observed to slow the hydration rate of the alite (C_3S) in the initial stages due to the Fly Ash aluminate ions presence but is later enhanced after an appreciable Ca^{2+} concentration has developed to nucleate CH and CSH on the surface of the ash grain (Halse, *et al.*, 1984). This gives rise to a lower strength at early stages but enhanced strength at later stages of curing.

Pozzolana, especially PFA, has been observed to lower the water to cement ratio (w/c) of the resultant blended cements. This has been attributed to the smooth and spherical nature of the PFA grains and decreased hydration products at the early stages (Taylor, 1997). Some pozzolanas are known to increase the w/c depending on their rheological character.

RHA and calcined SBE were observed to have a higher water demand. This is because the materials required excess water to wet, and then form workable pastes (Muthengia, 2003). The w/c ratio effect of pozzolana blended cement is important as this has a bearing on strength development which reduces as the w/c ratio increases (Taylor, 1997). w/c has also an effect on other concrete admixtures for example air-entraining agents (Taylor, 1997). A high w/c ratio is known to contribute to a higher permeability and hence antagonise the intended beneficial effect of blending the OPC. A higher water demand in concrete works is often taken care of by use of plasticizers. While blending the OPC with pozzolana, a careful consideration must be undertaken to verify both negative and positive effects of blending. Other factors that need consideration and are observed in the blended cement include dry shrinkage, setting times retardation, reduced segregation and bleeding, tensile strength and vertical cracking (Blanks and Kennedy, 1955).

Blending OPC with pozzolana has the effect of lowering the OPC content of the resultant blend. This in turn lowers the proportion of the OPC phases. Lowering C_3A phase reduces the heat of hydration of cement (Blanks and Kennedy, 1955) involved. This is important in large construction works where an enormous amount of concrete is required. Pozzolana therefore serves to reduce the phase and in most cases offer higher strengths at later stages. The phase, C_3A is also a point of focus in as far as the sulphates attack is concerned.

2.4 Degradation of Concrete

Concrete is subject to attack by corrosive agents be they physical, chemical or mechanical. The major physical cause of degradation includes abrasion, freeze and thaw. Chemical attacks may manifest themselves through corrosive environments such as chlorides, sulphates and acidic media. The attacks, which are the focus of this study, can either cause erosion and cracking of concrete, new product formation with cement hydration products or corrode the reinforcing bar, which in turn affect the durability of the concrete under consideration.

2.4.1 Sulphate attack

Attack by sulphate in concrete can either be through the SO_4^{2-} ion acting chemically or as an agent of deterioration through expansion. Sulphate and salts that convert to sulphate mainly attack the CH and CAH to form gypsum ($CaSO_4.2H_2O$) and ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$). CSH minerals are also attacked. Thaumasite ($CaSiO_3.CaCO_3.CaSO_4.15H_2O$) and MSH are formed as a result of attack on CSH which lead to loss of concrete strength. All these types of sulphate attack are dependent on conditions favourable for one product or the other to be formed. Thaumasite, for example, is much favoured by the presence of $CaCO_3$, mixing or contact water with SO_4^{2-} and low temperatures (Mingyu, *et al.*, 2006).

Mingyu, *et al.* (2006) proposed a mechanism of thaumasite formation in Yongan Dam through which $Ca(OH)_2$ react with SO_4^{2-} to form $CaSO_4.2H_2O$. The $CaSO_4.2H_2O$ in turn reacts with CSH and $CaCO_3$ (resulting from ingredient $CaCO_3$ or through carbonation of concrete) to form thaumasite. Thaumasite can also be formed through conversion from ettringite (Crammond, 2003).

Thaumasite form of sulphate attack (TSA) is more detrimental than the ettringite form of sulphate attack (ESA) as TSA can lead to even fluidizing of whole concrete mass

(Crammond, 2003) leading to white mushy non cohesive mass. This is because it involves attacking the CSH, the main source of cement strength. At least ettringite formation is limited to alumina content of cement which is not in as much proportion as CSH for TSA in OPC.

Ettringite formed during the early stages of cement curing is important in as far as fresh concrete is concerned to prevent flash set. The reaction is neither expansive nor destructive because the concrete is still elastic. More so, Hime and Mather (1999) argue that if all the reactants are from within the concrete system such a reaction leads to contraction from the reactants and products volumes point of view. But if the aluminate originates from different sources, then expansion is expected. Such sources include aluminate from CAH, monosulphoaluminate or chemically reactive alumina in pozzolana while calcium with sulphate from, for example, sodium or magnesium sulphates. The workers attributed the expansive reaction of ettringite to the reaction given in equation 2.20 (Hime and Mather, 1999)

$$6Ca^{2+} + 3SO_4^{2-} + Al_2O_6^{6-} + 32H_2O \longrightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O \qquad 2.20$$

$MgSO_4$ attacks concrete forming $Mg(OH)_2$ as per equation 2.21

$$MgSO_4 + Ca(OH)_2 + 2H_2O \longrightarrow CaSO_4.2H_2O + Mg(OH)_2 \qquad 2.21$$

The insoluble $Mg(OH)_2$ tends to offer protection to concrete only at early stages (Türker, *et al.*, 1997) and the resultant gypsum may not be expansive. But when the resultant $CaSO_4.2H_2O$ (equation 2.21) reacts with aluminate hydrate (Hime and Mather, 1999), then magnesium sulphate can cause damage because the resultant ettringite is expansive. The situation is worsened because reaction 2.21 leads to loss of concrete alkalinity (OH^-) as $Mg(OH)_2$ precipitates out and consequently, the CSH disintegrates to replenish it (Hime and Mather, 1999). This leads to loss of concrete strength. Furthermore, the resultant $Mg(OH)_2$ reacts with silicate hydrates giving rise to MSH (Mather, 1968) that has no cementious properties.

Salt crystallisation of $MgSO_4$ and Na_2SO_4 are deleterious in concrete. The salts cause a build up of osmotic pressure or large crystals that cause disruption of concrete. Hydration, dehydration and finally rehydration builds up these salts in concrete (like salt crystallisation). The processes also lead to expansion of the salts thereby destroying the concrete. Hydration of thenardite (Na_2SO_4) to mirabilite ($Na_2SO_4.10H_2O$), for example, is a very expansive process (Hime and Mather, 1999).

$C\overline{S}H_2$ resulting from the reaction of either sodium or magnesium sulphates with calcium hydroxide can consequently react with monosulfoaluminate or aluminates to form the expansive ettringite as shown in equations 2.22 and 2.23 (Al-Amoudi and Maslehuddin, 1993; Mather, 1968)

$$C_4A\overline{S}H_{12} + 2C\overline{S}H_2 + 16H \longrightarrow C_6A\overline{S}_3H_{32} \qquad 2.22$$

$$C_4AH_{13} + 3C\overline{S}H_2 + 14H \longrightarrow C_6A\overline{S}_3H_{32} + CH \qquad 2.23$$

Concrete deterioration can be prevented by reducing chances of cement being in contact with aggressive environment. But this is practically unattainable and, if so, only for a short period. Sulphate attack has been combated by using cements with low C_3A but this has never been the ultimate solution to sulphate attack. This only helps to address problems of ettringite as a result of attack by $CaSO_4$ and may be helpful in chances of Na_2SO_4 ($N\overline{S}$) leading to gypsum. Reducing C_3A implies a higher content of the C_3S and C_2S and thus a higher CH content upon hydration. CH again is prone to $N\overline{S}$ attack leading to $C\overline{S}H_2$ formation. Reduction of C_3A may not be effective in curbing attack of CSH or CH by $MgSO_4$ (Mehta, 1993). Low permeability and a low w/c have also been cited and applied as means of curbing the attack. This is mainly attributed to reduction in porosity and therefore reduction in diffusivity of sulphates into the concrete. Blending cement with pozzolana lowers permeability, but the pozzolana must have a low alumina content (Taylor, 1999). Pozzolana is also known to react with the $Ca(OH)_2$ thereby lowering concrete pH and hence affecting the formation of ettringite that is favoured by high pH, hence less expansion from ettringite if any (Al-Amoudi and Maslehuddin, 1993; Mather, 1968). A low w/c ratio has been reported to be a problem when $MgSO_4$ attacks the concrete. This is because with a low w/c, there would be no space to accommodate expansive $M\overline{S}H$ or gypsum (Al-Amoudi, 2002) and hence more deleterious effect of $MgSO_4$ in this case. Al-Amoudi (2002) observed that with low w/c, the deterioration was just on the concrete surface as the rebar at high depth of cover in the mortar in the worker's research did not show evidence of corrosion.

Ammonium sulphate, $(NH_4)_2SO_4$, attacks concrete through the reaction with $Ca(OH)_2$ forming expansive $CaSO_4.2H_2O$ and the highly soluble NH_4OH. The resultant NH_4OH can easily leave the concrete. This causes a decline in concrete pore pH. This can result in disintegration of the CSH to replenish the $Ca(OH)_2$ and hence a loss in concrete strength as observed with the case of $MgSO_4$ attack . The reaction involved is shown in equation 2.24 (Barnes, 1983)

$$Ca(OH)_2 + (NH_4)_2SO_4 + 2H_2O \longrightarrow CaSO_4.2H_2O + 2NH_4OH \qquad 2.24$$

Generally sulphate attacks are associated with expansion, loss of concrete strength and lowering of pH. The accompanying cation dictates the secondary effects of sulphates. Magnesium, for example, as accompanying ion of the sulphates has been shown to be associated with loss of concrete strength due to attack on CSH as compared to calcium sulphate, which mainly leads to expansive effects. The products formed from the primary sulphates also define the sulphates effects. Formation of NH_4OH or $Mg(OH)_2$, for example, leads to lowering of concrete pH as well as disintegration of CSH.

2.4.2 Carbonation

Carbonation is the process through which atmospheric carbon dioxide reacts with the cement hydration product in presence of water or moisture. Carbon dioxide can ingress the concrete via the pores or be transported through the ingressive solutions that diffuse or are absorbed into the concrete. Dry carbon dioxide is of no deleterious effect but in presence of moisture, it reacts with the pore OH^- and Ca^{2+} from the pore water or the CSH forming the $CaCO_3$ as shown in equations 2.25 – 2.28 (Hewlet, 1998)

$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad 2.25$$

$$H_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O \qquad 2.26$$

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2 \qquad 2.27$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O \qquad 2.28$$

It is apparent that some CO_2 will be required to keep the $Ca(HCO_3)_2$ in solution (equation 2.27) otherwise the reverse of the reaction takes place and $CaCO_3$ is precipitated until some CO_2 is availed to shift the equilibrium to the right. In light of this, aggressive CO_2 (CO_2^A or $\check{C}^A$) in cement is therefore defined as the CO_2 in excess of amount required to keep the $CH\check{C}_2$ [$CaO.H_2O.2CO_2$ or $Ca(HCO_3)_2$] in solution. The Carbon dioxide required to keep the $Ca(HCO_3)_2$ in solution is referred to as the stabilising carbon dioxide ($\check{C}^S$) (Collett, *et al.*, 2004). The amount of $\check{C}^A$ is dependent on the amount of $Ca(HCO_3)_2$ and also to some extent the pH of the solution and the accompanying cation if it varies from calcium (Hewlet, 1998). The $\check{C}^A$ is also affected by presence of other salts of calcium for example gypsum. This lowers it for a given content of CO_2. CO_2 dissolved in sea water can be beneficial to cement due to formation of protective coatings of the carbonates. In severe conditions, which may be accompanied by higher amounts of dissolved CO_2 for example in estuaries, the effects are deleterious since carbonic water is more acidic in seawater than fresh water. This is worsened by the decaying organic matter releasing CO_2 (Hewlet, 1998).

The attack by CO_2 precipitates Ca^{2+} (as $CaCO_3$) from $Ca(OH)_2$ causing disintegration of the CSH to replenish the $Ca(OH)_2$ as well as lowering the pore solution pH (Taylor, 1997). This again increases the chances of corrosion of the reinforcement if present as well as loss of concrete strength and durability. Carbonation has also been sited as a prevalent condition favourable for thaumasite formation (Collett, *et al.*, 2004; Mingyu, *et al.*, 2006) at low temperatures if the concrete is in contact with sulphates. Taylor (1997) observed that carbonation may be beneficial under certain circumstances where it improves compressive strength and decreases porosity. He attributed this to the precipitation of the resultant $CaCO_3$ from the carbonation process.

2.4.3 Alkali Aggregate Reactions (AAR)

AAR comprises of the series of reactions involving alkalis, sodium and potassium, in concrete or mortar, with some reactive aggregates (García, *et al.*, 2007). These types of reactions include (Oberholster, *et al.*, 1983)

I. Alkali-silica reaction: This is the reaction between the alkalis and active aggregates containing amorphous and metastable silica. The reaction is rapidly expansive

II. Alkali-siliceous rock reaction: This is the reaction between alkalis and rocks containing constituents of chalcedony, cryptocrystalline silica and strained quartz (García, *et al.*, 2007). The reaction is slowly expansive

III. Alkali-carbonate rock reaction involves the reaction between the alkalis and carbonate rocks for example argillaceous and dolomite limestone. The reaction varies from slow to rapidly expansive depending on the type of rock.

The AAR have been reduced mainly by a controlled inclusion of reactive aggregates, use of low alkali cement, control of voids in mortar through use of air entraining agents for example, as well as substitution of OPC with pozzolana (Bektas, *et al.*, 2004; García, *et al.*, 2007; Shehata and Thomas, 2002). The AAR reaction proceeds immediately after mixing the aggregates and cement with water and the short period of hours thereafter. It involves formation of highly caustic solution from solubilization of the alkalis owing to their high solubility. The highly caustic solution reacts with the reactive aggregates, rocks or carbonates forming gels at a rate dependent on the reactivity of the aggregates. As these gels absorb water, they swell and build up osmotic pressure. Finally they may rapture the paste surrounding the reactive particle. This in turn acts as a reservoir for the accumulation of gels and the process of building, hydrating and rapture of gels continues (Blanks and Kennedy, 1955). The result is swelling and micro-cracking of cement paste and aggregates. The damage can manifest itself in a variety of forms, from typical non-oriented surface cracking to highly oriented cracks (Saint - Pierre, *et al.*, 2007).

2.4.4 Chlorides Attack

Chlorides are made available into the concrete through contact water that has chlorides, for example brackish water, seawater and industrial effluents. They can also be introduced into the concrete through mixing waters. Chlorides will ingress into the concrete in a similar manner as other pollutants. This is mainly through diffusion in the pore water, adsorption (and desorption) onto the pore walls, and hydrodynamic dispersion and convection due to flow of the pore water (Johannesson, 1997). Adsorption occurs in concrete layers exposed to wet and dry cycles and is mainly limited to the 10 - 20 mm of the concrete surface. They can as well ingress and be transported into the concrete through capillary action via cracks and continuous pores except in saturated concrete material (Taylor, 1997). The rate of ingress of chloride is dependent on the cement type, especially on its chloride binding ability. OPC tends to have higher chloride ingress than blended cements. Blended cements, for example pozzolana based, are less permeable due to increased cementious material from the reaction between the included pozzolana and $Ca(OH)_2$ resulting from hydration of cement (Yiğiter, *et al.*, 2007). Blended cements have also exhibited higher binding ability of chlorides, because of the proportionate amount of alumina if it forms part of the reactive phase, and hence decrease chloride diffusion (Luo, *et al.*, 2003).

Chlorides remain in pore solution though they are partly bound by alumina via the formation of Friedel's salts (Pruckner and Gjørv, 2004) as shown in equations 2.29 and 2.30

$$CaCl_2 + 3CaO.Al_2O_3.6H_2O + 4H_2O \longrightarrow 3CaO.Al_2O_3.CaCl_2.10H_2O \qquad 2.29$$

Or

$$2NaCl + 3CaO.Al_2O_3.6H_2O + Ca(OH)_2 + 4H_2O \longrightarrow 3CaO.Al_2O_3.CaCl_2.10H_2O + 2NaOH \qquad 2.30$$

Chloride diffusivity is dependent on the balancing cation involved (Taylor, 1997). Ca^{2+} and Mg^{2+}, for example, show higher diffusion coefficients than with Na^{+}. This is because NaCl has first to react with $Ca(OH)_2$ to form $CaCl_2$. The resultant $CaCl_2$ then reacts with the aluminate phase (Arya, *et al.*, 1990) (c/f equation 2.29 and 2.30). Gjørv and Vennesland (1979) observed that although w/c ratio may affect the permeability of chlorides into concrete, the effect was only significant for a short period of exposure. They observed that, for a lengthy period of exposure, and in the bulk of the concrete, the effect was minimal. Similar observations were made by Yiğiter, *et al.* (2007) but working with blast furnace slag cements. The workers (Yiğiter, *et al.*, 2007) observed significant effects in OPC where chloride penetration increased with increase in w/c. Gjørv and Vennesland (1979) reported that the permeation had more to do with the property of the concrete and exchange anion. Pozzolana blended cements exhibit low permeability, lower OH^- concentration in the pore water and thus offers less exchange ion for the Cl^- hence low diffusivity of chloride ions (GjØrv and Vennesland, 1979). Furthermore, ingress of chlorides activates rehydration of residual cement as well as enhancing pozzolanic reaction. This makes the concrete denser thus lowering chloride diffusivity (Bai, *et al.*, 2003; Yiğiter, *et al.*, 2007).

Binding ability of chlorides by cements may be reduced by presence of sulphates. This is due to preferential reactions between sulphates and the alumina phases in cement (Calleja, 1980). Chlorides, especially from NaCl, have also been found to cause an increase in pH (Pruckner and Gjørv, 2004) as OH^- are released into solution to counter the anions removed in form of insoluble complex salts. This may result in higher chances of alkali aggregate reaction due to the high pH (Holden, *et al.*, 1983).

The diffusion of chloride in concrete is approximated from solution to Fick's second law (Crank, 1975) under non – steady state conditions assuming boundary conditions $C_{(x,t)} = 0$ at $t=0$, $0<x<\infty$, $C_{(x,t)} = C_s$ at $x=0$, $0<t<\infty$, constant effects of co-existing ions, linear chloride binding, one-dimensional diffusion into semi-infinite solid. The equation is given as 2.31 (Luping and Gulikers, 2007)

$$C_{(x,t)} = C_s\left[1 - erf\left(\frac{x}{\sqrt{4D_{app}t}}\right)\right] \qquad 2.31$$

Where

$C_{(x,t)}$ is concentration of Cl^- at any depth x in the concrete bulk at time t

C_s is the surface concentration

D_{app} is the apparent diffusion coefficient and

$$erf(Z) = \frac{2}{\sqrt{\pi}} \int_0^{Z} e^{-t^2}\, dt \qquad 2.32$$

Equation 2.31 has been used mainly to describe mathematically the experimental profiles of chloride concentration found in non-steady state laboratory test or from structures exposed in the field. By fitting the equation to experimentally-determined chloride profile concentrations, the D_{app} and C_s are determined mathematically (Collepardi, *et al.*, 1972). The D_{app} ranges from 10^{-11} to 10^{-13} m^2/s depending on the concrete under consideration (Bertolini, *et al.*, 2004). D_{app} and C_s can be used to predict the penetration of chloride over a long period of time.

Several chemical interactions between chloride and the cement constituents, do affect the chloride diffusion into the concrete or mortar bulk. The diffusion is also dependent on several parameters for example, concrete age, temperature, relative humidity, chloride binding capacity, convectional flow of chlorides and exposure conditions (Oh and Jang, 2007). Corrective terms are, therefore, usually applied to the simplified error function model to give the so called 'modified model' when calculating the diffusion coefficients (Bertolini, *et al.*, 2004; Luping and Gulikers, 2007; Nokken, *et al.*, 2006; Oh and Jang, 2007). When a corrective term is not applied, the approximation by the equation 2.31 yields the apparent diffusion coefficient, D_{app}. The corrective term is dependent on the type and property of cement. Luping and Gulikers (2007) found out that the simplified error function to Crank's solution gave a good approximation comparable to the modified models for OPC under ten years. The workers (Luping and Gulikers, 2007) observed that simplified model underestimated chloride penetration in PFA blended cements. Despite these shortcomings, the simplified error function model has been used by many engineers in predicting chloride penetrations and diffusion coefficients (Bertolini, *et al.*, 2004; Luping and Gulikers, 2007). Equation 2.31 was similarly used in this study to approximate the diffusion coefficients of the different cement categories.

Generally, Chlorides have no effect on the calcium silicate hydrates of cement although the accompanying cation may have (Barberon, *et al.*, 2005). They have only been shown to interact with the alumina content of cement. It is widely documented that chloride is extremely harmful to the reinforcement bar beyond certain critical threshold concentration where it induces pitting and propagates corrosion of the rebar (Alonso, *et al.*, 2000; Arya, *et al.*, 1990; Yeau and Kim, 2005).

2.4.5 Pure, Soft and Sea Water

Pure or soft water is expected mainly to dissolve $Ca(OH)_2$ from the cement bulk. This is followed by disintegration of the silicate hydrates to replenish the CH dissolved off. The extent and rate of damage is dependent on the rate of percolation of water into/out of the cement paste. Flowing water is known to cause severe damage as the concentration changes and flow cause physical damage as well. This makes rain water an aggressive agent. This explains why most concrete roofs have to be treated with protective coatings.

Soft water is also expected to be corrosive owing to dissolution of the atmospheric carbon dioxide giving rise to the more corrosive carbonic acid (Taylor, 1997). The carbonic water initially attacks $Ca(OH)_2$ forming the $CaCO_3$ as shown by equation 2.33 (Barnes, 1983)

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \qquad 2.33$$

The $CaCO_3$ dissolves slowly owing to formation bicarbonates as shown (see equation 2.27). This then follows the sequence of carbonation.

Water can also cause leaching of other cement constituents, mainly as ions, due to concentration gradient between the cement bulk and the water. This initiates dissolution of the CH, followed by the monosulphates, ettringite and finally the calcium silicate hydrates. This leaves an amorphous mass of silica with traces of calcium and aluminium ions (Adenot, 1992; Gérard, 1995). The mass has no cementitious value. Other workers (Long, *et al.*, 1998) while studying the hydration of C_3S in water, observed Ca^{2+} in the water confirming the leaching ability of water.

When concrete is exposed to seawater, it is subject to various forms of attack. These include physical in terms of freeze-thaw, salt weathering (exfoliation) and abrasion due to suspended sand. Chemical attack is manifested through the ingress Cl^- and SO_4^{2-} and subsequent reaction with hydration products of the cement (O'Farrel, *et al.*, 2000). Seawater contains variable amounts of salts of Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, SO_4^{2-} and other ions depending on the region of consideration. Standard seawater has the constituents shown in table 2.3 (ASTM, 2005c).

Table 2.3: Main Chemical Constituents of Sea Water

Constituent	g/l
$NaCl$	24.53
$MgCl_2$	5.20
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.695
$NaHCO_3$	0.201
KBr	0.101
H_3BO_3	0.027
$SrCl_2$	0.025
NaF	0.003
Chlorinity	19.38

Concrete damage through seawater is mainly dependent on submerged level, seawater flow or turbulence, tidal range as well as the physical and chemical properties of concrete (Wilkins and Lawrence, 1983). Concrete that has been fully submerged suffers very low corrosion of the rebar due to insufficient oxygen availability, but insufficiency of oxygen may also make it impossible to maintain the passive film. Corrosion potentials may be in the range of -800 to -1100 mV (silver/silver chloride electrode). The corrosion rates are much suppressed due to limited rate of oxygen reduction and spread over large surface area of the rebar (Wilkins and Lawrence, 1983).

Chemical attack is mainly manifested in the form of carbonation, sulphate and chloride ingress as well as leaching and intake of cations from sea water. The severity due to the separated aggressive ions varies compared to their mix in sea water. The formation of a protective layer that develops as a result of combined action of Mg^{2+} and HCO_3^- as well as the $CaCO_3$ (as aragonite not calcite due to Mg^{2+} ions) (Taylor, 1997) reduces the ingress of corrosive agents. The effects of sulphate attack to formation of expansive ettringite, for example, are reduced in sea water as chlorides lower the expansive potential of the ettringite. The expansive effect is also reduced due to consumption of a portion of the C_3A by the chlorides in the formation of Friedel's salt (Santhanam, *et al.*, 2006). In the same manner, the chloride binding ability of concrete subjected to sea water is lowered as there is preferential reaction of the sulphates with the chloride binding C_3A. More so, the presence of other ions, for example Na^+, K^+ which ingress into concrete together with SO_4^{2-} are known to enhance pozzolanic reaction as well as rehydration of residual cement which may change the matrix of the involved concrete (Guerrero, 2000; Lorenzo, 2003; Shi and Day, 2000).

The loss of strength due to cracks as a result of formation of expansive products, erosion of concrete materials due to turbulent waters and corrosion of rebar are severe damages that can result in concrete exposed to seawater especially in tidal zones. Tidal zones create scenarios of wet and dry seasons that helps build the salt concentration in the bulk of cement. This may be accompanied by osmotic pressure builds up which lead to concrete cracking or enhanced diffusivity of the salts due to crystallisation and hence concentrations build up (Oberholster, *et al.*, 1983). Pozzolana-based Portland cements have been recommended mainly for use in these corrosive environment among other cements (GjØrv and Vennesland, 1979; Memon, *et al.*, 2002; O'Farrel, *et al.*, 2000; Yiğiter, *et al.*, 2007) but they do have their limitations due to the harshness of the sea water.

2.5 Transport Process in Concrete or Mortar

Gases and fluids, for example carbon dioxide, oxygen and water ingress concrete and cause chemical and physical deterioration including corroding the reinforcement. The ingress of these substances is dependent on the permeability of the concrete or mortar. The process of ingress involves several mechanisms. The mechanisms include capillary suction, convection, permeation, diffusion and migration (Bertolini, *et al.*, 2004).

Capillary suction happens due to capillary action inside the cement paste capillaries. When water comes into contact with a porous material such as concrete, the concrete imbibes the water due to under-pressure in the pores caused by the capillary suction (Hooton and Hong, 1999). A more porous concrete absorbs more water, although the smaller the pore dimension the stronger the capillary action but the transport becomes slower with decreasing pore size due to friction (Bertolini, *et al.*, 2004).

The movement of the fluids and gases due to pressure gradient is referred to as permeation. Permeability in concrete increases with capillary porosity, which is dependent on w/c ratio. Migration as a transport process in concrete is caused by electrical potential difference. The migration of ions, for example Cl^-or Na^+, is similar to transport of the same in bulk solution. The difference arises because in concrete ions can only be transported through interconnected water-filled pores which may involve the ions to move a longer distance than would be in bulk solution. This is so because the pores are for one not always interconnected or straight as would have been in a bulk solution. Due to this, even in water-saturated cement based materials, the ion transport is some orders of magnitude lower compared to bulk solution (Luping and Gulikers, 2007). Ion migration plays an important role especially in rebar corrosion

Diffusion is caused by concentration gradient. CO_2, Cl^- and other ions ingress concrete and mortar through the pore solution on concrete/ mortar surface where they are present in high concentration to internal zones where their concentration is lower. The diffusion of Cl^- and SO_4^{2-} is rapid in water-filled pores as opposed to gases that do so in open pores.

2.6 Corrosion

Corrosion is a freely spontaneous reaction upon metal and its environment that tends to revert the metal into its natural or similar chemical nature as its original ore. It has thus been defined as extractive metallurgy in reverse (Jones, 1996). This is illustrated in figure 2.1 (Cotta, 2007).

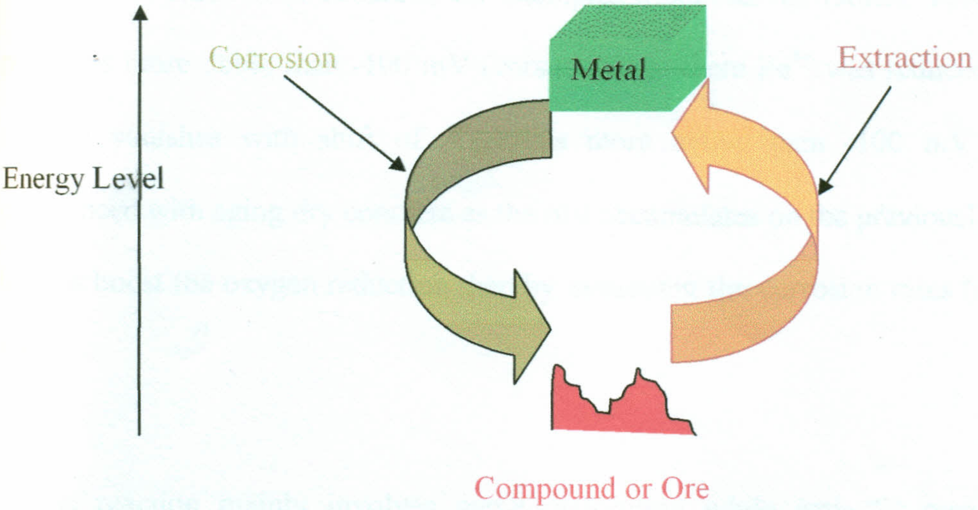

Figure 2.1: An Illustrative diagram for Corrosion – Extraction Processes of a metal (modified)

2.6.1 Electrochemistry and Corrosion

Corrosion involves cathodic and anodic reactions that take place on the same electrode. The anodic reaction and cathodic reactions can separately be represented by equations 2.34 and 2.35 respectively

$$M \longrightarrow M^{n+} + ne \qquad 2.34$$

$$Z + ne \longrightarrow Z^{n-} \qquad 2.35$$

Equation 2.34 represents metal dissolution while 2.35 involves reduction of electrolytic species if the reaction occurs in electrolytic media, dissolved oxygen in neutral or acidic media or water. In some instances reduction of high oxidation state of cations (Jones, 1996) can also occur as shown by equation 2.36.

$$M^{n+} + (n-m)e \longrightarrow M^{m+} \qquad 2.36$$

This type of reaction in concrete, for example, was observed (Jones, 1996) to occur at potentials more noble than -100 mV (versus SCE) where Fe^{3+} was reduced to Fe^{2+}. The reaction vanishes with shift of potentials more active than -100 mV (SCE). It is pronounced with aging dry concrete as the rust accumulates on the previously anodic sites. It helps boost the oxygen reduction thereby increasing the corrosion rates (Alonso, *et al.*, 1998).

Anodic reaction mainly involves metal dissolution while cathodic reaction is much dependent on the prevalent conditions. In an aqueous media, for example, where metal dissolution is the anodic reaction, the cathodic reaction may involve the reactions given by equations 2.37 and 2.38

$$2H^+ + 2e \longrightarrow H_2 \qquad 2.37$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad 2.38$$

These reactions take place at potentials more active than $E^{\theta}_{H^+/H_2}$ (SHE) and involve hydrogen evolution. At more noble potentials, reactions 2.39 and 2.40 are involved

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O \qquad 2.39$$

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^- \qquad 2.40$$

At more noble potentials than $E^{\theta}_{O_2/H_2O}$ (SHE), water is oxidised to oxygen (oxygen evolution) (Jones, 1996) to give the anodic reaction. The reaction involved is 2.39 but while proceeding in the left hand side.

The reactions and the exact species formed are dependent on pH and potentials as well as the equilibrium conditions. Pourbaix (1966), for example, established equilibrium between the various components of many water/metal systems in terms of potential and pH of which the results are represented in potential – pH diagrams (Pourbaix, 1966). Figure 2.2 is such an illustration of Fe/water system (Wolynec, 2003).

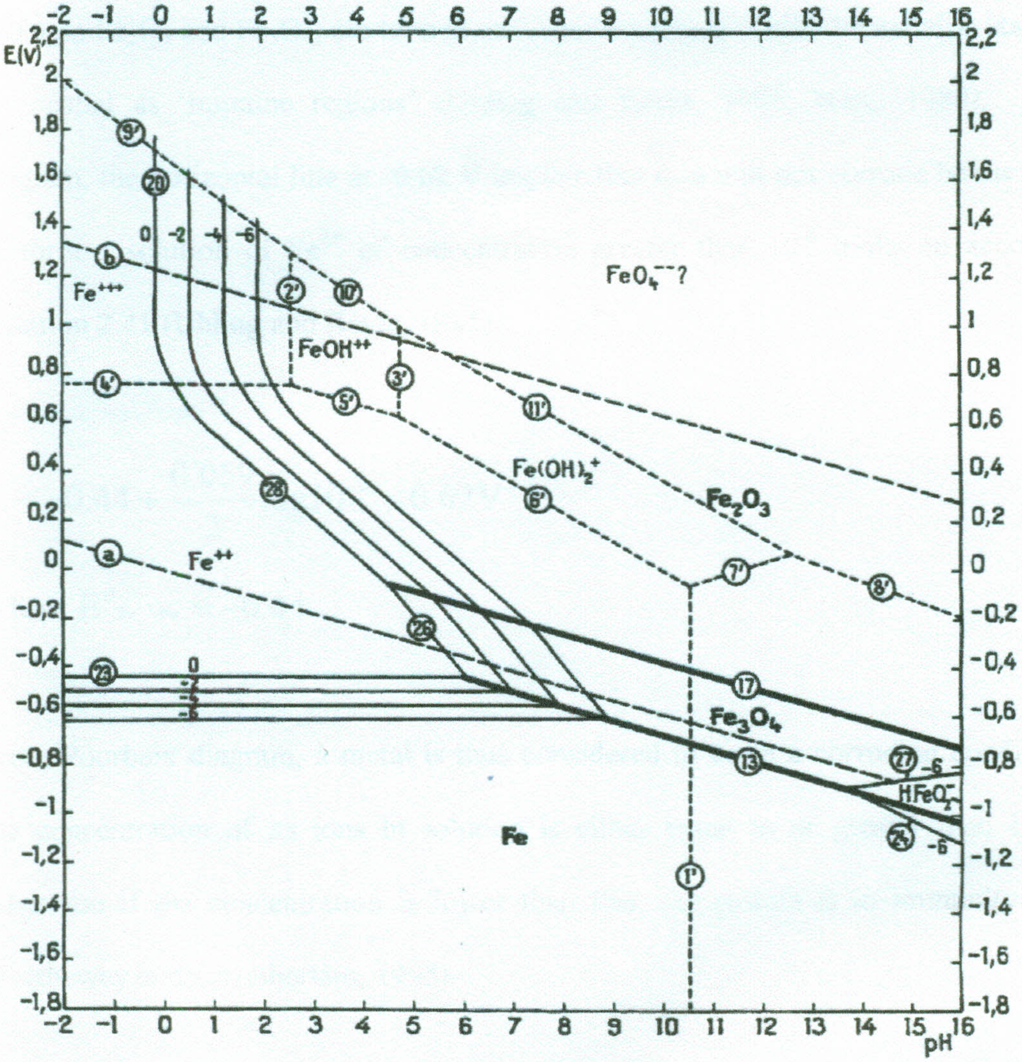

Figure 2.2: Potential – pH Equilibrium Diagrams for the Iron-Water systems at 25 °C.

The diagram shows general state of thermodynamic behaviour with no kinetics or rates of reactions. The lines a and b are the usual H_2 and O_2 evolution. The diagram indicates the experimental conditions of potential (versus SHE) and pH for which iron, its various solvated ions and oxides are stable at 25 °C. The stability region of $Fe^{2+}_{(aq)}$ for example, is bound by two horizontal lines representing the equilibrium between $Fe_{(s)}/Fe^{2+}$ and Fe^{2+}/Fe^{3+}, two sloping lines representing $Fe^{2+}/FeOH^{2+}$ and $Fe^{2+}/Fe(OH)_2^{+}$, and a vertical line representing Fe^{2+}/Fe_3O_4 (West, 1980). The diagram can also be used to deduce regions of corrosion behaviour. The region corresponding to stable ionic state, for example Fe^{2+} and Fe^{3+}, are referred to as 'corrosion regions', those corresponding to passivating films, for example Fe_2O_3 and Fe_3O_4, are termed as 'passive regions' while the metallic state, Fe, are designated as 'immune regions' (Uhling and Revie, 1985; West, 1980). From the diagram, the horizontal line at -0.62 V implies that iron will not corrode below this value to form a solution of Fe^{2+} of concentration greater than 10^{-6} molar in accordance to equation 2.41 (Uhling and Revie, 1985)

$$E = -0.44 + \frac{0.059}{2}\log 10^{-6} = 0.62V \qquad 2.41$$

Where $E^{\theta}_{Fe^{+2}/Fe} = -0.44$

From Pourbaix diagram, a metal is thus considered to be in a corroding condition when the concentration of its ions in solution is either equal to or greater than 10^{-6} molar, otherwise if the concentration is lower than this, the system is in immunity condition (Trethewey and Chamberlain, 1995).

2.6.2 Rebar Corrosion Electrochemistry

Properly designed, constructed and maintained concrete structures are expected to yield the natural service life, that is the expected serviceability life of a structure (Ahmad, 2003). This is because the rebar, which usually leads to collapse of reinforced concrete if attacked; is usually protected against corrosion due to the high alkalinity of concrete, of pH > 12. At the high pH, the rebar is in a passive state (Verbeck, 1975), with negligible corrosion rates. The protective layer is a film of the gamma ferric oxides (γ-Fe_2O_3), iron oxide hydroxide ($FeO(OH)$) and magnetite (Fe_3O_4) which prevent Fe^{2+} from entering into the solution as well as oxygen from diffusing to the steel surface (Al-Amoudi and Maslehuddin, 1993). The layer has also been found to be rich in lime with inclusions of C-S-H gel (Leek and Poole, 1990; Page, 1975). The high electric resistivity of concrete is also another aspect that helps in corrosion resistance of the rebar. This acts by reducing the flow of current between the cathodic and anodic sites of the rebar.

Corrosion of the rebar leads to concrete fracture through cracking, loss of bond strength between concrete and rebar, reduction of rebar cross-section area, loss of strength, delamination and spalling of concrete cover and therefore loss of concrete serviceability life (Cabrera, 1996; Fang, *et al.*, 2006; Zhang and Lounis, 2006). A good example of concrete cracking due to rebar corrosion is shown in plate 2.1.

Plate 2.1: Concrete Cracking due to Rebar Corrosion Products. Picture of a Grilled Concrete Wall of the Simon Building Corridor of the University of Manchester

The plate shows cracks that have brownish depositions indicating that there was corrosion of the rebar. The concrete crack may therefore be attributed to the expansive corrosion products of iron oxides. The crack could not be associated with expansive products of the concrete or ingressive agents. This is because the regions surrounding it did not show signs of cleavage.

Several factors can lead to corrosion initiation and propagation of the rebar, and the metal passage from passive to active state of corrosion. These include lowering of the pH either due to carbonation, acid or acid-like attacks. Chloride attack also initiates and propagates pitting type of corrosion. Internal sources of impurities, for example from the aggregates, can also cause corrosion. External factors that may propagate corrosion of the rebar once initiated include the environmental constituent mainly oxygen, humidity, temperature fluctuations, bacterial attack et cetera. Stray current, current that follows paths other than intended circuit, is also known to cause rebar corrosion. They mainly originate from electric-powered railway lines, electric welding machines et cetera. If currents of this kind enter a metallic structure, they cause corrosion at the areas where they enter soil or water (Uhling and Revie, 1985). Anaerobic bacteria reduce inorganic sulphates to sulphides in presence of hydrogen or organic matter. In this process, the bacteria are aided by the presence of iron surface where hydrogen is adsorbed (Uhling and Revie, 1985). In the process, iron is oxidised to Fe^{2+} and FeS hence corrosion of the metal.

Hardened or hardening cement paste will contain gel pores and capillary pores whose dimensions are particularly dependent on the w/c ratio. Gel pores, which constitute about 20- 30 percent by volume of hardened paste and are of about 2.5 mm in diameter, develop from shrinkage of hardening paste. They are non-continuous and thus do not act as en-route for entry of aggressive solution or gas into the concrete. On the other hand, capillary cavities which are continuous but smaller than the gel pore (about 1 – 10 μm diameter) and constituting a lower percentage by volume of hardened paste (about 1 – 10 percent) act as entry points for the corrosive agents (Biczok, 1967; Locke, 1982). Capillary cavities develop as a result of evaporation of excess, unbound water and thus they are dependent on the w/c ratio.

In ordinary reinforced concrete, the pore water behaves as the electrolyte while the rebar (Fe) behaves as the anode undergoing chemical dissolution (Bazant, 1979). The prevalent type of reaction is dependent on pH, presence of aggressive anion and the electrode potential of the rebar (Ahmad, 2003). The anodic reactions involved can be summarised as given by equations 2.42 – 2.45 (Ahmad, 2003)

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 8e + 8H^+ \qquad 2.42$$

$$2Fe + 3H_2O \longrightarrow Fe_2O_3 + 6H^+ + 6e \qquad 2.43$$

$$Fe + 2H_2O \longrightarrow HFeO_2^- + 3H^+ + 2e \qquad 2.44$$

$$Fe \longrightarrow Fe^{2+} + 2e \qquad 2.45$$

The cathode reactions are more dependent on oxygen availability, rebar potential and the pH. The possible reactions include 2.37 and 2.40 above. Reaction 2.37 is even more dangerous because it induces pressure build up due to the gas evolved as well as hydrogen embrittlement (Hope and Alan, 1993). The occurrence of this reaction is minimal due to the potential and pH of the concrete being too high, but may occur in cathodically protected rebars.

When reinforced concrete comes into contact with chlorides at levels beyond certain critical conditions, pitting corrosion ensues. Pitting is a form of localized corrosion in which small pit/holes result in the corroding metal surface. Corrosion occurs in these pits but not on the entire surface of the metal. The process is autocatalytic as it produces conditions that are both stimulating and necessary for its continuity. In an aerated chloride solution, at certain critical [Cl$^-$] threshold, the chlorides cause dissolution of the protective layer of the oxides of iron (Fontana, 1987) and thus dissolution of the metal in the pit. This creates charge difference, as a result of excess positive metal ions, forcing Cl$^-$ ions to rapidly migrate into the pit giving rise to metal chloride. This reactions involved are given in equations 2.46 – 2.48

$$Fe(OH)_2 + 2Cl^- \longrightarrow FeCl_2 + 2OH^- \qquad 2.46$$

$$Fe(OH)_3 + 3Cl^- \longrightarrow FeCl_3 + 3OH^- \qquad 2.47$$

$$Fe_2O_3 + 6Cl^- + 3H_2O \longrightarrow 2FeCl_3 + 6OH^- \qquad 2.48$$

The resultant metal chloride undergoes hydrolysis, as shown in equation 2.49, consequently causing a build up of the hydrogen and chloride ions that stimulate dissolution of the metal.

$$FeCl_n + nH_2O \longrightarrow Fe(OH)_n + nHCl \qquad 2.49$$

Where n = 2 or 3 depending on the oxidation state of Fe.

Iron hydroxide is a weak base to neutralise such a strong acid as HCl (Jones, 1996). This leads to the suggested low pH in the pit. Since there is limited dissolution of oxygen in the pit solution, the cathodic reduction of dissolved oxygen on the metal surface adjacent to the pit sustains the pit growth (Fontana, 1987). The cathodic site, the metal surface, is very large compared to the pit size, and this makes the pit grow at a fast and an ever increasing rate.

The presence of chlorides in solution or in concrete will always tend to modify the anodic behaviour of steel as shown in figure 2.3. This reduces the passivity range from as much as +600mV to values sometimes below -500 mV (SCE). As the concentration of chlorides increase, the passivation phase fades and the E_{pit} drastically drops (Bertolini, *et al.*, 2004).

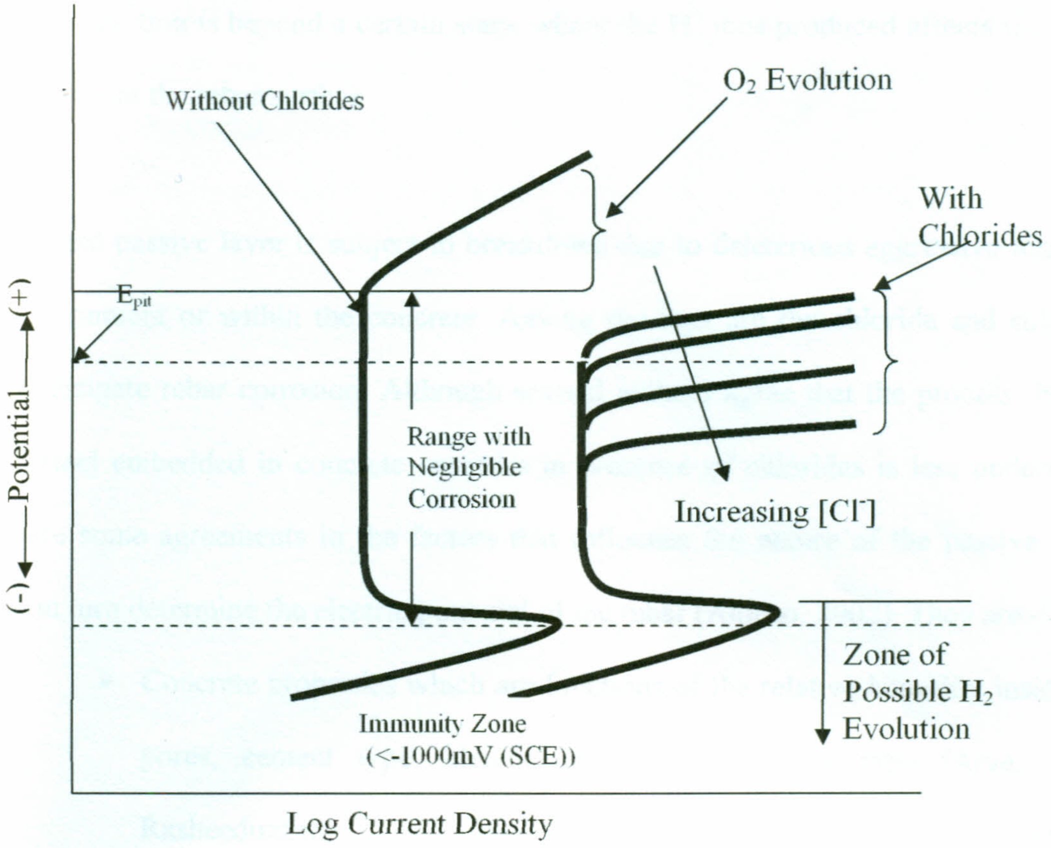

Figure 2.3: Anodic polarisation for steel in chlorides contaminated media (≈ -1 to 0.4 V versus SCE) (Modified)

In the potential range between equilibrium and -800 mV (SCE), the anodic dissolution rates are negligibly low due to proximity to equilibrium and hence the corrosion rates are negligible. Rebar at this potential range is said to have a quasi-immunity. Above + 600 mV (SCE), the oxygen evolution, equation 2.50, becomes the anodic reaction hence the rebar does not corrode (Bertolini, *et al.*, 2004).

$$2H_2O \xrightarrow{\hspace{3cm}} O_2 + 4H^+ + 4e \qquad 2.50$$

This potential is highly unachievable in a normal state unless under stray current influence or under other external polarization. The rebar can only corrode if the resultant oxygen evolution reaction is beyond a certain stage where the H^+ ions produced affects the pH of the concrete at the rebar surface

The formed passive layer is subject to breakdown due to deleterious aggressive ion from the environment or within the concrete. Among the ions are the chloride and sulphate, which instigate rebar corrosion. Although several authors agree that the process through which steel embedded in concrete corrodes in presence of chlorides is less understood, there are some agreements in the factors that influence the nature of the passive layer, which in turn determine the electric potential of the rebar (Alonso, 2002). They are:-

- Concrete properties which are functions of the relative humidity inside the pores, cement type, blending materials and w/c ratio (Arya, 1995; Rasheeduzzafar Al-Saadoun, *et al.*, 1990). These in turn affect the binding property of the cement, porosity, the pore water pH and chloride diffusivity (Thomas, 1996).
- The aggressiveness of the environment which is dependent on the temperature (Hussain, *et al.*, 1995; Lopez, *et al.*, 1993), the chloride content and its accompanying cation (Macias and Andrade, 1990).
- The steel metallurgical composition and oxygen availability
- The Cl^-/OH^- threshold of the mortar or concrete. This has generally been agreed to be about 0.6, although some authors have observed different values (Alonso, *et al.*, 2000).

2.7 Analytical Techniques

2.7.1 Chloride Profile Analysis

Chloride profiling is widely used for analysis of chloride ions concentration, be they free, bound or total versus depth of ingress in to cement mortar or concrete. This helps to monitor the level of chloride ingress as well as diffusivity of the same in cement mortar or concrete bulk. As chlorides ingress into the cement mortar or concrete, some of them are chemically bound by the cement alumina phase while some are 'free'. These represent the two types of chlorides in cement mortar or concrete; the free (water soluble) and bound chlorides (acid soluble). Their methods of extraction are different. For bound chlorides, several methods have been in place. They mainly involve dissolution of a powdered mortar through use of concentrated nitric acid with an ionic strength adjuster (ISA) or soxhlet extraction technique which involve refluxing of boiling water on the cement powder for 24 hours (Bertolini, *et al.*, 2004). The water-soluble chlorides are obtained from pore solution or using cold water or alcohol dissolution from powdered sample. The methods of analyses of the chlorides from the extracts vary from one laboratory to the other depending on the availability of facilities. Some of the common analytical techniques include chloride analyzer (Atkins, *et al.*, 1996; Suryavanshi, *et al.*, 1996), potentiometric titration, chloride ion selective electrode, inductively coupled plasma spectroscopy and colour based titrations (Bertolini, *et al.*, 2004). In this study, chloride analyzer was used after extracting the chlorides from cement mortar using concentrated nitric acid.

2.7.2 Linear Polarisation Resistance (LPR)

This technique has found use in obtaining the corrosion rates of a given working electrode in terms of corrosion current density, I_{corr}. In this technique, the working electrode is usually the corroding bar whose I_{corr} is measured versus a suitable reference electrode and a counter electrode usually graphite. The electrolyte is mainly the solution in which the working electrode is immersed. The technique involves the polarisation of the working electrode and counter electrode from free corrosion potential, E_{corr}, of the working electrode while holding the potential of reference electrode constant. The polarisation is done by applying an external current (I_{app}) to a small over - potential E. For an anodically polarised system, the anodic current increases to a value of I_a, and the cathodic current (I_c) decreases by a corresponding amount. This is given by the relationship in equation 2.51 (Uhling and Revie, 1985)

$$I_{app} = I_a - I_c \qquad 2.51$$

This is shown in current-potential relation diagram at corrosion potential, E_{corr}, in figure 2.4 (Uhling and Revie, 1985)

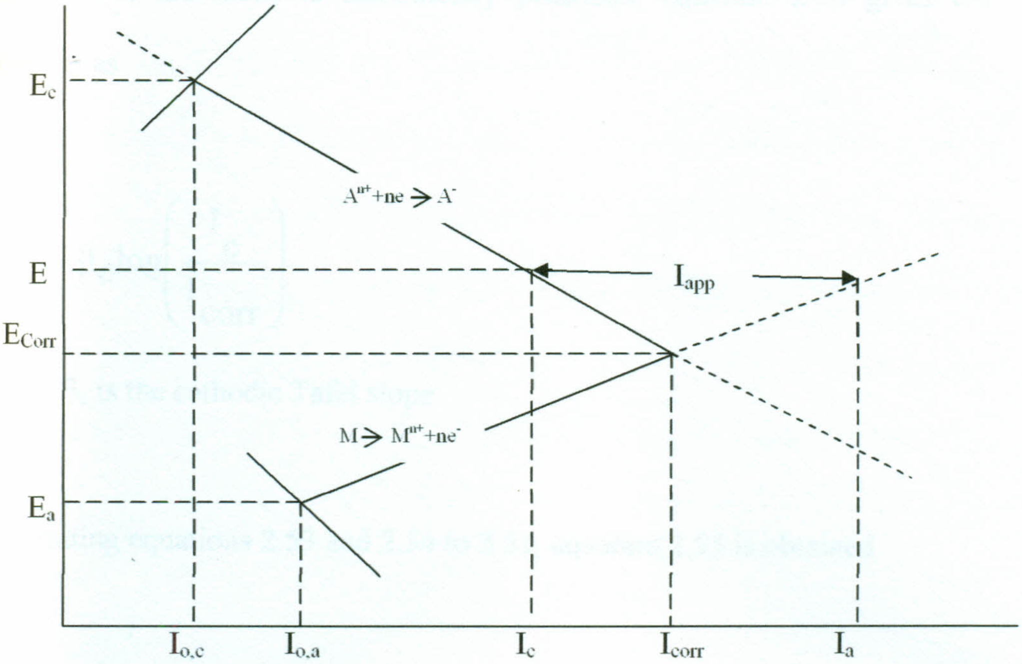

Figure 2. 4: Current – Potential Relation Diagram (Modified)

For anodic polarisation over small over – potentials, the equation can be expressed as

$$E - E_{corr} = \Delta E = \beta_a \log\left(\frac{I_a}{i_{o,a} A_a}\right) - \beta_a \log\left(\frac{I_{corr}}{i_{o,a} A_a}\right) \qquad 2.52$$

Where A_a is the fraction of area that is anode and $i_{o,a}$ is the exchange current density for the anodic reaction, while β_a is the anodic Tafel slope (Shreir, *et al.*, 1994; Yalcyn and Ergun, 1996). Equation 2.52 simplifies to equation 2.53

$$\Delta E = \beta_a \log\left(\frac{I_a}{I_{corr}}\right) \qquad 2.53$$

Similarly, if the metal is cathodically polarised, equation 2.54 gives the change in potential as

$$\Delta E = -\beta_c \log\left(\frac{I_c}{I_{corr}}\right) \qquad 2.54$$

Where β_c is the cathodic Tafel slope

Substituting equations 2.53 and 2.54 to 2.51, equation 2.55 is obtained

$$I_{app} = I_{corr}\left(10^{\Delta E/\beta_a} - 10^{-\Delta E/\beta_c}\right) \qquad 2.55$$

To obtain the Stern and Geary equation, a Taylor series expansion for small over-potentials, η, the value $\Delta E/\beta_a$ and $\Delta E/\beta_c$ are so small such that equation 2.55, simplifies to equation 2.56

$$I_{app} = (2.3)I_{corr}\Delta E\left(\frac{1}{\beta_c} + \frac{1}{\beta_a}\right) \qquad 2.56$$

Making I_{corr} the subject from equation 2.56, gives equation 2.57

$$I_{corr} = \frac{I_{app}}{2.3\Delta E}\left(\frac{\beta_a\beta_c}{\beta_a + \beta_c}\right) = \frac{1}{2.3R_p}\left(\frac{\beta_a\beta_c}{\beta_a + \beta_c}\right) \qquad 2.57$$

Where R_p is called the polarisation resistance. R_p is obtained as a slope of the plot of the resultant polarisation current against the over – potential. The plot is linear in the region of η approaching zero and thus the polarisation is usually done at very small ranges away from the E_{corr}, generally ± 10 – 20 mV (Rothwell and Tullmin, 2000; Yalcyn and Ergun, 1996) with scan rates of about 0.1 mV/sec (Al-Amoudi and Maslehuddin, 1993; Erdogdu, *et al.*, 2001). The corrosion rate (in terms of I_{corr}) is thus calculated from equation 2.57 which can be simplified to equation 2.58 (Fontana, 1987)

$$I_{corr} = \beta / R_p \qquad 2.58$$

where β is the Tafel constant given as equation 2.59 (Fontana, 1987)

$$\beta = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \qquad 2.59$$

In common practice, the values of 52 and 26 mV (Al-Amoudi and Maslehuddin, 1993; Erdogdu, *et al.*, 2001; Page, *et al.*, 1986), or values approximating the same for mild steel, are used for β values for system under passivation and active states respectively (Al-Amoudi and Maslehuddin, 1993; Erdogdu, *et al.*, 2001; Page, *et al.*, 1986). The authors (Al-Amoudi and Maslehuddin, 1993; Erdogdu, *et al.*, 2001; Page, *et al.*, 1986) warn that for the usage of the technique one requires to account for solution resistance at low conductivity levels and apply the right constants. The technique does not deduce the mode of corrosion, whether localised or uniform. The method has been used by a number of a authors of which Yalcyn and Ergun (1996) used it in predicting the corrosion rates of rebars while other authors (Al-Amoudi and Maslehuddin, 1993; Al-Tayyib, *et al.*, 1988;

Erdogdu, *et al.*, 2001; Page, *et al.*, 1986; Yalcyn and Ergun, 1996) have used the technique in the study of corrosion of reinforcing bar with success. Working electrodes that have attained an I_{corr} value of greater than or equal to 0.1 $\mu A/cm^2$ are considered to have attained active corrosion (Erdogdu, *et al.*, 2001; Liu and Weyers, 1998). Erdogdu *et al.* (2001) used the scheme presented in table 2.4 as a criterion for using linear polarisation resistance results to study the state of corrosion of a system

Table 2.4: Criterion for using LPR for corrosion assessment

Corrosion Current Density ($\mu A/cm^2$)	Corresponding rates in μm/year	Corrosion State
$I_{corr}<0.1$	1.2	Passive Condition
$0.1< I_{corr}<1$	11.7	Moderate Corrosion rate
$1< I_{corr}<10$	116.8	High Corrosion Rate
$10< I_{corr}<100$	1167.5	Very High Corrosion Rate

Some authors (Liu and Weyers, 1998) have also used the scheme in predicting the age after which damage of the concrete structure is expected. An I_{corr} value greater than 11 $\mu A/cm^2$ for example, is predicted to cause damage within less than two years.

2.7.3 Potential Measurement

Perhaps this is the most common method that has been applied in monitoring corrosion of reinforcement steel. The technique helps obtain the free corrosion potential, E_{corr}, of a working electrode versus a suitable reference electrode. The technique can be carried out in two modes; One involves placing a reference electrode in contact with the concrete surface via a suitable electrolyte and connecting to a high impedance voltmeter. The second terminal is connected to a bare surface of the reinforcement. In this mode, the electrolyte may be a sponge soaked in an appropriate electrolyte, either commercially available or prepared (ASTM, 2005d). Readings are taken at specified points along the surface of the concrete via placement of the reference electrode along the specified surface. Some authors (Park, *et al.*, 2005; Thiong'o, 1995) have used the technique but the reference electrode is placed at a fixed position in the corrosive media under investigation. In the second mode of the technique, two reference electrodes are used, one of which is held at fixed position while the other is placed along different surfaces of the concrete. Contact with the reinforcement bar is not important in this mode. This technique mode may be useful in helping to detect localised corrosion, for example, pits in which high – potential gradients may develop (Page and Cunningham, 1988).

Potential measurements basically gives corrosion probabilities and not the kinetics of corrosion (Erdogdu, *et al.*, 2001; Page and Cunningham, 1988). ASTM C – 876 (ASTM, 1992) defines the following observations on potentials of the rebars against saturated calomel electrode (SCE)

- Potentials greater than -120 mV indicate that there is a probability greater than 90 percent that the system does not corrode
- Potentials in the region of between -120 and -270 mV give uncertainity of whether the system is under or no corrosion
- Potentials less than -270 mV indicate that there is probability greater than 90 percent that the system is corroding

Page and Cunningham (1988) observed that corrosion potential measurements are applicable in systems under good oxygen supply, which may not be the case with reinforcement and especially in submerged structures where E_{corr} of less than -270 mV (SCE) have been observed but the systems were under negligible corrosion. The results of the method are also dependent on the type of reference electrode. Copper – copper sulphate electrodes (CSE) has been known to give inconsistent results in alkaline as it forms precipitates. The CSE give variance results in seawater with a variance of up to 100 mV from its theoretical value due to contamination with chloride ions. SCE and silver – silver chloride electrodes give consistent results as long as they are properly maintained (Page and Cunningham, 1988).

2.7.4 Atomic absorption Spectroscopy (AAS)

The technique has traditionally been used to quantitatively measure mainly the group two and higher groups elements mainly from solution or solubilised samples. The technique involves measurement of the attenuation of radiation absorbed by gaseous atoms of analyte. Valence electron transition whose radiation wavelength appear in the ultra-violet region of the light spectrum are the most important in AAS (Van Loon, 1980). If an electron undergoes transition from a higher energy level E_x to a lower energy state E_y the wavelength, λ, of the emitted radiation is given by equation 2.60 (Van Loon, 1980)

$$\lambda = {}^{hc}\!/_{E_x - E_y} \qquad 2.60$$

Where h is the Planck's constant and c is the velocity of light. The parameters ΔE (corresponding to $E_x - E_y$ from the above equation) and λ are unique values for a given transition. Resonance transitions, which involve absorption and release of the same quantity of energy are the most useful for AAS.

If light of intensity I_o is irradiated through a cell containing atomic species of an element, the transmitted radiation I will show a frequency perturbation whose relationship with the original intensity is related through the coefficient of absorption k_v defined by the equation 2.61

$$I = I_o e^{-Nk_v b} \qquad 2.61$$

Where b is the thickness of the absorption thickness or the length of the cell holding the sample and N the total number of free atoms

The absorption of monochromatic light is governed by the Beer-Lambert law which relates the concentration c, of the sample to absorbance A, at a given wavelength λ. The relationship is represented by equation 2.62 (Welz and Sperling, 1999)

$$\text{Log}\,(I_0/I) = A \qquad 2.62$$

Where

$$A = \varepsilon_\lambda bc \qquad 2.63$$

ε_λ = molar absorption coefficient of the sample at a wavelength λ while b is the path length

Basically, the method involves nebulisation or introduction of sample by other means into an atomising chamber where the sample is volatilised, decomposed, atomised appropriately and absorption of the radiating incidence, I_0. The final stage then involves the measurement of absorbance which is proportional to concentration. From equation

2.62, the absorbance A, should be linearly related to concentrations c, of the analyte (Lewis and Evans, 2001).

2.7.4.1 The Basic Principles of AAS

The source of radiation is characteristic of analyte atom of interest. The characteristic radiation, from hollow cathode lamps (HCL) for example, is produced when the argon or neon gas in the lamp (about 2 torr) are ionised. When the ionised argon or neon gas collides/interacts with the analyte metal surface (which is the analyte metal or its alloy, although in some cases, multi-elemental lamps are available), the metal atoms absorb energy to undergo excitation as they get sputtered into the tube. When they relax to ground state, a characteristic radiation is emitted (Van Loon, 1980). The main source of radiation used are hollow cathode lamps (HCL), electrodless discharge tubes and vapour discharge lamps among others (Welz and Sperling, 1999), with the first two being commonly used.

The second stage involves aspiration and atomisation of the samples. Commonly, premix – nebuliser cum burners are used. In this case, premix chambers in the nebuliser are designed to mix the fuel, oxidant and sample and aspirate into the atomisation chamber, the burner head flame. In the atomisation chamber, the aspirated solution's droplets are vaporised and atomised. The atomisation chamber produces the path length for the characteristic radiation from the cathode lamp. Other forms of atomisation include cathode sputtering in which case the sample, usually an electrical conducting sample or a non – conducting one is incorporated in a conducting matrix like silver or copper then made to be the cathode. Ionised inert gas is then accelerated towards the cathode to knock out the sample atoms. Electro-thermal atomisers include for example electrically heated graphite furnaces and rods. It is in the atomisation chamber that a portion of the incident radiation from the source of radiation is absorbed (Van Loon, 1980). The proportion of incident radiation is related to the concentration of analyte in the sample.

The attenuated radiation from the atomisation chamber is passed through an optical system, a monochromator, which separates the resonance line as well as decreasing the emission intensity from the atomizer. The radiation from the monochromator is then passed on to the photomultiplier, where an electrical signal is generated. The signal generated is proportional to the absorption of the analyte atoms (Welz and Sperling, 1999).

CHAPTER THREE

EXPERIMENTAL

3.1 Analytical Procedure

Unless otherwise specified, whenever water appears in this chapter, it refers to distilled water (for cases where aggressive media were analysed) and de-ionised water (for cases where chloride profile analysis is mentioned). Analytical grade chemicals were used. Glass wares and plastic containers used were washed with a suitable detergent using running water, rinsed with water and dried appropriately.

3.1.1. Sampling and preparation of test materials

Materials were sampled from their respective regions in Kenya; SBE from point of dispatch of Kasuku Packers-Athi River (KAPA), ALS from British Oxygen Company (BOC)-Industrial area of Nairobi, RH from Mwea rice milling station, sea-water from Bamburi beach in Mombasa, OPC and PPC from the parking yard of Bamburi Cement Factory, BB from Kenya Clay Products in Ruiru Municipality while sand was sampled from Githurai distributors in Ruiru Municipality.

Corrosion and chloride profile analyses were carried out at the University of Manchester, UK. OPC, PCDC and a blend of OPC with PFA were used for these analyses. OPC and PFA were therefore obtained from the Mechanical and Civil Engineering School of the University of Manchester. The 'combined ash' used in PCDC for these analyses were prepared in Kenyatta University, Kenya.

'Combined ash' preparation and incineration were carried out following a procedure described by Muthengia (2003) using a fixed bed kiln (Ochung'o, 1993): 5 kg of RH were neatly spread on the floor of a fixed bed kiln followed by a spread of 8 kg of ground BB. 5 kg of RH were spread on the BB then 8 kg of SBE spread on the RH. Finally, 30 kg of RH were spread on the SBE. A little paraffin was poured on the RH around the firing window and the whole mass ignited. The incineration temperature was controlled below 700 °C by closure and opening of the kiln windows. After 48 hours, the whole mass had completely been incinerated and cooled. Any unburnt upper surface layer was skimmed off carefully. The remaining ash was removed from the kiln via the mesh below the kiln and the firing window. The resultant ash, referred to as 'combined ash' was ground using a laboratory ball mill mode TR 850 W and thoroughly mixed using trowels by making cones that were dismantled from sides to form other cones in a seven series of cones. The resultant ash was reground in the ball mill until the percent retention on a 100 μm shaker sieve was less than 10 percent.

Acetylene lime sludge as obtained from the sampling site, was allowed to settle after which excess water was carefully poured off. The resultant lime slurry was dried at 110 °C to a constant mass. The resultant powdery material was ground using a laboratory blender. This was labelled DALS.

The 'combined ash' and DALS were further inter-ground in a ratio of 2: 1 respectively for ten minutes in the laboratory ball mill to ensure uniformity. The resulting mixture was parked in sealed plastic bags and stored in moisture-free cotton paper lined bags. This was labelled 'test ash' for identity purpose.

The 'test ash' in mix with commercial OPC in a ratio of 9: 11 respectively were inter-ground using the laboratory ball mill for ten minutes to ensure complete mixing. The resultant cement was labelled PCDC. Separately, OPC and PPC were similarly ground to ensure a similar fineness.

Sand as obtained from the sampling site was washed by spraying with tap water and sun-dried for two days to a constant weight. The dry sand was sieved to remove coarse material through a 5 mm sieve. To ensure uniformity, the sand was mixed using trowels by making cones that were dismantled from sides to form other cones in a series of seven times.

Sea water as obtained from the sampling site was stored in clean plastic bottles. About 500 ml were sampled for analyses of Na^+, K^+, Ca^{2+}, Cl^- and SO_4^{2-}. Laboratory solutions of chlorides and sulphates were made by dissolving requisite amounts of anhydrous magnesium chloride and sodium sulphate salts in water (in separate volumetric) and diluting respectively to make solutions having a corresponding concentration to that in sea water. These solutions were labelled Cl1 and SO1 respectively. A second set of solutions was similarly prepared but with double the concentration of chlorides and sulphates in sea water. These solutions were labelled Cl2 and SO2 respectively. Sea water was labelled SW.

Sodium and potassium ion concentration was analysed using flame photometry (Golterman, 1978), while Ca^{2+} was analysed using atomic absorption technique (Golterman, 1978). To prepare ionisation suppressors for the analyte ions, requisite amounts of La_2O_3 and CsCl were dissolved in 20 ml water – 25 ml HCl mix and diluted to a 100 ml in a 100 ml volumetric flask to make 100 and 50 ppm solutions respectively. To make 1000 ppm stock solutions, respective salts of interest were dried accordingly; NaCl, KCl and $CaCO_3$ at 140, 110 and 180 °C respectively for one hour. Requisite amounts of the dried salts were dissolved in 1 ml HCl-50 ml water mix. The resultant mixes were diluted to 1000 ml in a volumetric flask. $CaCO_3$ was first dissolved in 10 ml concentrated HCl. To prepare standard solutions, 100 ml of each stock solution was pipetted into a 1000 ml volumetric flask and diluted to the mark. Out of the standard solution, proportionate amounts of each solution and 10 ml Cs-La solution were pipetted into 100 ml volumetric flasks to make 0 – 100 ppm calibration solutions. The flame photometer and AAS machines were set in accordance to their instructional manual. Each time an analysis was done, the standard solutions were prepared afresh. A corresponding diluent of sea water was similarly treated with the Cs-La solution. This procedure was always repeated each time the concentration of Na^+, K^+ and Ca^{2+} was determined from aggressive media.

Chloride concentration in sampled sea-water was determined using the usual potentiometric method: Standard chloride stock solutions were prepared by dissolving requisite amounts of NaCl in water and diluting to the mark of a one litre volumetric flask. Standard solution was prepared by diluting the stock solution. From the standard solution, calibration solutions of 0 – 100 ppm were prepared. An ionic strength adjustment buffer (ISAB) solution was prepared by dissolving requisite amounts of KNO_3 solution in water and diluting to one litre in a volumetric flask to make a 0.1 molar solution. Calibrations were done by mixing the calibration solutions with the ISAB solution in a 1: 1 ratio. Diluents of sea water were similarly treated and analysed. This procedure was always repeated each time the concentration of Cl^- was determined from aggressive media (Dilution of the aliquots of SW, Cl1 and Cl2 was necessarily done).

Sulphate concentration in sample solution was determined using the usual turbidimetric procedure (Golterman, 1978): Requisite amounts of dried anhydrous sodium sulphate solution was dissolved in water to make a 100 ppm stock solution from which calibration solutions of 0 – 50 ppm were made by diluting calculated amounts accordingly. A conditioning reagent was prepared by mixing 50 ml of glycerol with a solution containing 30 ml HCl, 300 ml water, 100 ml of isopropyl alcohol and 75 g sodium chloride. The sulphate concentration was determined by taking a suitable amount of aliquot (further dilution was done for the SO1 & 2, and SW) and diluting to 50 ml into a 250 ml conical flask. 2.5 ml of the conditioning reagent was added and the resulting solution magnetically stirred for one minute. The turbidity of the mixture was determined and recorded as turbidity without barium chloride. The sample was put back into the flask and a spatulaful (about 0.25 g that was determined to be excess) of $BaCl_2$ added. The resulting mixture was stirred for a further one minute and the turbidity determined and recorded as turbidity with $BaCl_2$. A calibration curve was drawn by plotting the response of the turbidometer (Turbidity with $BaCl_2$ – Turbidity without $BaCl_2$) versus the concentration of the standard solutions and the resultant slope of the graph determined. To calculate the concentration of the sample, the following formulae given as equation 3.1 was used

$$\text{Concentration(ppm)} = \frac{\text{Turbidity with BaCl}_2 - \text{Turbidity without BaCl}_2}{\text{Calibration graph slope}} \qquad 3.1$$

Chemical analysis for the OPC, PFA and Test Ash was done using Axios XRF machine using IQ+ part of the superq package that operates the XRF machine.

3.1.2 Pozzolanicity Test

The test was done in accordance with the International Standard for Organisation (International Standard for Organisation, 1990). Reagents were prepared by separately dissolving requisite amounts of ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA), concentrated HCl and NaOH in water to make 0.025 M EDTA, 0.1M HCl and 5M NaOH solutions respectively. The 0.025 M EDTA solution was standardised against dried calcium carbonate while 0.1M HCl was standardised against dried sodium carbonate. Murexide indicator was prepared by inter-grinding 0.5 g of murexide and 100 g of dried potassium chloride using a pestle and mortar.

Curing of the test sample for the test was done by pipetting 100 ml of freshly boiled water into a 0.5-litre plastic container and the sealed container placed in a thermostatic enclosure at 40 ± 0.2 °C until equilibrium was reached in about an hour. The container was removed from the thermostatic enclosure and 20.00 g of test cement poured into it using a wide funnel. The container was then immediately sealed and shaken vigorously for a bout 20 seconds. A horizontal rotary motion was adopted thus preventing any sample or liquid from being thrown up and remaining separated from the rest of the solution. The container was then placed back to the thermostatic enclosure. After a period of testing (4, 8, 21 or 28 days), the container was removed from the enclosure and filtered immediately under vacuum. A butchner funnel, a vacuum flask and dry whatmann filter paper were used for the filtration. The flask was then sealed immediately to avoid carbonation. The filtrate was allowed to cool to room temperature in about ten minutes.

To determine the concentration of the OH^- ions, 50 ml of the filtrate were pipetted into a 250 ml conical flask and about five drops methyl orange indicator added. The resulting solution was titrated against 0.1M HCl. The OH^- concentration in millimoles per litre was calculated using equation 3.2

$$[OH^-] = \frac{1000 \times 0.1 \times V}{50} \qquad 3.2$$

Where V was the volume of the 0.1M HCl used for the titration.

To determine the concentration of CaO, about 5 ml of 5 M NaOH and 50 mg of the murexide indicator were added to a measured solution that remained after completion of OH^- determination. The resulting solution was titrated against the 0.025M EDTA solution. During titration, the pH of the solution was maintained at 13 by the addition of the NaOH solution. The pH was monitored through a pH meter. The concentration of $Ca(OH)_2$ was calculated using equation 3.3

$$[CaO] = \frac{1000 \times 0.025 \times V}{50} \qquad 3.3$$

Where in this case, V was the volume of EDTA solution used for the titration.

3.1.3 Preparation of Mortar Cubes

Six 100 mm mortar cubes were prepared at a go. For each category, a total of 21 mortar cubes were prepared. The cubes were prepared by taking 3141.0 g of cement and 9423 g of sand and mixing them through a seven cone succession in a steel basin. After the mixing, 1440 ml water were added and a further mixing done using two trowels until a uniform mortar was formed in about five minutes. The mortar was transferred into the 100 mm mould cubes using the trowels and compacted using a vibrating porker model B25DS for two minutes. In any case where the mortar was seen to be levelling below the cube fill, mortar was added during the compaction period. The porker was never stopped during the compaction period. After the two minutes, the mortar was levelled by vibrating the porker on a horizontal slant over the cube for thirty seconds. The mortar was then cured for 24 hours after which it was de-moulded and submerged in lime rich water in a curing room maintained at 23 °C for 27 days. Three specimens from each category of cement were taken for compressive strength determination using the compressive strength machine model number Mie 2742. In each category of the remaining cubes, three of them were separately immersed in 500 ml of each category of aggressive solution (distilled water [labelled as DW], SW, Cl1, Cl2, SO1 and SO2) in separate 2-litre plastic containers. An aliquot of the aggressive medium was sampled each time for analyses of the selected ions (Ca^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-}). An equal amount of the original solution of each category was replenished after sampling. The pH of the aggressive medium was monitored by use of pH meter model number 3405. After the sixth month of monitoring the cubes in aggressive media, the three cubes of each category were taken out for compressive strength analyses.

3.1.4 Corrosion Monitoring and Chloride Ingress Measurement

10 mm by 80 mm mild steel rods, whose chemical composition is given in table 3.1 (as analysed by the Bureau Veritas Consumer Products Services UK LTD), were cut, and smoothened on the edges with a smooth file. The rods were polished with emery papers 80-600 grit in succession. The resulting metal rods were washed with distilled water, rinsed with acetone and blow dried. They were stored in a dessicator that used anhydrous silica as desiccant.

Table 3.1: Chemical Analysis of Mild Steel

Element	% w/w	Method of Analyses
C	0.18	Combustion Analysis
Si	0.23	ICPOES
Mn	0.77	ICPOES
P	0.016	ICPOES
S	0.011	Combustion Analysis
Cr	0.03	ICPOES
Mo	<0.02	ICPOES
Ni	0.04	ICPOES
Al	0.032	ICPOES
Co	<0.005	ICPOES
Cu	0.09	ICPOES
Nb	<0.005	ICPOES
Pb	<0.02	ICPOES
Sn	<0.02	ICPOES
Ti	0.005	ICPOES
V	<0.02	ICPOES
W	<0.02	ICPOES
Fe	Balance	

ICPOES: Inductively Coupled Plasma Optical Emission Spectroscopy

3:1 sand to binder (100 % OPC, OPC-25 % PFA or PCDC) ratio was used in preparation of the mortar. In the initial stages, it was presumed that mortar with 0.4, 0.5 and 0.6 w/c ratio would be prepared. It was however noted that the amount of water added to correspond with the above w/c ratios, could not make consistent pastes. This was because the sand was oven dried. An amount of water required to wet the sand was determined through addition of excess water to the sand and leaving the sand to dry in a normal laboratory set up for three days. The residual water was calculated to be about 0.077 percent by weight. A 0.8 w/c ratio mortar proved to be the best workable mix in all cement categories. A lower w/c ratio of 0.73 was also used but the paste was quite difficult to work with. A higher w/c ratio of 0.85 was also prepared. A corrected w/c ratio after subtracting the sand wetting water would correspond to 0.5, 0.57 and 0.62 for 0.73, 0.8 and 0.85 respectively. To avoid confusion, the later w/c ratios have been used in this write-up.

Six 30 mm by 100 mm by 100 mm high density PVC were machine-cut. Six 10 mm holes were drilled through the PVC blocks. From one edge of a block, two holes were drilled at 20 and two more at 15 mm from the other edge. A hole was drilled through on the remaining edges at 10 mm from the edge. One of the PVC block used is shown in plate 3.1.

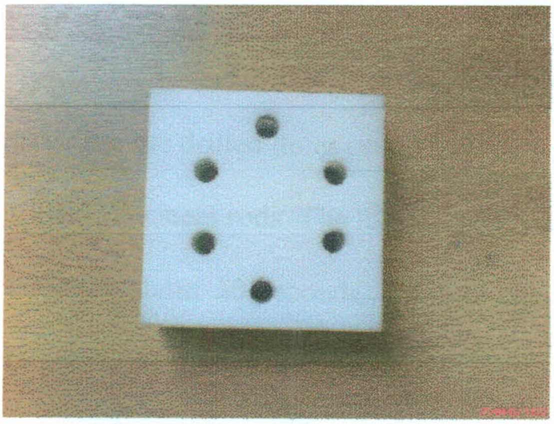

Plate 3.1: PVC Block with the Holes Drilled Through

A quantity of mortar enough to make five mortar cubes was prepared for each category of mix at a go. This was done by transferring 7800 g of standard building sand followed by 2600 g of binder (cement + ash: Ash was either PFA or test ash) into a mechanical mixer

'Creteangle Multi-Flow Mixer', commonly referred to as Pan Mixer. The dry powder was mixed for about half a minute. An amount of water, as shown in table 3.2, was slowly added to the powder as the mixer continued. After a minute, the mixer was stopped and the mortar scrapped from the side with the help of a trowel. The mixer was then continued for about 30 seconds. The mortar was again scrapped from the side of the mixer and mixed with a trowel. The mortar was now ready for placement.

Table 3.2: Amount of water added for each batch of cement category made

Cement Label	Ash Used	w/c ratio	Amount of water added (mls)
1A	None	0.73	1900
1B	None	0.8	2100
1C	None	0.85	2200
2A	Test Ash	0.73	1900
2B	Test Ash	0.8	2100
2C	Test Ash	0.85	2200
1A	PFA	0.73	1900
2B	PFA	0.8	2100
3C	PFA	0.85	2200

The PVC block was placed at the bottom of the cube mould. Six polished steel rods were placed in the drilled holes on PVC. The mortar was finally shovelled in to the cube with or without the steel rods. The mortar was compacted into the cube by vibrating on a vibrating table for about 30 seconds. All five cubes of a category were vibrated at a go. Excess mortar was cut off from the cube using a shovel and the surface smoothened off using the same. After 24 hours the cubes were de-moulded. The PVC block could not be separated from the mortar. The above procedure was repeated but this time the mortar was allowed to cure for 48 hours in the mould before de-moulding. The PVC block, again, could not be separated from the mortar.

Holes with dimensions and distances from the edges, similar to the PVC block, were made on a 0.5 mm by 100mm by 100 mm polythene sheet. The PVC block was lightly spot-oiled with an oil-dump tissue paper. The polythene sheet was placed on the PVC block and the holes on either matched. The cut polythene sheet adhered very well to the PVC block. The PVC block plus the polythene sheet were placed at the bottom of a cube mould. The polished mild steel rods were carefully and gently pushed into the PVC block holes. A photo picture of one of such cubes is shown in plate 3.2. Two such cube moulds and other three others (without PVC block and rods) were placed on a vibrating bench. Mortar was carefully shovelled into the cubes and compaction done for about 30 seconds. The mortar was levelled using a trowel and vibration continued for about 10 seconds. Final levelling was done. The resultant mortar was cured for 24 hours (in case of 0.73 and 0.8 w/c ratio) and 48 hours (in case of 0.85 w/c ratio) after which they were de-moulded. The simulated reinforced mortar cubes are shown in plate 3.3.

Plate 3.2: PVC block with Polythene sheet lining in the Mortar Cube

Plate 3.3: Mortar Cubes Simulating Reinforced Concrete

On the second day after preparation of individual mortar cubes, 6 mm nichrome wires with 5 mm heat shrunk tubings were spot-welded at about 8 mm from the top side of the protruding rebar. After the sixth day of preparing all the cubes, steel reinforcement protector 841, obtained from Flexcrete Technologies Limited (UK) was applied to the mortars with embedded steel rods. This was done by first gritting the exposed surface of the rods with emery paper grade 80 then de-oiling the protruding rebar ends with acetone-soaked cloth. Steel reinforcement protector was prepared by mixing 3: 1 by volume of cementious powder to polymer dispersion provided and thoroughly mixing it with the help of a provided wooden stick to a brushable paste. The resultant paste was thinly applied to about 1 mm with a 25 mm pure bristles brush on the exposed ends of the rebars. The steel reinforcement protector 841 paste was similarly applied on to the mortar cube to the face with the exposed rebar surface. This is shown in plate 3.4.

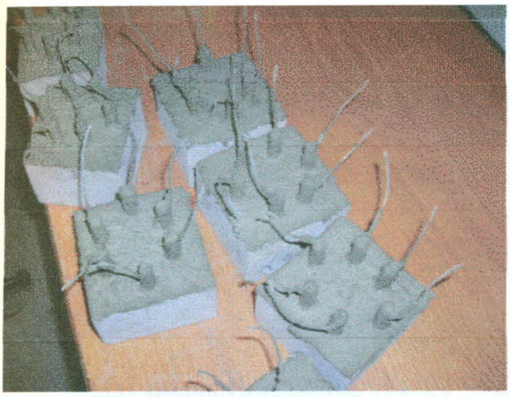

Plate 3.4: Steel reinforcement Protected Mortar Cubes

The first coat was allowed to cure for about 45 minutes before application of a similar second coat on top of the first one. After an additional 45 minutes, any voids were brushed with the steel reinforcement protector 841 paste. The mortar cubes were allowed to cure overnight. Similarly, steel reinforcement protector 841 paste was applied to all faces, except on two opposite sides, of the mortar cubes without reinforcements. All mortar cubes were cured for an additional 21 days in saturated calcium hydroxide solution.

After the 28th day of curing, 2-metre insulated copper cables were connected to the nichrome wire spot welded to the embedded steel rods with the help of joint clips. The open ends of the clips were sealed with silicon-based sealant Dow Corning 732. The insulated copper cables were labelled with a seven code identity. The first two letters identified the cement type (PC for PCDC, OP for OPC and PF for OPC + PFA), the third and fourth members of the code which were numbers identified the w/c ratio (12 for 0.73 w/c ratio, 31 for 0.8 w/c ratio and 29 for 0.85 w/c ratio), the fifth member which was a letter identified the rebar depth of cover (Y for 10 mm, B for 15 mm and G for 20 mm depth of cover) while the last two which were either L1, L2 or L3 was just to distinguish the three similar rebars. PC12BL1 identified the first 15 mm depth of cover rebar of a PCDC cement mortar cube of 0.73 w/c ratio.

All cubes were subjected to one week alternate wet – dry tank for a period of six months. The wet alternate week involved complete immersion of the mortar cubes in 3.5 percent sodium chloride solution.

For visual inspection of the rebars, the simulated reinforced mortar were dismantled with help of a hammer and a chisel and visually examined after the 168th day.

3.1.5 Corrosion Potentials and Linear Polarisation Resistance Measurements

It was initially designed that OPC-25 % PFA, OPC and PCDC reinforced simulated mortar cubes would be analysed for corrosion potential (versus SCE) and Linear Polarisation resistance (LPR) measurement. But after about two alternate cycles, it was noticed that the portions of the rebars to which the steel reinforcement protector 841 paste was applied had not protected the OPC-25 % PFA mortar rebars. These measurements were therefore not done henceforth.

Corrosion potentials were measured using SCE as reference electrode with a high impedance voltmeter. The LPR was done using a laboratory-made potentiostart (Leeds, 2007) using SCE and graphite rod as reference and counter electrode respectively. The LPR and potential measurements were done for a total of 12 wet-dry cycles which coincided with 168 days. E_{corr} and LPR measurements were done during the wet seasons. During the E_{corr} and LPR measurements, the reference electrode was always maintained at a fixed position. It was held in position by a clamp affixed to a retort stand by a boss head. The counter electrode was always positioned next to the simulated reinforced mortar of interest.

In LPR measurements, the potential was manually shifted from E_{corr} to ± 20 mV in intervals of about 5-8 mV. Corrosion current readings were taken after stabilisation which took about 45 – 60 seconds. A graph of over-potentials, η, verses corrosion curent was plotted and its gradient, R_P, calculated. Corrosion current density, I_{corr}, was determined as per equation 3.4

$$I_{corr} = 52/(S_A*R_P) \qquad 3.4$$

where S_A is the specific surface area of the rebar, approximated from ($\pi Dh + \pi r^2$) in which case D, h and r represent diameter, height and radius of the rebar respectively. The height, h, taken was for the length of the rebar embedded in the mortar cube.

52 is the Tafel constant and has that meaning throughout the text.

3.1.6 Chloride Ingress profile Analysis

The analysis was done in accordance to ASTM C 1152 (ASTM, 2005e) with slight modifications: Corning chloride analyzer M926 apparatus was used instead of the prescribed silver-silver chloride electrode for determination of chloride concentrations. The resultant nitric acid extracts from the cement mortar were therefore adjusted to pH of about 7. The rest of the procedure was adopted. 0.05 M NaCl, 0.05 M $AgNO_3$ and 5 M NaOH reagents were prepared in the usual manner. The two opposite sides to which steel reinforcement protector 841 paste was not applied, an emery paper 80 grit was used to polish to about 1 mm layer. A 15 by 15 mm by 100 mm core was obtained from each cured mortar cubes without reinforcement. This was done by cutting the mortar cubes using a Slabbing saw with a 14 inch blade using water as lubricant. The obtained core was cut first into two equal portions of 15 mm by 15 mm by 50 mm. The two halves were cut into four equal slices to give samples at approximate depths of 12.5, 25, 37.5 and 50 mm using CS 10 Logitech saw with a 10 inch blade. The obtained slices were ground using a Tema equipment grinder for approximately two minutes. Between each sample grinding, the grinder was thoroughly cleaned to avoid cross contamination. The ground samples were placed in a 20 ml glass sample holder and shaken to mix.

About 10 g of the sample from the mortar cube drills was obtained for analyses. The sample was dispersed in 75 mL of water in a 250 mL beaker. 25 mL of [1:1] nitric acid was slowly added while stirring with a glass rod to break any lump of cement forming. The beaker's content, with a watch glass cover lid on, was rapidly brought to boiling using a hot plate. The resultant solution was allowed to cool for about ten minutes then its pH adjusted to between 6.80 and 7.10. The near neutral solution was then filtered through a pre-rinsed 9-cm course textured filter paper into a 250-mL beaker. The filter paper and the beaker were rinsed four times with water. The filtrate was diluted to 200 ml in a volumetric flask.

The resultant solution was then analysed for chlorides using the Corning Chloride Analyzer M926 of serial number 1845. The chloride analyzer M926 was first conditioned with 5µl of a 200 ppm standard chloride solution in mix with 30 ml of buffer solution, containing CH_3COOH (<100 g/l), HNO_3 (9 g/l), anticoagulant and agent moullant in accordance to Corning Limited Instruction Manual booklet (Corning-Limited, 1980). A standard calibration curve was obtained from 0 to 200 ppm standard chloride solutions. 5 µl of 200 ppm chloride solution (provided with the apparatus) was pipetted into a 30 ml buffer solution. The machine was then conditioned by pressing the 'run – condition' button. Additional 5 μl of 200 ppm chloride solution was pipetted in to the buffer solution and the machine set to analyse. The procedure was repeated until a reading of 200 ± 2 units was obtained. For sample analyses, 5 μl of 200 ppm standard chloride solution (provided with the apparatus) were pipetted into a 30 ml buffer solution and the machine conditioned as above. 5 μl of sample was then pipetted in to the resultant solution and the machine set to analyse. The conditioning and calibration was always run each time a new series of sample was analysed. For each analysis, quadruplicate results were run for every three samples of a given cement type.

Since there was a slight deviation from the prescribed standard (ASTM, 2005e) procedure, confirmatory tests were run. This was first through carrying out the above sample digestion process of a mortar sample and obtaining the residue after filtration. The residue was washed further for three more times and re-acidified to a pH of 2 using the 1: 1 HNO_3. To the re-acidified sample, a few drops of silver nitrate solution were added. No white precipitates were observed as would have been expected of a chloride-containing solution. A second confirmatory test involved a mortar sample that was divided into two portions. To one portion, 40 ml of 200 ppm chloride solution was added as part of the 75 ml dispersing water and the normal sample digestion and chloride analysis done. This was done in triplicates. The results showed a corresponding response to the added chloride standard as compared to the un-spiked samples.

Apparent chloride diffusion coefficients D_{app} were derived from the fitting curves of equation 2.31 on the chloride penetration depth verses chloride concentrations graphs

(Abramowitz and Stegun, 1972; Collepardi, *et al.*, 1972). Curve fitting was done using the method of least squares.

3.1.7 Data Analyses

Since at least triplicate results were obtained for each category of results, averages to obtain means were done. Graphical representations were done in the usual manner for data necessitating the same. These included results for chloride profile, compressive strength, corrosion current densities and potentials analyses. Compressive strength analyses results were first analysed for their change from the 28th to the 180th day. The change between each category of sample was analysed for significant difference between the same and different samples using T-test (Anderson, 1987; Miller and Miller, 1988). Results from chloride profile analyses and corrosion current densities were subjected to paired T-test (Anderson, 1987; Miller and Miller, 1988).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, results for the analyses of the test cements, PCDC, OPC and PPC in selected corrosive media are reported. The corrosive media, which were in a laboratory set-up, included sea water, distilled water, sodium sulphate, magnesium chloride and sodium chloride solutions. Discussions are presented for each category of results. In all the tests, a high w/c ratio and concentration of the sulphate and chloride solutions were used to accelerate the tests. This is a usual practice (Pech and Castro, 2002; Trejo and Monteiro, 2005) in laboratory tests.

Generally, mortar cubes that were prepared from respective cements were cured for 28 days in saturated calcium hydroxide solution. After the curing period, compressive strength was determined from three mortar cubes representative for each category of test cement. The average strengths were 25.8333, 22.1379 and 19.2273 MPa for OPC, PPC and PCDC respectively. Three other cubes of each category of cement were subjected to the corrosive media of sea water, magnesium chloride, sodium sulphates and distilled water. After about six months of monitoring of the Ca^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-} ions and pH changes in the corrosive media, compressive strength of the three mortar cubes representative of each category was determined. The change in compressive strength from the 28th day to the sixth month was calculated using equation 4.1.

$$\%C.S_{gain} = \frac{C.S\,(n^{th}\ Day) - C.S\,(28^{th}\ Day)}{C.S\,(28^{th}\ Day)} \qquad 4.1$$

Where % $C.S_{gain}$ was the calculated percent gain in compressive strength, C.S (n^{th} Day) was the compressive strength at the n^{th} day, which in this study was 180th day and C.S (28th Day) was the strength at the 28th day. This percent gain in compressive strengths will be discussed in their respective sub-sections.

4.2 Chemical Analyses of the Test cements

Table 4.1 gives the results for chemical analyses of oxides in percent by mass (except for Cl^-) of OPC, PFA and the test ash. The main chemical components of cements and pozzolana are the silica, iron, aluminium and calcium oxides. They provide the main binding cementitious phases, for example, calcium silicates. The alkali and alkali metal oxides are important because they provide alkalinity in hydrated cement and/or concrete pore systems. The alkalinity protects reinforcing bars against corrosion.

Table 4.1: Results for Chemical Analyses of OPC, PFA and Test Ash

Sample / Oxide %	OPC	PFA	Test ash
SiO_2	16.163	39.417	39.711
CaO	64.615	3.691	23.742
Al_2O_3	3.831	16.951	4.849
Fe_2O_3	2.527	3.000	4.043
Na_2O	0.252	0.242	0.173
K_2O	0.572	1.482	0.824
MgO	0.832	1.06	0.524
SO_3	3.573	0.734	0.485
Cl^-	0.027	0.02	0.061

The test ash had a higher Cl^- content as compared to the other materials. This was more than two times the content of the OPC and PFA. The chlorides may have resulted from the activation process of the bleaching earth. The earths are mainly thermally and acid activated with HCl, HNO_3 or H_2SO_4 (Mana, *et al.*, 2007; Oboh and Aworh, 1988; Sabah, *et al.*, 2007). Exposure of the test ash based cement to chloride environments may thus require caution.

The CaO phase in OPC, which was the highest in this case, was mainly in the form of calcium silicates, ferrites or aluminates (Blanks and Kennedy, 1955). It is thus less vulnerable to the aggressive ion attacks although the resultant $Ca(OH)_2$ upon hydration of the phases is vulnerable (Blanks and Kennedy, 1955). The test ash showed a higher calcium oxide content than PFA. This was originally in the form of $Ca(OH)_2$ via DALS. The $Ca(OH)_2$ in pozzolana-based cements may provide pozzolanic reaction thus making the cement more durable, less permeable and increase its strength (Blanks and Kennedy, 1955).

The test ash had a higher silica content, comparable to PFA despite being blended with DALS. The silica would be expected to react with the added $Ca(OH)_2$ to form more cementious material as a long term benefit. This would make the cement mortar more durable. Active silica in pozzolana is an important component as it constitutes one of the major phases for pozzolanic reaction (ASTM, 1991).

4.3 Pozzolanicity Analyses

Figures 4.1 and 4.2 give the results of the CaO and OH^- concentrations as analysed from the accelerated curing of the test cements. The test gives the progressive residual $Ca(OH)_2$ as a result of continued cement hydration. Pozzolanic cements are known to continuously consume and hence reduce $Ca(OH)_2$ in hydrated cement or concrete as opposed to OPC. The test, therefore, gives a measure of pozzolanicity of a given cement (International Standard for Organisation, 1990).

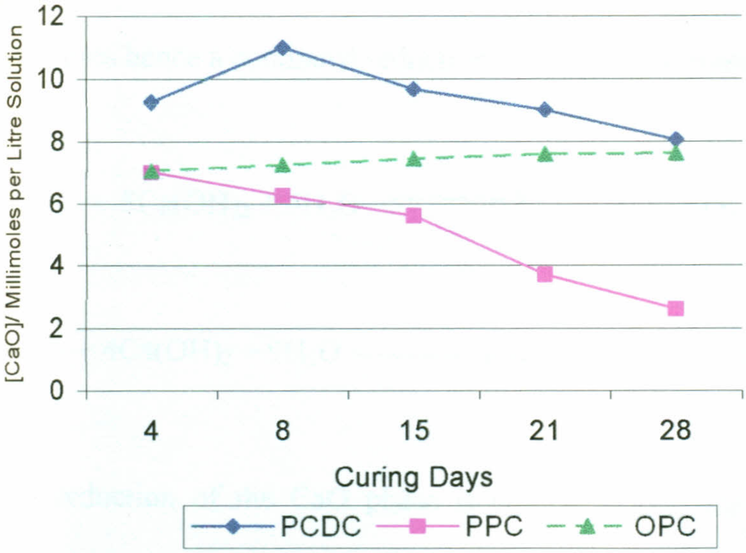

Figure 4.1: CaO Concentration Change as a Function of Curing Period

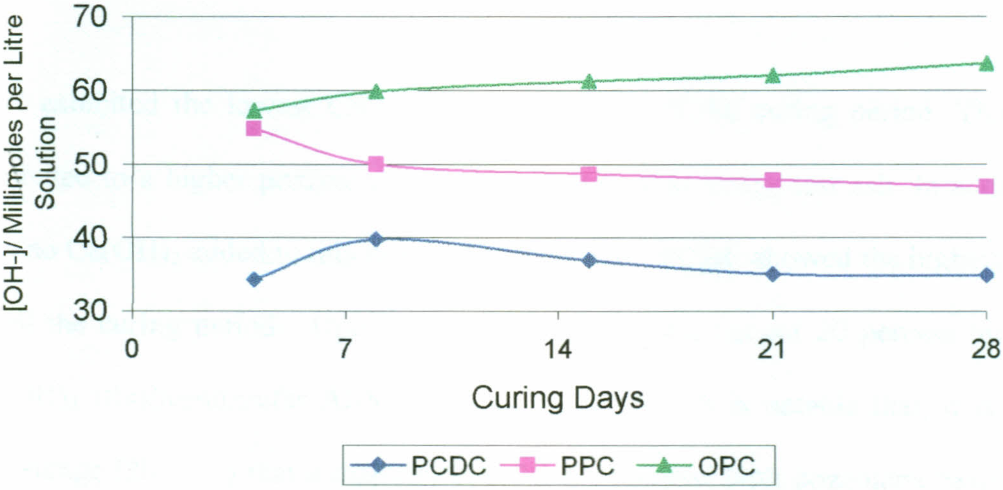

Figure 4.2: OH^- Concentration Change as a Function of Curing Period

As can clearly be seen, in the replaced cement, there was an appreciable reduction in CaO while OPC had an almost constant amount of the same. This was in line with the expectations as pozzolanic reaction consumes the $Ca(OH)_2$ produced from the hydration of Portland's C_3S and C_2S phases (Czernin, 1962; Taylor, 1997). The silica and aluminate phases, for example in pozzolana consume $Ca(OH)_2$ as given by equations 4.2 and 4.3 (Young, *et al.*, 1998). The reactions are slower than the normal Portland hydration processes hence a continued reduction in the same is observed over time.

$$2SiO_2 + 3Ca(OH)_2 + 5H_2O \longrightarrow 3CaO.2SiO_2.8H_2O \qquad 4.2$$

$$Al_2O_3 + 4Ca(OH)_2 + 9H_2O \longrightarrow 4CaO.Al_2O_3.13H_2O \qquad 4.3$$

The reduction of the CaO phase is crucial as this lowers the phase that is prone to aggressive attack. The resultant silicate hydrates have cementitious properties thus increase the strength of the pozzolana based cements. More so, the additional cement products make the cement mortar denser and hence less permeable and more durable (Ampadu and Torii, 2002; Cheng, *et al.*, 2005; Taylor, 1999).

PPC exhibited the lowest CaO content at the end of the curing period. This could be attributed to a higher pozzolanic reaction as compared to the test ash. In addition, there was no $Ca(OH)_2$ added to this mix as was in PCDC. PCDC showed the highest CaO level at all the curing period. Upon hydration, OPC releases about 20 percent by weight of $Ca(OH)_2$ (Rasheeduzzafar Al-Saadoun, *et al.*, 1990). It is notable that, it is about this percentage (20 – 25) that a majority of OPC are blended with pozzolana based materials (Muthengia, 2003). By summing up the included DALS and resultant $Ca(OH)_2$ from OPC upon hydration, through a conservative estimate, PCDC contained about 26 percent by weight of $Ca(OH)_2$. In PCDC, the replacement levels were higher than this percentage. It was therefore important to add extra $Ca(OH)_2$ to counter for the excess pozzolana added. The added $Ca(OH)_2$ was expected to react at least to a greater extent if not to completion with the included pozzolana, although over time as pozzolanic reaction are known to proceed slowly. It was therefore expected, as observed, that PCDC would show the highest CaO at the early days of curing, followed by OPC then finally PPC. It was however notable that by the end of the testing period, the CaO content in PCDC was reaching almost the same level as OPC. This was a clear indication that there was, albeit slow, continued pozzolanic reaction in PCDC.

OPC showed the highest levels of the OH^- levels with no appreciable change over the curing period. PCDC on the other hand exhibited the lowest levels. Pozzolanic reaction has been cited by many workers (Arya, *et al.*, 1990; Sagoe-Crenstsil and Glasser, 1993) to reduce the pore water pH. This is despite the observation by Diamond (Diamond, 1975) that it is governed by the alkali hydroxides. In a different research, Diamond (Diamond, 1981) studied the pore solution pH, Na^+, K^+ and Ca^{2+} content for OPC and PFA blended OPCs. The PFA's used had insignificant water-soluble alkalis but appreciable amounts were released by the $Ca(OH)_2$ reaction in the test for available alkalis. He observed a lower pH level accompanied by lower alkali ions in the blends. He attributed this to dilution effect stemming from replacement of the OPC as well as activity of the pozzolana that removed a limited portion of the alkalis from the pore water. The worker observed that incorporation of alkalis into the cement products removed them from the pore solution in blended cements. He concluded that the alkalis from test PFA's did not contribute to the alkalinity of pore water. Byfors (1987) conducting similar studies, but with silica fumes and PFA blended OPC observed similar trend of lowered pH. He attributed the observations to the same reasons as Diamond.

Figures 4.1 and 4.2 showed that PPC and PCDC exhibited continued decrease in $Ca(OH)_2$ while OPC had an increase of the same as the curing period progressed. The consumption of the $Ca(OH)_2$ in the pozzolanic reaction reduces the buffering effect of the pore solution pH. Thus when a slight decrease in OH^- is witnessed, rebar in pozzolanic cement would be at high risk of attack by chlorides if available. Other workers have observed a similar scenario; Byfors (1987) and Thomas (1996) studying the chloride thresholds (Cl^-/OH^-) for OPC and blended cements, observed that the value decreased with the extent of OPC replacement. Byfors (1987) actually observed a decrease to a half and a third with silica fumes replacement levels of 10 and 20 percent by weight of OPC respectively. The advantage of the pozzolanic reaction though is to decrease permeability, increase binding ability and hence lower diffusivity of the chlorides. This in turn protects the rebar from pitting type of corrosion (Cheng, *et al.*, 2005; Hossain and Lachemi, 2004; Page, *et al.*, 1986; Taylor, 1999).

4.4 Results for Test Cements in Chloride Solutions

4.4.1 Compressive Strength

After the curing period in saturated $Ca(OH)_2$, corresponding cubes of each category were continuously immersed in the different corrosive media of study after which their compressive strength was determined. Figure 4.3 represents the percent gain in compressive strength versus test cement in simulated magnesium chloride solutions.

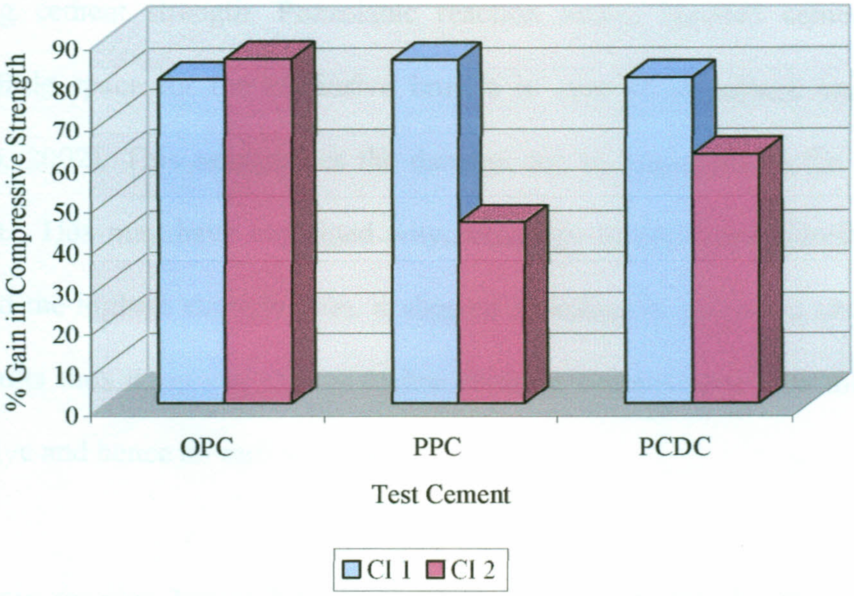

Figure 4.3: Percent Gain in Compressive Strength versus Test Cement in Chloride Solutions

There was an observed increase in strength for the test cements immersed in Cl^- simulated solutions but it was significantly lower when the Cl^- concentration was doubled in PPC and PCDC. (T_{Cal} = -15.03 and -7.50 respectively). PPC had the highest strength gain in simulated solution 1. Lorenzo, *et al.* (2003) while studying the flexural strength changes in Portland and blended cements in marine simulated media, observed an increase in flexural strength particularly in the blended cements. They attributed this to ingress of the chloride and the sulphate ions. Similar studies, although with pozzolana lime cements, were carried out by Shi and Day (2000). They (Shi and Day, 2000) also attributed the increase in the strength to the same ions. Lorenzo, *et al.* (2003) observed that the chlorides are more active in enhancing the strength gain than sulphates due to both their small charge and ionic sizes. The workers note that this enhances its diffusivity.

The attack by $MgCl_2$ on mortar introduces both the chlorides and Mg ions. Brucite is associated with Mg-attack. Brucite is expansive and can lead to cracking and hence lowering cement strength. Pozzolanic reaction makes blended cements denser. This leaves little space for the expansive brucite in case of Mg-attack on the mortar (Al-Amoudi, 2002). This exaggerates the damage due to Mg-attack in the pozzolana based cements. This may have explained why, although, at the lower chloride concentration, PPC had the highest strength gain, it showed a decline in simulated chloride 2 solution. The results thus suggested that at higher chloride concentration, the medium was more aggressive and hence an earlier Mg-attack.

Pozzolanic reaction leaves limited $Ca(OH)_2$ for the Mg-attack. The reduced $Ca(OH)_2$ leaves the CSH as the immediate culprits (Al-Amoudi, 2002). The result is formation of non-cementious MSH. The attack was not severe in PCDC compared to PPC. The less severity could be attributed to the level of substitution. Thus the pozzolanic-$Ca(OH)_2$ reaction was not expected to have consumed all the $Ca(OH)_2$ or made the mortar as dense as PPC. More so it would seem that the introduced $Ca(OH)_2$ as DALS may have offered a phase for Mg-attack prior to silica.

The results of this study were similar to ones made by Al-Amoudi (2002). The worker (Al-Amoudi, 2002) observed Mg-media to be more deleterious to blended cements than OPC. This lowers their strength development. He attributed this to the reaction of the Mg-solution with CSH as the CH had been consumed by the pozzolana included. He also observed that limited space for the expansive brucite made Mg - attack more severe in pozzolana based cements.

4.4.2 Selected Ions Analyses in Chloride Simulated Solutions

4.4.2.1 Chloride Intake and Leaching

After the 28 days curing in saturated $Ca(OH)_2$ solution, each category of mortar cube was immersed in different corrosive media for six months. The corrosive media were analysed for selected ions at certain intervals of time over the monitoring period. Figures 4.4 – 4.5 give the progressive intake and leaching of the chloride ions in magnesium chloride simulated solutions against monitoring period by mortar cubes of each category.

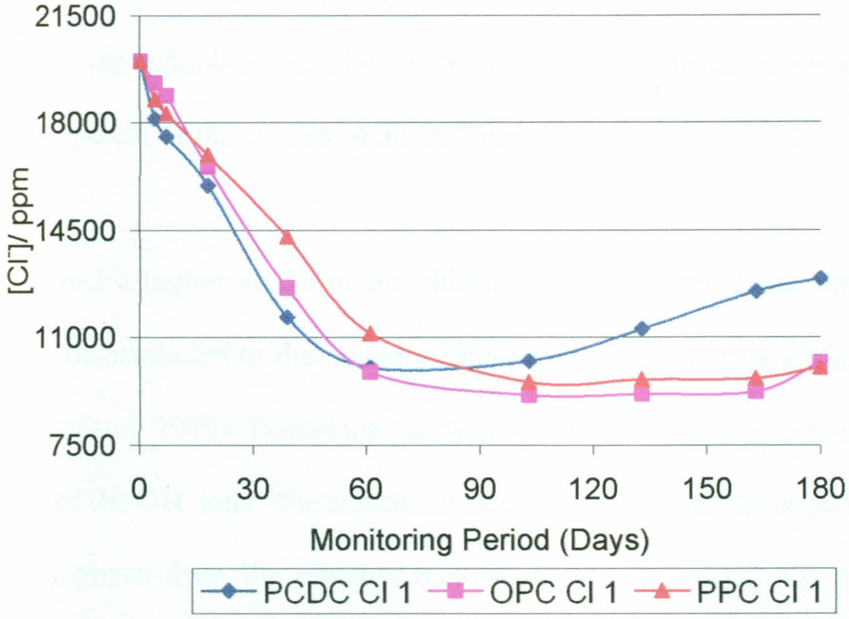

Figure 4.4: Cl⁻ Analyses in Chloride Simulated Solution 1

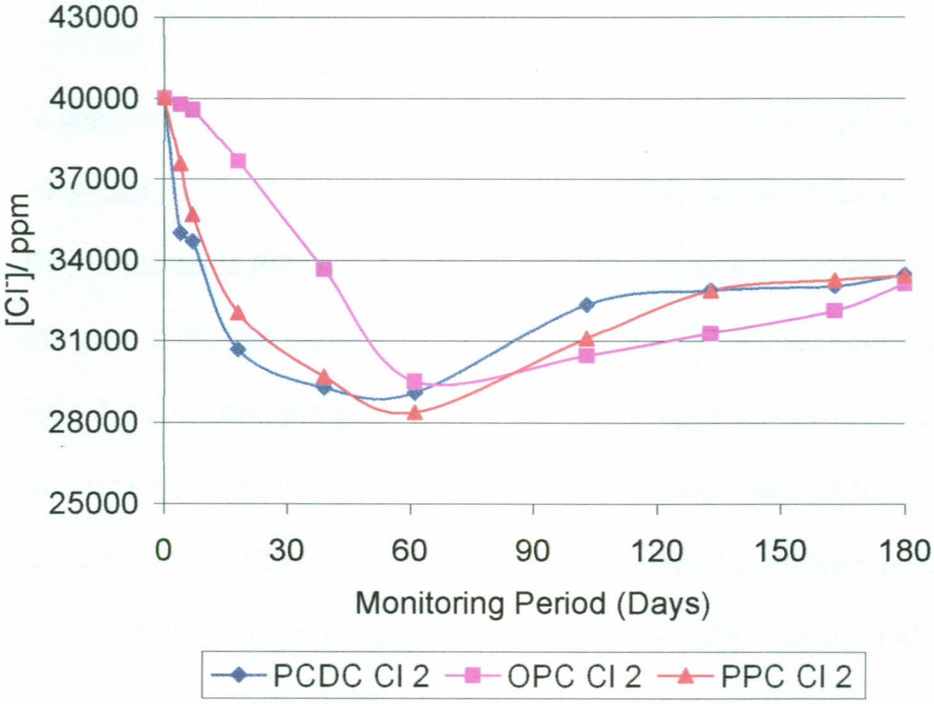

Figure 4.5: Cl⁻ Analyses in Chloride Simulated Solution 2

It was observed that in chloride simulated solution 1, the PCDC had the highest initial intake followed by an early subsequent leach in chloride ions. The high intake in PCDC could be associated to higher permeability due to the high levels of substitution coupled with lower pozzolanic reaction. This can be inferred from the lowest compressive strength development of the cement at the 28th day.

OPC had a higher intake of the chlorides than the PPC from simulated solution 1. This could be attributed to the higher exchange capacity due to a higher OH^- ions (Gj0rv and Vennesland, 1979). Pozzolana reaction lowers the $Ca(OH)_2$ content and hence the buffer store of the OH^- ions. The additional cementious material from pozzolanic reaction, higher Al_2O_3 phase from the reactive constituents of pozzolana and packaging of pozzolana grains between cements aggregates lower the diffusivity of chlorides into the bulk. This in turn lowers the intake of the ions in pozzolana based cements.

As the concentration of the chlorides is doubled, OPC showed a decreased intake of the chlorides than the PPC. Perhaps the beneficial effects above of denser mortar, reduced $Ca(OH)_2$ levels made PPC less resistant to the $MgCl_2$ attack. As observed in compressive strength gain, OPC had higher strength gain than PPC as the solution concentration was doubled. Actually, strength gains in PPC and PCDC significantly reduced as the chloride concentration was doubled. This was attributed to availability of the $Ca(OH)_2$ in OPC thus less attack on its CSH compared to PPC. PPC being denser, from pozzolanic reaction may have left little space for expansive brucite from Mg – attack (Al-Amoudi, 2002; Kurdowski, 2004)

Subsequent leaching of the chloride ions was observed in all cements. The attack by magnesium-based chlorides introduces expansive brucite in the cement mortar. This results in micro-cracking. The cracks may have availed pathways for leaching of the ingressed ions. As was observed with a reduced percent compressive strength gain, there was a higher and earlier leach from PPC as compared to OPC as the concentration of the chlorides was doubled. Lack of space for the expansive brucite in PPC may have largely contributed to micro-cracking and hence the earlier leach.

There was an observed early leach on the chlorides as the concentration of the chlorides in the media was doubled. The leach was more pronounced from chlorides 2 than from chlorides 1 solution in all cements. Perhaps this could have been due to the solution being more aggressive as the concentration was doubled.

Generally, OPC had higher strength gain and lower Cl^- intake especially at higher chloride concentrations. This is because, at initial stages of the $MgCl_2$ attack, pozzolanic reaction reactivation due to the chloride ingress improves on the microstructure of pozzolana-based cements. At later stages, as depicted by the lower strength gain at high chloride concentration, the deleterious effects of the Mg^{2+} ion in the $MgCl_2$ takes preference in the blended cements.

4.4.2.2 Sulphates Intake and Leaching from Chloride Simulated Solutions

Sulphates concentrations in the magnesium chloride simulated solutions were analysed over the monitoring period for each category of cement mortar cube. Figures 4.6 – 4.7 show the sulphates leach and intake from the chloride simulated solutions. The sulphates were observed to increase in the corrosive media rapidly up to about the 11th and 25th day in simulated chloride solution 1 and 2 respectively. The ions then showed a fast decline to an almost constant amount.

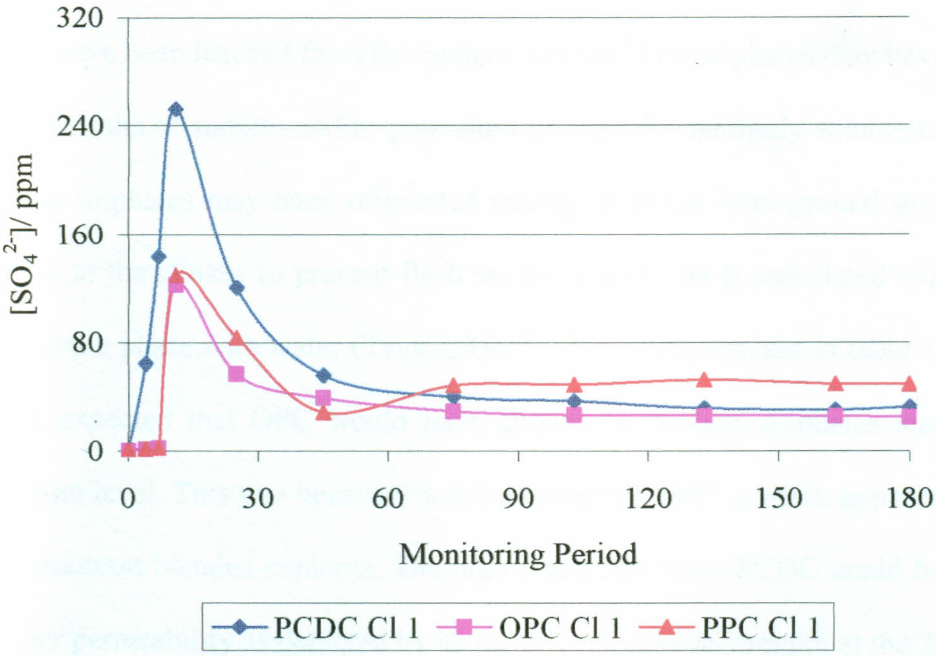

Figure 4.6: SO$_4^{2-}$ Analyses in Chloride Simulated Solution 1

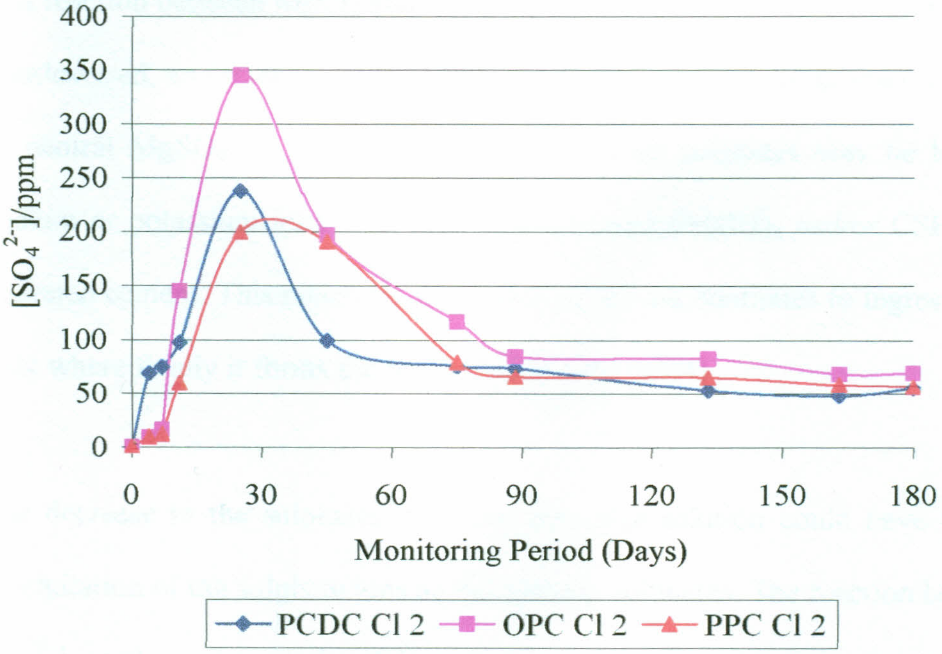

Figure 4.7: SO$_4^{2-}$ Analyses in Chloride Simulated Solution 2

The chloride solutions did not have sulphate ion in the first place and therefore the ions must have been leached from the cement mortars. The sulphates may have been leached as soluble salts of sodium and/or potassium or even the sparingly soluble calcium sulphates. These sulphates may have originated mainly from the inter-ground gypsum. Gypsum is added to the clinker to prevent flash set of cement that is associated with the reaction of aluminate phase with water (Taylor, 1997). From SO_3 content in table 4.1, it would have been expected that OPC would have shown the highest sulphates leach from its high gypsum level. This was because by substituting the OPC, a lower gypsum was expected in the resultant blended cements. The high leach thus from PCDC could be attributed to its higher permeability as depicted by its lower compressive strength at the 28th day.

The reaction between $MgCl_2$ and $Ca(OH)_2$ lowers the pH of the concrete mass. As the pH was lowered, an increase in the soluble sulphate was observed (Brown and Doerr, 2000), as neutral $MgSO_4$, in pore solution. The resultant sulphates may be leached out with sodium or potassium ions. The Mg^{2+} attacks more $Ca(OH)_2$ and/or CSH from the inner hydrated cement. This maintains Mg-attack as the ion continues to ingress into the mortar bulk where finally it forms the MSH (Kurdowski, 2004).

The decrease in the sulphates from the corrosive solution could have been due to the precipitation of the sulphate ions as the calcium sulphates. The reaction between Ca^{2+} and SO_4^{2-} is as shown in equation 4.4

$$Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2H_2O_{(l)} \longrightarrow CaSO_4.2H_2O_{(s)} \qquad 4.4$$

The sulphates could have also been precipitated due to the effect of the chlorides and hydroxides in the media. Sulphates, especially of alkalis and alkaline earth metals have a diminishing solubility in the presence of chlorides and hydroxides (Seidell and Linke, 1952).

As the concentration of the chloride solutions were doubled, the OPC showed the highest sulphates leach. This may have been attributed to a higher level of gypsum in OPC that became a vulnerable phase as the chlorides concentration increased. The substitution of the OPC with pozzolana reduces the amount of available sulphates from cements. It was notable that in both cases of chloride concentrations, the amount of leached sulphates from PCDC was about the same at the early days of subjection in corrosion media.

As monitoring period progressed, it was observed that the test-mortar cements exhibited a decline in SO_4^{2-} leach. The decline was most pronounced in PCDC especially with increased chloride concentration. With time, pozzolana-based cements become denser due to pozzolanic reactions. As observed from pozzolanicity test, PCDC showed a continued decrease in CaO, suggesting that the pozzolanic reaction proceeded, albeit slowly. Thus, PCDC became less permeable and hence less vulnerable to the aggressive media.

The increase of the chloride concentration in the aggressive media was more deleterious to OPC. The leaching of the sulphates from OPC almost doubled with the doubling of the chloride concentration. The leaching of the sulphates from PCDC reduced as monitoring period proceeded. This showed that there was continued pozzolanic reaction.

4.4.2.3 K^+, Na^+, Ca^{2+} and pH Analyses in Chloride-Simulated Solutions

Figures 4.8 – 4.10 show the results of K^+, Na^+ and Ca^{2+} analyses. Figure 4.11 shows the results of pH variation of chloride simulated solutions over a period of six months. K^+, Na^+ and Ca^{2+} are important constituents in as far as pore solution pH is concerned (Diamond, 1981). Pore solution provides the medium for cement phases reaction as well as providing alkalinity for protection of rebar against corrosion. A disruption, either by leaching or causing an imbalance of the pore system and its constituent would therefore affect the property of cement mortar or concrete involved.

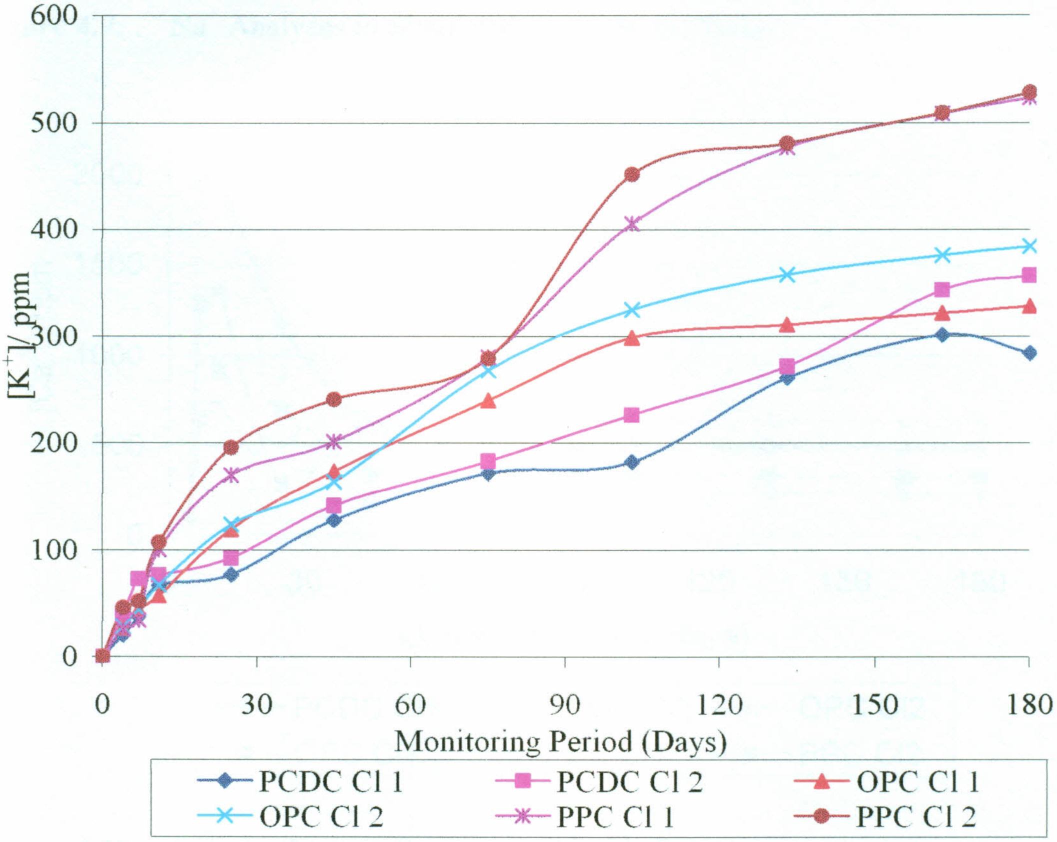

Figure 4.8: K^+ Analyses in Chloride Simulated Solution

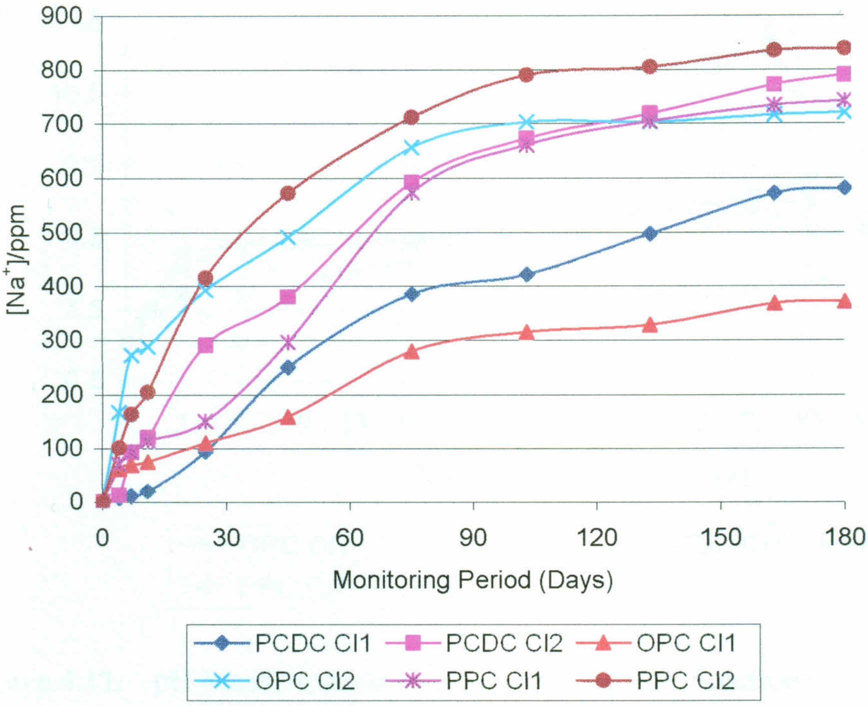

Figure 4.9: Na^+ Analyses in Simulated Chloride Solutions

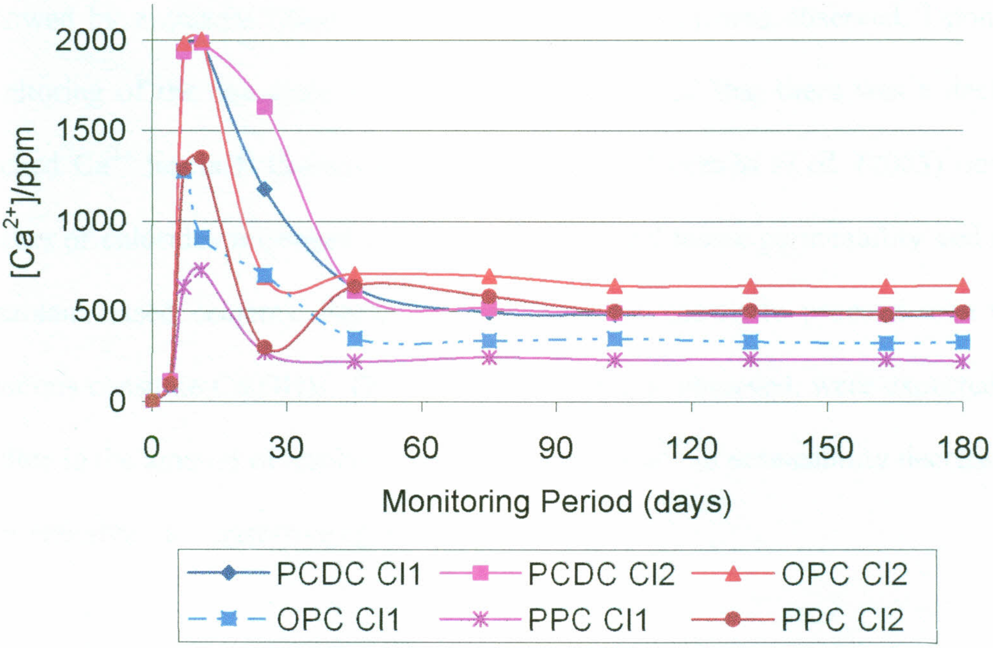

Figure 4.10: Ca^{2+} Analyses in Simulated Chloride Solutions

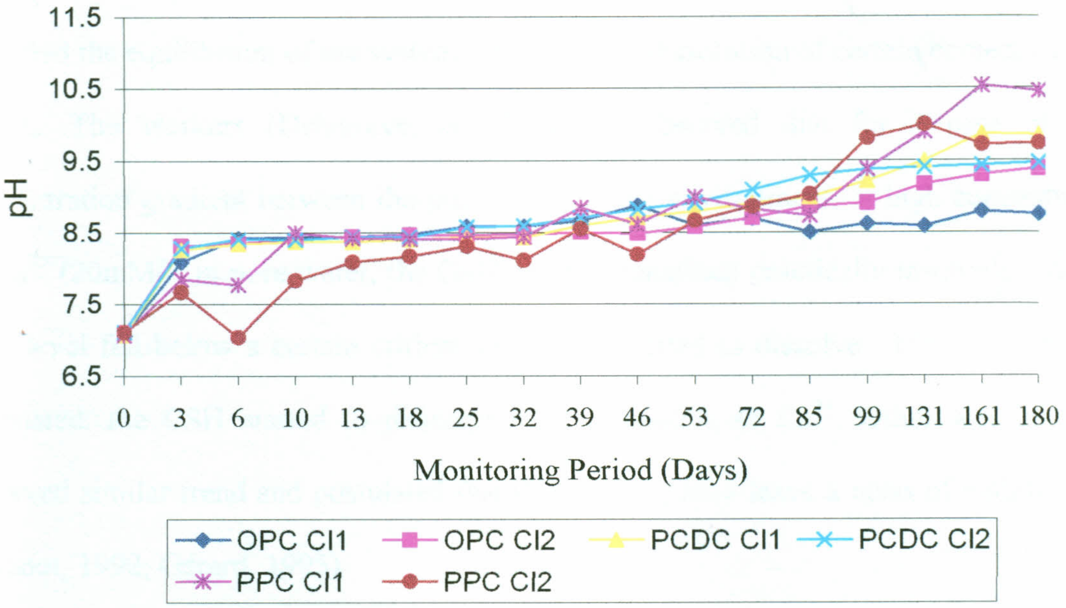

Figure 4.11: pH Measurements in Simulated Chloride Solutions

In the test solutions, an increase in the amount of leached Ca^{2+} from the mortar cubes followed by a decline immediately around the 11th day was observed. Upon continued monitoring of the test cement mortars, it was observed that there was a decline on the leached Ca^{2+} leached. Guerrero, *et al.* (2000) and Lorenzo *et al.* (2003) observed that ingress of chlorides improved the microstructure and hence permeability and strength of pozzolana-based cements. Pozzolanic reactions are known to proceed with time. The reactions consume $Ca(OH)_2$. Thus blended mortars as observed, were expected to show a decline in the amount of leached ions, for example Ca^{2+} as permeability decreased because their resistivity to aggressive agents had increased.

The leaching of the ions could be attributed to concentration gradient between the mortar cube and environmental media. This was also observed by Delagrave, *et al.* (1995). They observed that when concrete was immersed in a given medium, the chemical potential gradient between the pore solution and the environment was characterised by diffusion in and out of the material. Changes in the chemical composition of the pore solution modified the equilibrium of the system. This leads to dissolution of certain cement hydrate phases. The workers (Delagrave, *et al.*, 1995) observed that for a case of Ca^{2+} concentration gradient between the pore solution and environment, at high concentration of Ca^{2+} (20mM/l) in pore water, the CSH and CH remained practically insoluble. As the Ca^{2+} level fell below a certain critical value, CH started to dissolve. If all the CH was exhausted, the CSH started to disintegrate and dissolve as Ca^{2+}. Other workers have observed similar trend and postulated that the leaching may leave a mass of mainly silica (Adenot, 1992; Gérard, 1995).

In all the mortar cube holders containing chloride simulated solutions, there was a noticeable amount of precipitates. Some dirty white precipitates were distinguishable from traces of cement mortar deposit. The PCDC had the highest quantities of the dirty white particles. Kurdowski (2004) during examination of corrosion of different types of cements in strong chloride solutions of Magnesium observed formation of a skin upon which new products were formed. He proposed that the skin formation was due to the rapid diffusion of the chloride ion in to the interior of the paste which must have been counterbalanced by the diffusion of the OH^- in the opposite direction. Thus two fronts of high concentrations of OH^- and Cl^- met and quick precipitation of magnesium compounds occurred. This skin, he observed was mainly composed of gibbsite, Friedel's salt, halite, brucite, aragonite and basic magnesium and calcium chlorides. The worker observed that the skin was very temporary in Portland and slag cements. The white dirty precipitates may have been attributed to the above process. The temporary skins may have scaled off during the stirring times while sampling and hence the precipitates observed.

Despite PPC exhibiting a lower leach in Ca^{2+}, its compressive strength gain was least in simulated chloride solution 2. The formation of $Mg(OH)_2$ from the reaction between $MgCl_2$ and $Ca(OH)_2$ lowers the concrete pH by decreasing the buffer store of OH^- and hence the OH^-. This forces the disintegration of the calcium silicate hydrates to replenish the $Ca(OH)_2$. The resultant $Si(OH)_n$ (from disintegration of CSH) and $Mg(OH)_2$ react to give rise to MSH (Brown and Doerr, 2000) that has no cementious property. The reaction of MH with CSH is given by equation 4.5 (Mather, 1968).

$$4MH + SH_n \xrightarrow{\qquad} M_4SH_{4.5} + (n-4.5)H \qquad 4.5$$

The action is aggravated by the absence of the $Ca(OH)_2$ as the Mg^{2+} can attack CSH directly (Al-Amoudi, 2002). This makes blended cements to be more susceptible to this form of attack as pozzolana reaction consumes the $Ca(OH)_2$.

There was a marked increase in pH of the chloride solution accompanied by leaching of the alkali metal ions from the test cement mortars. Generally, contact water with concrete is expected to attain a pH value above 9 or almost at equilibrium with the pore water. This corresponded with the leach of the alkali ions observed in all the test cements.

The ingress of the Cl^- is accompanied by leaching (in exchange) of the OH^- from the cement paste. This introduces OH^- from the pore solution into the corrosive media which attains pH equilibrium between the pore water and cement mortar environment. This could also be achieved through ionic transfer (Adenot and Buil, 1992). The pore solution has been found to be mainly constituted of alkali hydroxides, SO_4^{2-} and small amounts of Ca^{2+} (Constantiner and Diamond, 1992). These ions can thus be leached with OH^- to help attain pH equilibrium with the external solutions. In all the cements, the K^+ ion was highly leached from the mortar cubes, perhaps due to its higher concentration than the Na^+ in the pore solution (Diamond, 1975).

The leaching of the alkali ions continued up to a certain point where it almost attained a constant amount. This is a similar scenario observed by Herold (1995), who analysed for the Ca, Mg, Fe, Al, Si, Na and K in solutions where hardened pastes of OPC with w/c ratio of 0.5 were immersed. The worker (Herold, 1995) observed that there was a marked reduction in leaching in stationary systems. The worker attributed this to the growth of residual protective layer which changed the dissolution rate from reaction controlled to a diffusion controlled process. The worker also attributed the decline in leaching of the ions to the growth of temporary concentration build up in the corrosive media which caused a depression of the dissolution behaviour of the paste.

It was observed that the alkali metal ions were preferentially leached in PPC. The higher leaching of alkalis in PPC may be attributed to the observed higher pH in the chlorides solutions. Perhaps the micro-cracking associated with Mg-attack was more severe in PPC as exhibited even by the compressive strength especially at higher concentration levels. This may have made the cement more porous and hence highly leached.

The leaching of the alkali and alkali earth metal ions is deleterious as it may lead to disintegration of the CSH. The leach could also lead to loss in concrete strength, lowering of the pore pH hence breakdown in passivity of reinforcement. It would also lead to disruption of the media through which concrete phases and reactions are held. PPC exhibited the highest main ions loss for maintenance of the pore pH, for example Na^+, an important aspect in concrete system.

4.5 Chloride Profiling

Figures 4.12 – 4.14 show the chloride profiles against depth of cover of each category of the mortar cubes. Chloride profile analyses in this study involved the determination of the concentration of the ions (Cl^-) at different depths of cement mortar bulk of PCDC, OPC and OPC + PFA. The analyses were carried out after about six months of subjecting the mortar cubes to alternate dry and wet cycles (in this case complete immersion) of 3.5 percent sodium chloride solution. The analyses were done at different w/c ratios of each cement type. Generally, blended cements are expected to show reduced chloride ingress in to the bulk compared to OPC. This was observed in this study.

As the w/c ratio increased, there was a marked rise in the total chloride ingress in all the profile depths of the test cements. Blended cements, OPC + PFA and PCDC, showed a lower total chloride ingress than OPC. The order was OPC + PFA< PCDC<OPC. PCDC showed a sharp decrease in chloride ingress as the depth of cover increased. This was even more pronounced as the w/c ratio reduced.

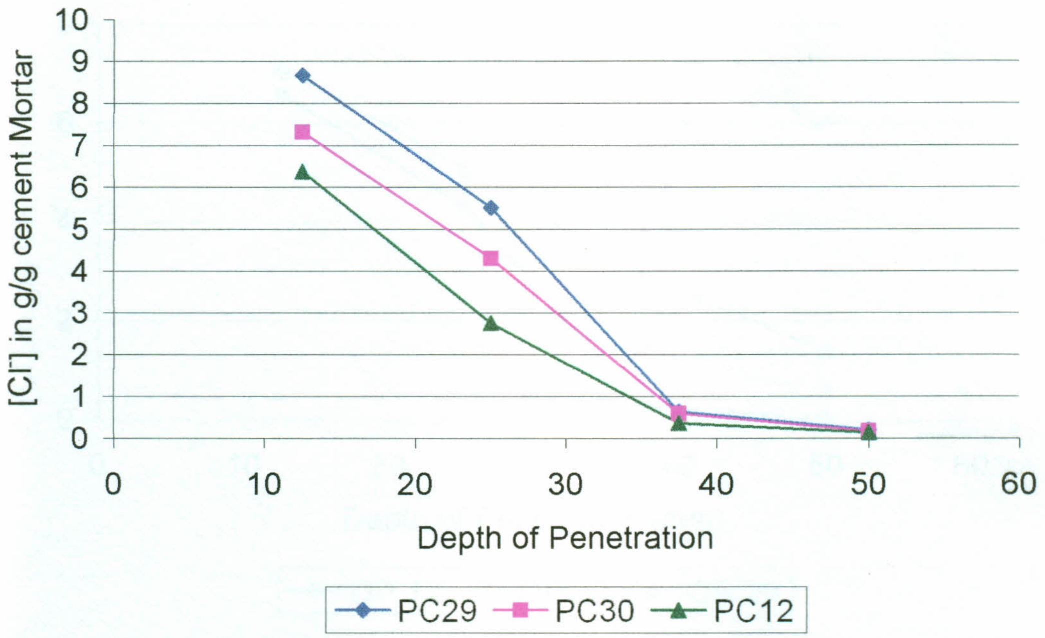

Figure 4.12: Chloride Profile for PCDC against depth of cover

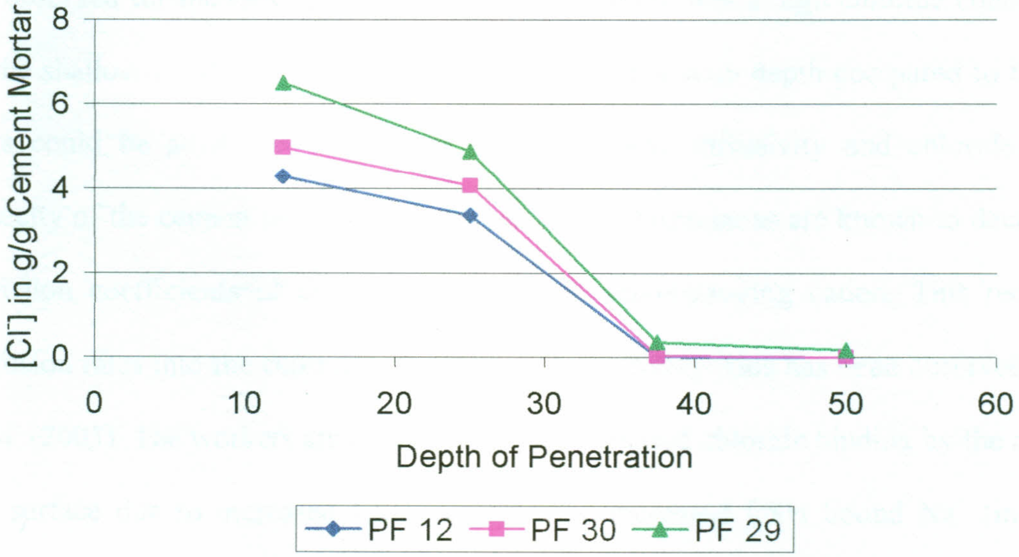

Figure 4.13: Chloride Profile for OPC- 25 %PFA against depth of cover

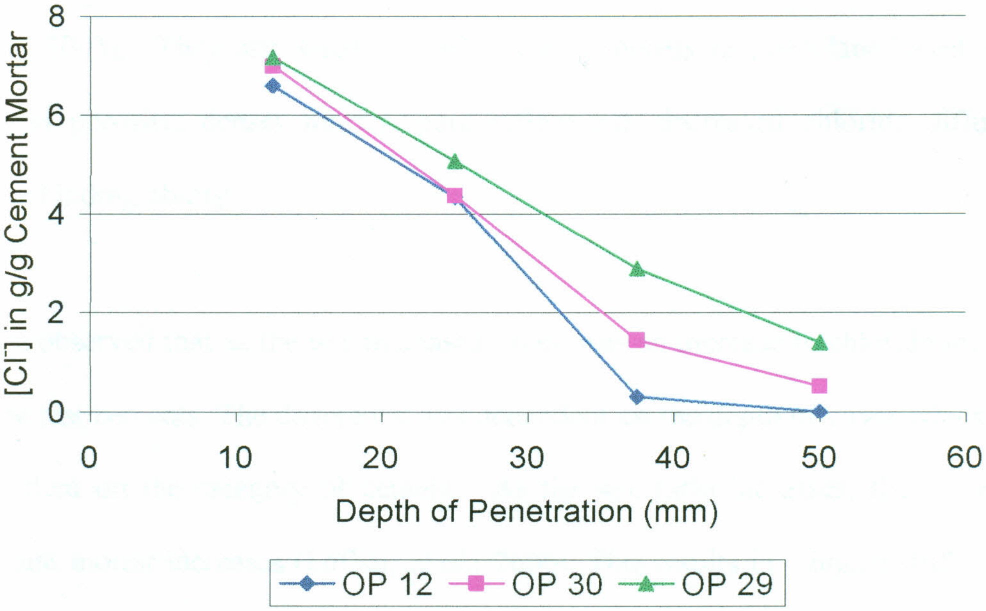

Figure 4.14: Chloride Profile for OPC against depth of cover

As observed for the OPC-25 % PFA and PCDC, there was a high chloride concentration at the shallow depths of cover, which decreased more with depth compared to the OPC. This could be attributed to changes in the intrinsic diffusivity and chloride binding capacity of the cement involved (Bai, *et al.*, 2003). Pozzolanas are known to decrease the diffusion coefficients of chlorides for a given accompanying cation. This reduces its diffusion rates into the cement bulk (Oh and Jang, 2007). This has been observed by Bai, *et al.* (2003). The workers attributed this to the increased chloride binding by the mortar at the surface due to increased CSH content. The increased CSH bound Na^+ (in case of NaCl) (Barberon, *et al.*, 2005) and hence retarded the diffusion of the chloride.

As the depth of profile increased, it was observed that the OPC exhibited the highest chloride ingress especially at higher w/c ratios. Since blended cements have lower $Ca(OH)_2$ and hence OH^- store than OPC in their pore solution, the exchange capacity between the OH^- and the chlorides in the pore water is thus lower (GjØrv and Vennesland, 1979). Several workers have made similar observations (Hossain and Lachemi, 2004; Luo, *et al.*, 2003). They attributed the reduction in ingress in pozzolana-based material to reduced porosity, denser mortar, pore refinement, decreased chloride diffusivity and higher binding ability.

It was observed that as the w/c increased, there was an increase in chloride ingress across all the test cements. The difference was dependent on the depth of cover which was again dependent on the category of cement. As the w/c ratio increases, the porosity of the resultant mortar increases (Lafhaj, *et al.*, 2006). This results in a higher diffusivity of the chloride into the mortar (Midgley and Illston, 1984). Figures 4.13 and 4.14, for example, showed that for blended cements, the difference was experienced at the shallow depths of cover (T_{cal}-value for OPC -25 % PFA between the 0.80 and 0.73 w/c ratio is 79.29 way above the T_{crit} = 12.71 for the shallow depths of cover). For OPC, the difference due to w/c was within the bulk. These observations were similar to ones by Gjørv and Vennesland (1979). They observed that the difference was only pronounced at depths of less than 20 mm for blended cements. Yiğiter *et al.* (2007) observed a similar trend where the OPC chloride penetration depths were affected by varied w/c ratio as opposed to silica fume blended OPC.

From the study, it was found necessary to plot comparative graphs between the different cement types for each w/c ratio. This helped to obtain a clear picture of the differences, if any, on the ingress of the chlorides into the cement mortars. Figures 4.15 – 4.17 show the chloride profiles of the different categories of cements at specified w/c ratios.

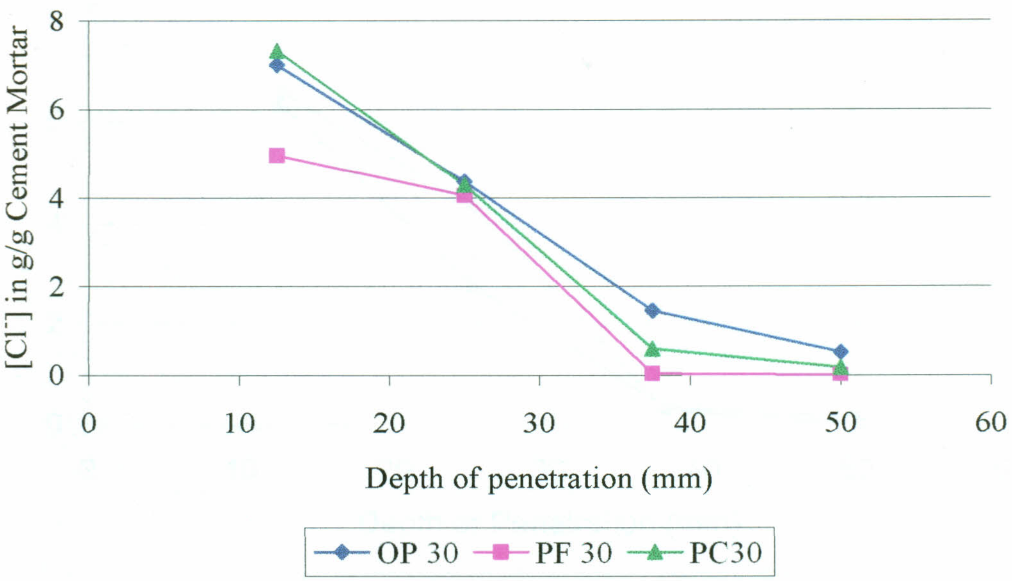

Figure 4.15: Chloride Profile for the Test Cements at 0.8 w/c Ratio

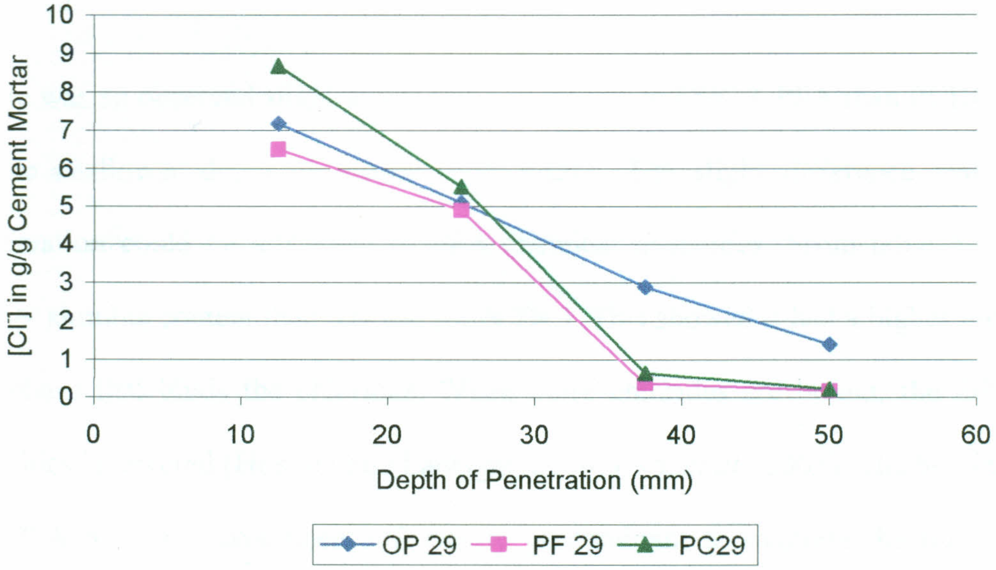

Figure 4.16: Chloride Profile for the Test Cements at 0.85 w/c ratio

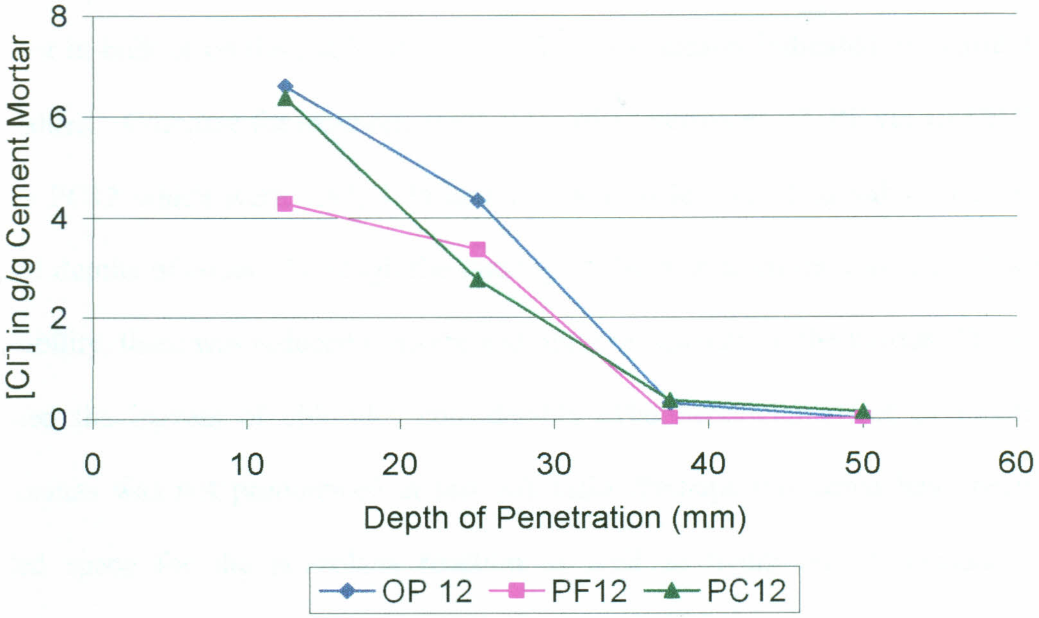

Figure 4.17: Chloride Profile for the Test cements at 0.73 w/c ratio

There was an observed slight lower chloride ingress in OPC + PFA than PCDC especially in the shallower depth of profile (<25 mm). The slight difference and hence the observation could be attributed to PFA chemical properties. From table 4.1, PFA had higher alumina content than test ash (in PCDC). This showed it had a higher proportion of the phase that binds the chlorides. When more chlorides are bound, the diffusivity of chlorides is lowered (Hossain and Lachemi, 2004; Luo, *et al.*, 2003). The binding effect of the PFA may not have been sufficiently predominant to override the other beneficial effects of pozzolana in improving the resistance of the blended cements. It would then seem that the reduction in porosity due to additional cementious material from pozzolanic reaction and the packaging of the pozzolana grain between aggregates and cement grains played a significant role in improving the resistance of the blended cements (Cheng, *et al.*, 2005; Hossain and Lachemi, 2004). Bai *et al.* (2003) observed that due to pozzolanic reactions, the pores become finer and hence the chloride diffusivity dropped.

At the least w/c ratio (0.73), the difference between cement type was not significant whether in bulk or on the shallower depths. This was clearly indicated by figure 4.17 and T_{cal} values. Compare for example, the T_{cal} for PF12 versus PC12, PF versus OP12, OP12 versus PC12 which were 0.87, 1.75 and 1.01 way below the T_{Crit} value of 3.18 for the overall depths of cover. Although the making of the mortar cubes was marred with poor workability, there was reduced porosity and higher resistivity of the mortar. These aspects reduced the ingress of chlorides considerably. The beneficial effect of incorporating pozzolanas was not pronounced at this w/c ratio. Perhaps this could have been due to limited space for the pozzolana reaction as well as hydration of residual cements. Decreased w/c ratio is a well known factor in increasing the resistance of concrete/mortar by lowering permeability and porosity (Lafhaj, *et al.*, 2006; Midgley and Illston, 1984).

It was generally observed that PCDC and OPC + PFA, offered a greater resistance to chloride ingress compared to OPC. The beneficial factor for blended cements was more pronounced in the bulk of the mortar as opposed to the surface. The opposite was true for OPC. The blended cements were thus observed to exhibit resistance to chloride ingress as expected. PCDC exhibited a significant drop in chloride ingress in its bulk. This showed that PCDC would offer a long term resistance to chloride ingress. This could be attributed to its continued hydration from pozzolanic reaction.

4.6 Apparent Diffusivity Coefficients

Figure 4.18 shows one of the error fitting curves for apparent chloride diffusion coefficients (D_{app}) of the OPC cement mortar. Similar curves were used for determination of the apparent diffusion coefficients for each cement category. These curves are given in appendix A. In this study, the equation to the solution of the Fick's second law under non

– steady state conditions for diffusion in a semi – infinite solid was used. D_{app} values in the range of 10^{-11} to 10^{-13} m^2/s depending on concrete (Bertolini, *et al.*, 2004) are normally obtained. Table 4.2 shows the D_{app} and corresponding r^2 values obtained from the error fitting curves for the different cement categories and w/c ratios.

Blended cement mortar exhibited lower chloride apparent diffusion coefficients (D_{app}) than OPC except for OPC + PFA at w/c of 0.73 where it was higher than its corresponding OPC. The D_{app} increased with increasing w/c ratio in all cement mortar categories. The increase was even more pronounced for OPC especially from the 0.8 to 0.85 w/c ratio. Apparently, as would have been unexpected from higher chloride ingress in the mortar chloride profiles, the PCDC exhibited lower D_{app} than its corresponding OPC-25 % PFA and OPC. OPC-25 % PFA did not really show a predominantly classical Fickian diffusion process of chlorides.

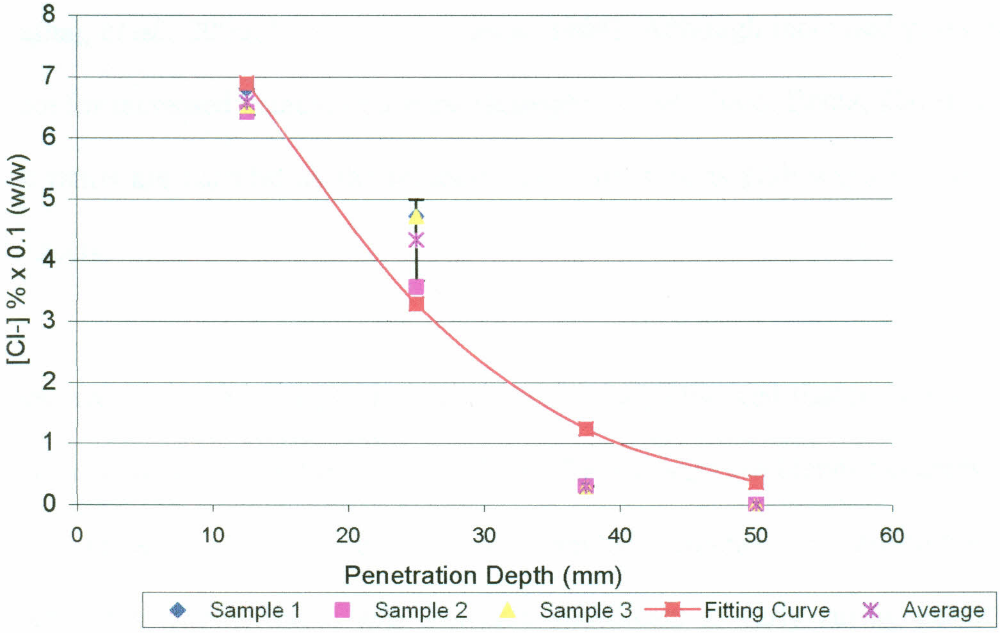

Figure 4.18: Error Function fitting for OPC (w/c ratio 0.73), D_{app}= 1.85 x $10^{-11}$$m^2/s$, and C_s = 1.117 % (r^2 = 0.9346)

Table 4.2: D_{app} and r^2 – Values for different cement mortars and w/c ratios

Cement type	w/c	D_{app} (x $10^{-11} m^2/s$)	r^2 - Value	C_s (%)
PCDC	0.73	1.34	0.9934	1.219
	0.8	1.81	0.968	1.285
	0.85	1.91	0.9506	1.513
OPC	0.73	1.85	0.9346	1.117
	0.8	2.5	0.9864	1.111
	0.85	4.27	0.9945	1.008
OPC + PFA	0.73	2.01	0.87	0.76
	0.8	2.09	0.8505	0.879
	0.85	2.12	0.8969	1.124

Increasing w/c ratio increased diffusivity of chloride. High w/c ratio affects porosity (Lafhaj, *et al.*, 2006; Midgley and Illston, 1984). Although increased porosity gives more room for increased cement hydration (Baroghel, *et al.*, 2006; Bentz, 2006), extremely high w/c ratios are harmful as the increased porosity acts as path ways for harmful ions and products.

Some workers, for example, Hossain (2003; 2005) observed that high w/c ratio increased porosity and hence the diffusion coefficient for volcanic ash blended cement. He (Hossain, 2003; Hossain, 2005) noted that for blended cements, the difference in diffusion coefficients with different w/c was only significant at early curing period but became insignificant with time. The opposite was observed for OPC which was found to decrease up to a certain time then increase thereafter with the increase being very dependent on the w/c ratio.

From the chloride profiles, there were no significant differences in the bulk of the mortar between the different w/c ratios for the blended cements. As observed by other authors (Hossain and Lachemi, 2004; Nokken, *et al.*, 2006; Yeau and Kim, 2005), the beneficial effects of blended cements were pronounced with curing time. This contributed to the increased resistance to chloride penetration even over varied w/c ratios for blended cements (Nokken, *et al.*, 2006). It was observed that there was significant difference in chloride profile for the OPC between the w/c 0.73 and 0.85 as well as 0.8 and 0.85 but no significant difference between 0.8 and 0.73. This showed that chloride diffusivity significantly increased with increase in w/c for OPC in the bulk.

Table 4.2 shows corresponding higher surface concentrations (as C_s %) for PCDC mortar than the other test cements for a given w/c ratio. But as was observed from the chloride profiles, the diffusion into the bulk diminished (figures 4.15 – 4.17). This was clearly indicated by the D_{app} in all w/c ratios which were the lowest for PCDC. Hossain and Lachemi (2004) observed a decreased diffusion coefficient with curing time for the highly substituted cements. The observations were similar to PCDC that had a high cement replacement level. The phenomenon could be explained by the lower pozzolanic reaction that becomes important with time. The reaction results in additional cementious material that makes the concrete denser with increased resistivity and hence lower chloride diffusivity. Kim and Yeau (2005) observed a similar scenario but with ground granulated blast furnace slag (GGBS). They observed a reduction in diffusion coefficient of chloride that was continuously lowered with increased curing time and replacement levels.

It was observed that in trying to fit the error function in OPC + PFA chloride profile results to obtain the D_{app}, the fitting was not as good as in the other cement mortar categories as depicted by the correlation coefficients, r^2 – values, which were the lowest. It would seem that the diffusion did not match a classical Fickian curve. It may have implied that there were processes other than pure diffusion involved. Thus the behavior could not be explained by, for example, changes in porosity (which would just change D_{app}), but it may imply something such as Cl^- adsorption that essentially takes Cl^- out of action. Some workers (Thomas and Matthews, 2004) attributed the poor approximation of the diffusion coefficient of PFA blended cements, using the error function, to capillary suction rather than diffusion alone. Perhaps the most probable explanations would be the binding ability as well as adsorption of the PFA blended mortar due to the high aluminium content as observed from the chemical analyses in table 4.1. The binding and/or adsorption may have played a predominant role especially at the surface of the mortar, thereby building a high surface concentration and creating an extremely lower bulk concentration. It would then imply that the binding and/or adsorption affected the diffusion process in a manner that it occurred in 'step – wise' diffusion. In this way, there would have been like a build up of chloride concentration steps after which the chlorides would diffuse into the bulk. It has been observed that PFA chloride binding capacity has a significant effect on the chloride diffusion and diffusivity (Martín-Pérez, *et al.*, 2000; Oh and Jang, 2007).

It was observed that the blended cements showed lower apparent diffusion coefficients with PCDC exhibiting the lowest D_{app} at all w/c ratios. The low D_{app} would thus be expected to mean lower chloride ingress. But as the chloride profile showed, the ingress was significantly lowered at greater depths of cover in the blended cements. It would thus imply that while using the cements in structures requiring reinforcement bars, then caution has to be taken on the depths of cover.

4.7 Corrosion of Rebar in Simulated Reinforced Concrete

In this analysis, mortar cubes were subjected to dry and wet cycles of NaCl solution. Corrosion current densities and potentials were measured during the wet cycles. Rebars with corrosion current densities of above 0.1μA/cm^2 were considered to have attained active corrosion. Similarly, rebars with corrosion potential below -270 mV (versus saturated calomel electrode) were considered to have attained active corrosion. These have been shown as the 'limit lines' in log corrosion current densities and corrosion potentials verses monitoring period graphs respectively in figures 4.19 – 4.26. Figures 4.19 – 4.22 show the average log corrosion current densities and corrosion potentials of rebars versus monitoring periods in simulated reinforced mortar cubes made from PCDC and OPC at w/c 0.85.

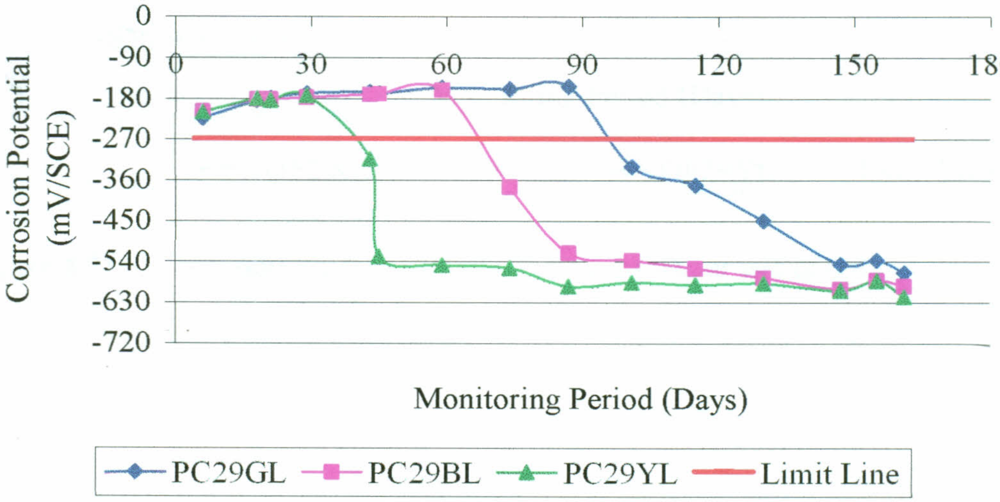

Figure 4.19: Corrosion Potential Verses Time for PCDC at w/c of 0.85

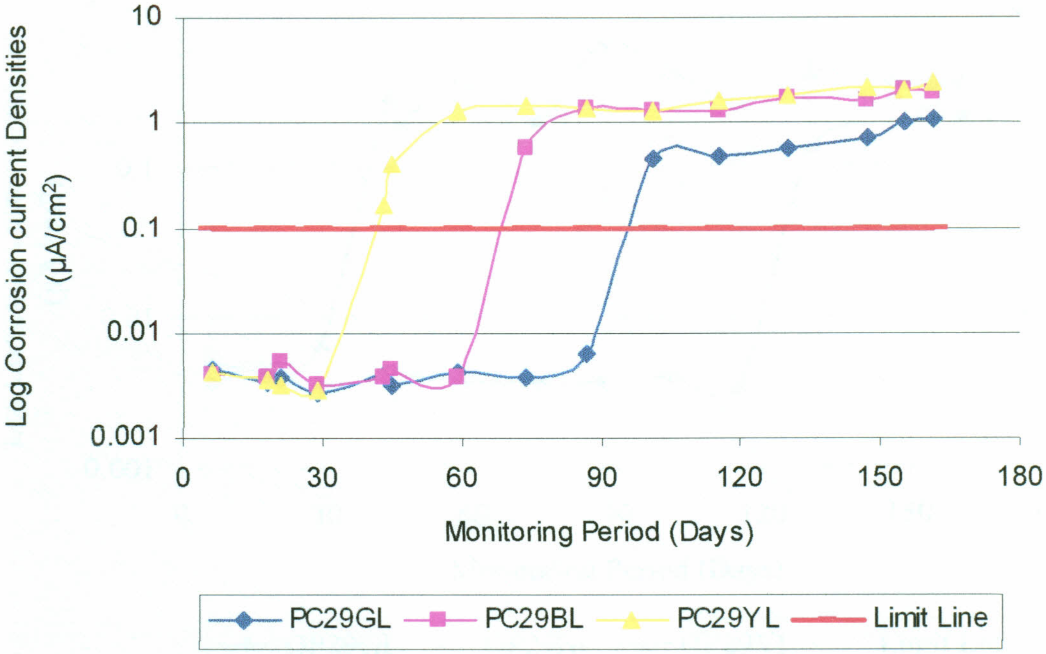

Figure 4.20: Log Corrosion Current Densities Verses Time for PCDC at w/c 0.85

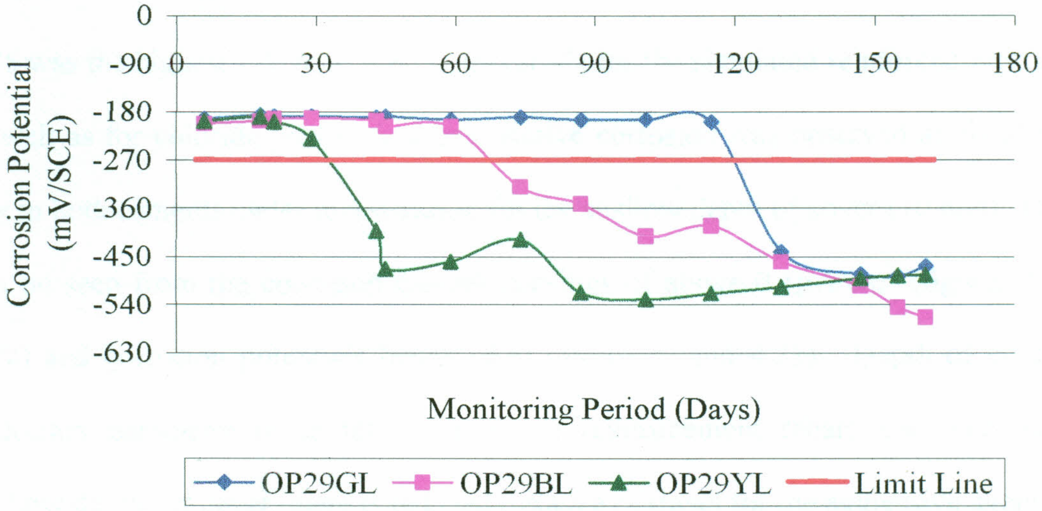

Figure 4.21: Corrosion Potential Verses Time for OPC at w/c of 0.85

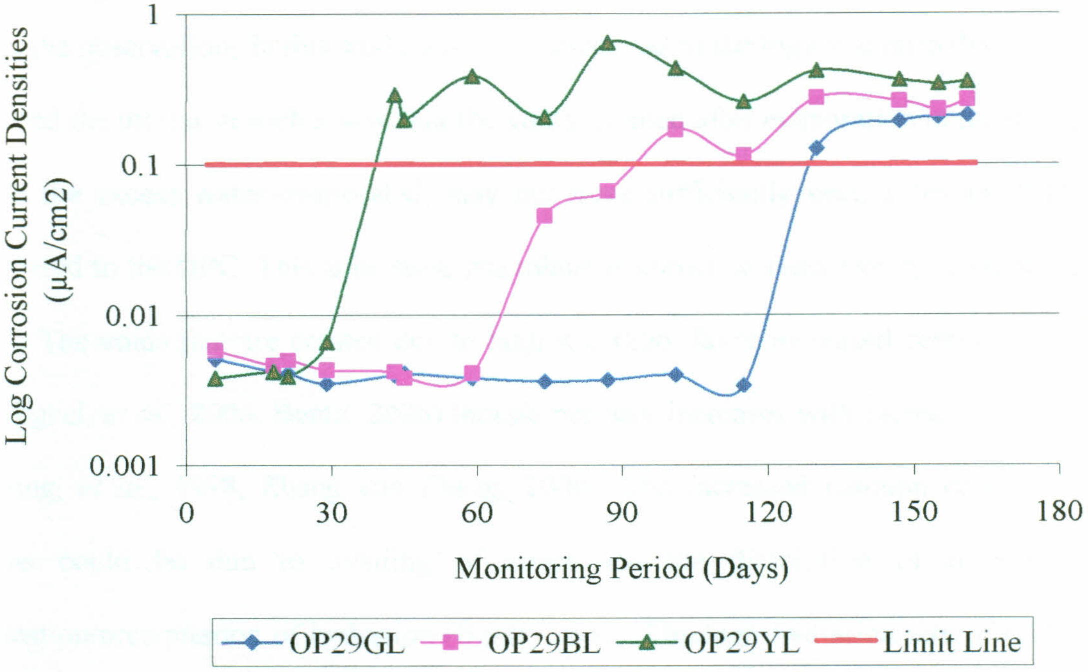

Figure 4.22: Log Corrosion Current Densities Verses Time for OPC at w/c 0.85

0.85 was the highest w/c ratio used in this study for the simulated reinforced mortar cubes as well as for chloride profile analyses. Active corrosion was observed at about the 43rd day in both cements under investigation for the shallow depth of cover (10 mm). This is as can be seen from the corrosion current densities of above 0.1µA/cm^2 (figures 4.20 and 4.22) and corrosion potentials below -270 mV (4.19 and 4.21). Depth of cover is an important parameter in as far as corrosion reinforcement rebars are concerned. For shallow depths of cover, there is reduced distance of travel for the aggressive agents.

From chloride profile analyses (figure 4.16), it was observed that PCDC had higher chloride ingress levels than OPC at this w/c ratio at the shallower depths of cover (below 20 mm). It was therefore expected, as observed, that initiation of active corrosion of the PCDC's rebar would occur earlier than OPC's. Blended cements with pozzolana (not with $Ca(OH)_2$ as in this case) show greater resistance to chloride ingress than OPC

(Cheng, *et al.*, 2005; Page, *et al.*, 1986; Thomas, 1996; Thomas and Matthews, 2004). Then the observations in this study would be attributed to the high w/c ratio that may have affected the mortar in such a way that the voids, created after evaporation in the dry spells when the excess water evaporated, may not have sufficiently been filled in PCDC as compared to the OPC. This is because pozzolana is known to react slowly as compared to OPC. The voids that are created due to high w/c ratio, favor increased cement hydration (Baroghel, *et al.*, 2006; Bentz, 2006) though porosity increases with increase in w/c ratio (Young, *et al.*, 1998; Zhang and Zhang, 2006). The increased reaction of the cement grains could be due to availing of space for the dissolution of reactants and nucleation/precipitation of hydration (Bentz, 2006). The high hydration rate of OPC may have substantially reduced its porosity compared to the PCDC. The beneficial effect of pozzolana blend may have been overridden by the porosity due to high w/c ratio.

The inclusion of lime in cements is known to increase porosity (Arandigoyen and Alvarez, 2006; Arandigoyen, 2007; Mosquera, *et al.*, 2006). Mosquera, *et al.* (2006) studied the effect of incorporating slaked lime in Portland - PFA cements. He observed that the higher the Portland – PFA binder was substituted with the lime, the higher was the porosity and vapor transport of the resultant mortar. PCDC has a significant proportion of lime added in form of DALS. This may have served to increase porosity of the cement mortar at the initial stages of curing. As observed from the chloride profiles, the chloride ingress was reduced as the depth of cover increased. This would suffice to suggest that there was continued pozzolanic – lime reaction as curing proceeded, which reduced the porosity of the PCDC mortar. The observations were further supported by the pozzolanicity analyses which showed a decreasing CaO as curing proceeded.

Upon attainment of active corrosion by the 0.85 (w/c) cements, PCDC's rebar registered higher I_{corr} than corresponding OPC's rebar. Some workers have attributed this to the lowering of pore pH by the pozzolanic reaction (Arya, *et al.*, 1990). Arya and Xu (1995) studied the chloride binding ability and its influence on the rate of corrosion on OPC and its blended cements of GGBS, PFA and SF. The workers (Arya, 1995) observed that despite higher chloride binding ability of blended cements and higher chloride concentration in OPC's pore solution, the corrosion rates of the rebars in OPC were lower than the blended cements. They attributed the higher corrosion rates to a lower OH^- in the blended cements pore solution. Byfors (1987), Diamond (1981) and Arya, *et al.* (1990) have attributed the decline in pore solution OH^- to both dilution factor (lower OPC content) and chemical activity of the fly ash. These factors may have affected the PCDC cements and hence its rebars exhibited higher corrosion rates compared to OPC's.

Figures 4.23 – 4.26 show the corrosion potentials and log corrosion current densities versus monitoring period for the cement of specified category at w/c 0.8. As the w/c ratio was reduced from 0.85 to 0.8, there was increase in the period before which the rebars attained active corrosion.

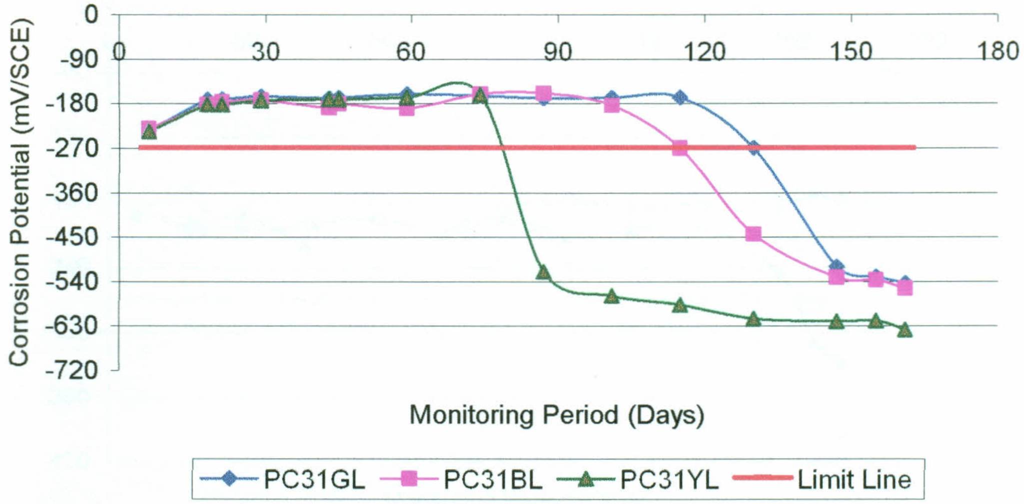

Figure 4.23: Corrosion Potential Versus Time for PCDC at w/c of 0.80

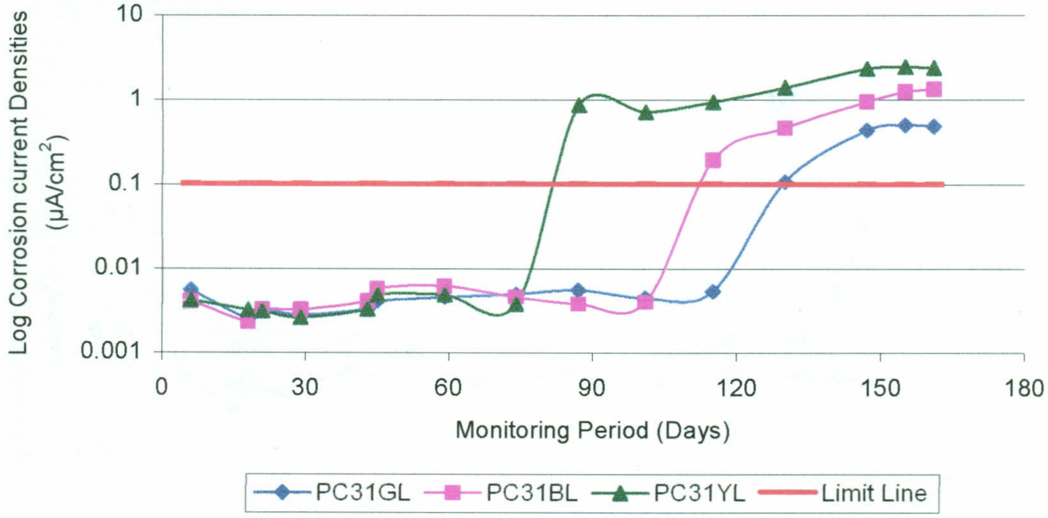

Figure 4.24: Log Corrosion Current Densities Verses Time for PCDC at w/c 0.80

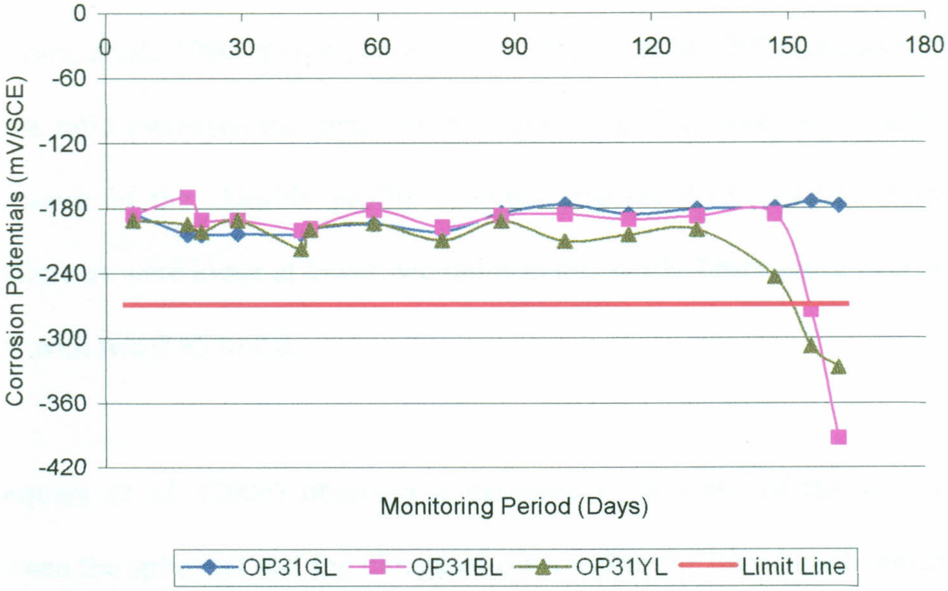

Figure 4.25: Corrosion Potential Verses Time for OPC at w/c of 0.80

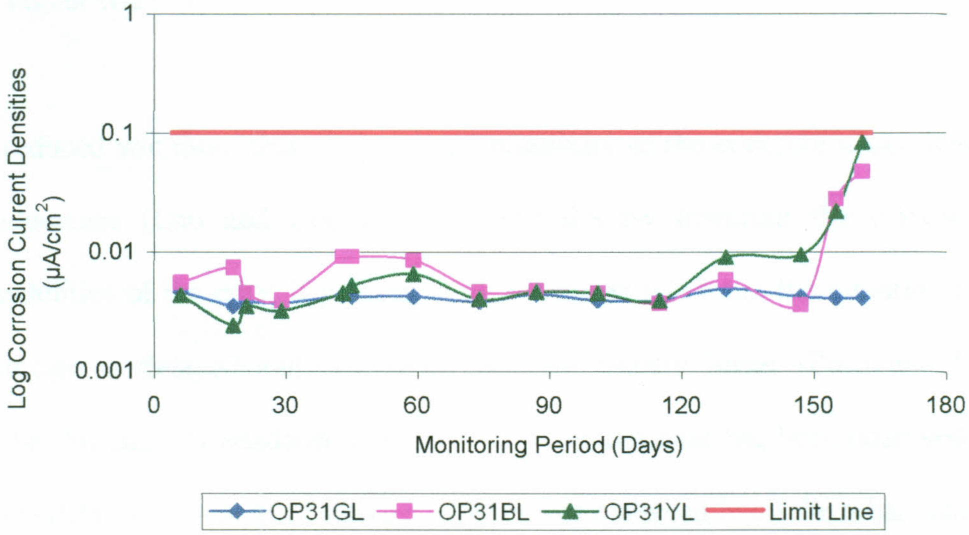

Figure 4.26: Log Corrosion Current Densities Verses Time for OPC at w/c 0.80

At this water to cement ratio (0.8), there was delay in rebar corrosion initiation time for both cements compared to the w/c of 0.85. This was due to reduced porosity and hence diffusivity of the chlorides and oxygen. Lower w/c is a well known factor that reduces the permeability of concrete and hence diffusivity of aggressive agents (Rasheeduzzafar Al-Saadoun, *et al.*, 1990; Yiğiter, *et al.*, 2007). Yiğiter *et al.* (2007) observed that an increase in w/c ratio increased the penetration of chlorides. This was also clearly observed from this work in the chloride profile analyses (figures 4.15 – 4.17). Apparent diffusion coefficients were lower at lower w/c ratios in this work. There was a decrease in D_{app} from OPC with w/c 0.85 to 0.8.

Mosquera *et al.* (2006) observed a decrease in porosity of the interconnected pores between the spherical and the elongated ones within the lime-based cement mortar as the w/c ratio reduced. Since there was lime added to the PCDC as DALS, the effect of reduced porosity due to lower w/c ratio must have been experienced in the PCDC. This may have resulted in the increase in initiation time for the rebars corrosion as compared to the higher w/c ratio.

At reduced w/c ratio, there is increased resistivity of the concrete which lowers the ionic conductance (Cao and Chung, 2005) and thereby lowering the corrosion rates and possibilities of the rebar if present. With a reduced w/c ratio, the initiation time of active corrosion is delayed and corrosion rates are usually lower (Pech and Castro, 2002; Rasheeduzzafar Al-Saadoun, *et al.*, 1990). A similar case has been observed in this study where delayed initiation of active corrosion was observed in all the rebars compared to the higher w/c (0.85).

Increasing w/c ratio is known to increases the oxygen diffusivity into the mortar cubes (Kobayashi and Shuttoh, 1991). Oxygen diffusion is an important factor that plays a major role in the corrosion of the rebar. This is because oxygen is the main cathodic reaction in rebar corrosion (Kobayashi and Shuttoh, 1991). At higher oxygen diffusivity, the cathodic reaction is high, so is the anodic (rebar corrosion) and therefore the corrosion rate. Oxygen dissolved in the pore solution is important in as far as maintaining the passivity (iron oxides films on the rebar). This prevents the rebar from corrosion. Sustenance of corrosion (pitting type in this case) is dependent on the sufficient supply of oxygen through the cathodic reaction on the passive film (Page, 1988).

PCDC's rebar still showed an earlier active corrosion initiation of the rebars at 15 and 20 mm depths of covers compared to OPC's. At the 87th and 115th day for 10 and 15 mm depths of cover respectively, PCDC's rebar had shown a shift from the 0.001 to 0.1 μA/cm^2 corrosion current densities and a shift of corrosion potential to more active values of below -270 mV (versus SCE). This implied active corrosion as per Erdogudu *et al.* (2001) and ASTM C – 876 (2005d) (versus SCE) criteria. As observed in the chloride profile studies in this work, PCDC had the effect of decreasing chloride ingress. At this w/c ratio, up to about 25 mm depth of cover, there was no significant difference in chloride ingress between OPC and PCDC. Byfors (1987), Diamond (1981) and Arya, *et al.* (1990) while studying the effects of pozzolana based materials in blend with OPC on pore solution observed that blended cements exhibit lower pore pH than pure OPC. Below pH 13.5, the Cl^-/OH^- threshold is drastically reduced (Gouda, 1970). Byfors (1987) observed that the reduction in pore pH would not cause corrosion of the rebars without presence of chlorides or carbonation. A reduction of the OH^- in presence of chloride, on the other hand, the worker noted, will result in a lower threshold value for the chloride. The author (Byfors, 1987) warned that at a certain chloride concentration which would not cause corrosion in OPC's rebars could suffice to initiate corrosion in concrete with the blends. At a lowered pH, the calcium chloroaluminate solubility is lowered and hence the bound chlorides are let free into the pore solution and hence can initiate corrosion (Arya, *et al.*, 1990). It would then appear that the PCDC's rebars in this study attained active corrosion at a chloride concentration that did not initiate corrosion in OPC's rebars as postulated by Byfors (1987).

OPC rebars at this w/c ratio did not attain active corrosion as indicated by the corrosion current densities. Observations from the corrosion potentials (versus SCE) and visual examination of rebars, after dismantling the cubes, indicated that there was active corrosion of the rebars at the depth of 10 mm and a very slight corrosion on rebars at 15 mm. Probably the time interval of dismantling of the mortar cube and last measurement of the rebars may have attained appreciable corrosion.

A significant difference in the corrosion rates between the rebars of PCDC and OPC was shown from their T_{cal} value (T_{cal} for OPC/PCDC31GL, OPC/PCDC31BL and OPC/PCDC31YL are 2.02, 2.21 and 2.99 respectively compared to T_{Crit} = 2.14). The difference increased with decrease in depth of cover. The difference could be deduced from the time the rebars attained active corrosion which was earlier for the PCDC's rebars compared to OPC's. The insignificant difference between the rebars at the deepest depth of cover of PCDC and OPC (i.e OPC/PCDC31GL which had T_{Cal} value of 2.02) could be attributed to the time of onset of active corrosion which was towards the end (for the PCDC) or longer than the experimental period (for OPC).

Figures 4.27 – 4.30 show the corrosion potentials and log corrosion current densities versus monitoring period for the cement of specified category at w/c 0.73. With a decreased w/c ratio, the resistivity and hence duration before attainment of active corrosion of the cement mortar is generally expected to improve. This was not the case. It was noted that from the mortar preparation, the 0.8 w/c ratio was best suited for making a workable mix. Below this w/c, the mix obtained had poor workability. It was then expected that the mortar would not be properly compacted.

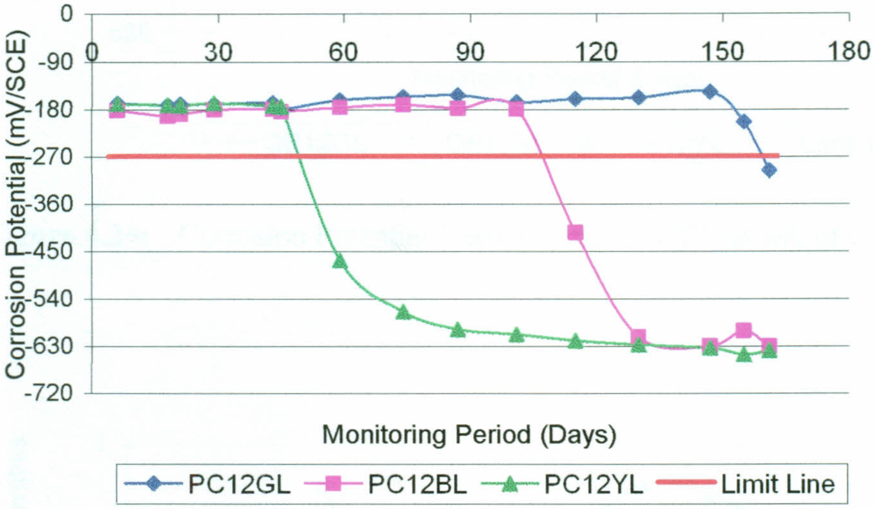

Figure 4.27: Corrosion Potential Verses Time for PCDC at w/c 0.73

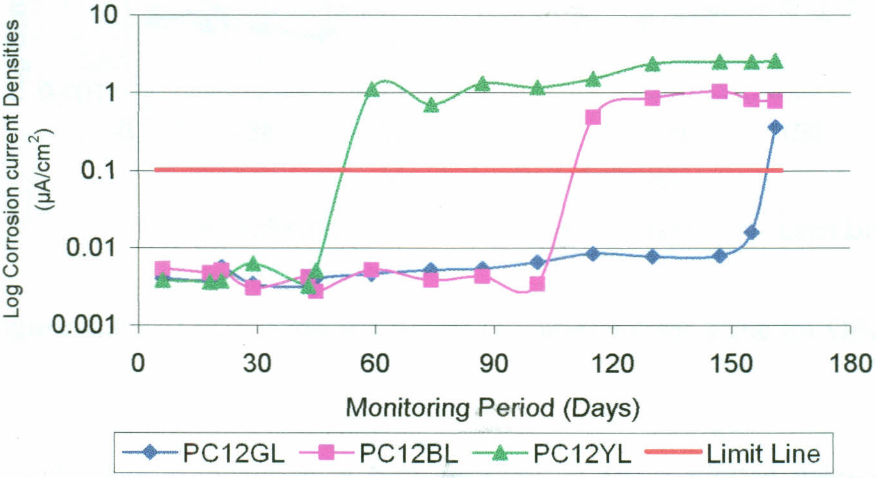

Figure 4.28: Log Corrosion Current Densities Verses Time for PCDC at w/c 0.73

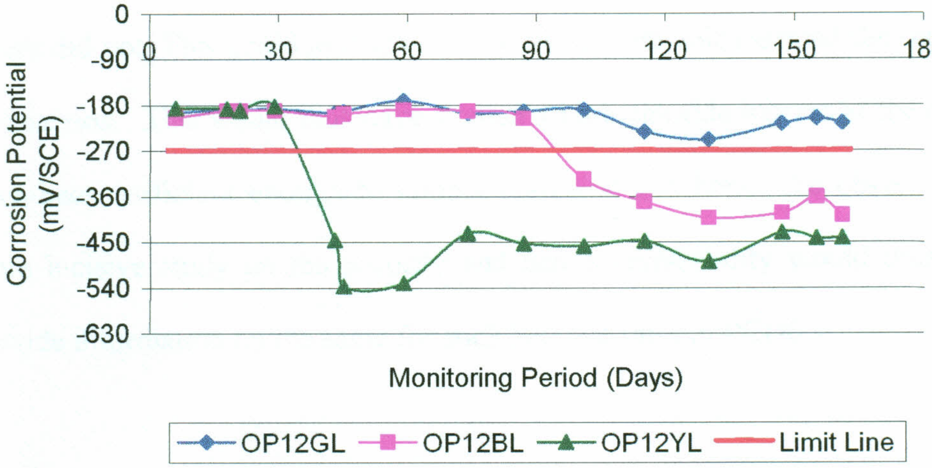

Figure 4.29: Corrosion Potential Verses Time for OPC at w/c of 0.73

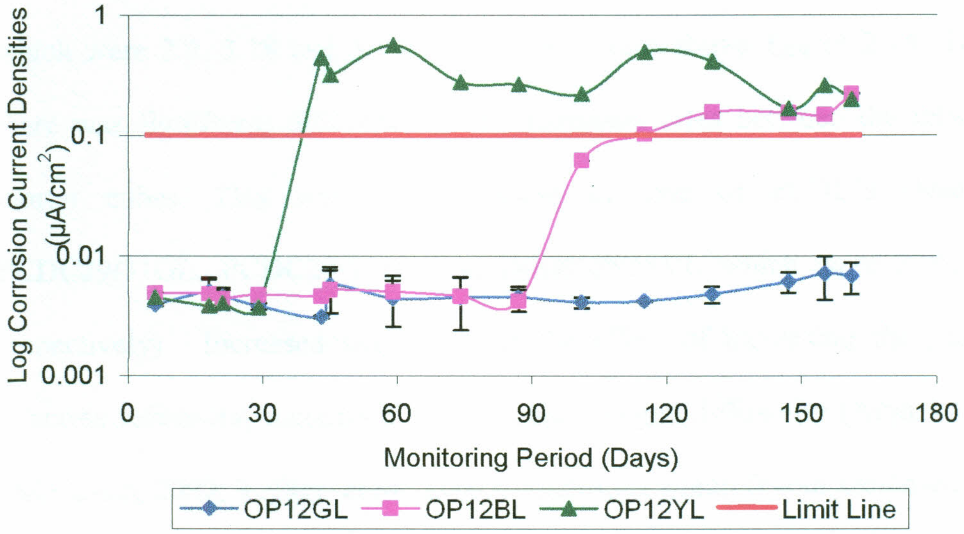

Figure 4.30: Log Corrosion Current Densities Verses Time for OPC at w/c 0.73

Despite poor compaction in both mortars, PCDC exhibited delayed initiation of active corrosion at the 10 and 15 mm depth of cover compared to OPC. This could also be observed from the chloride profile (figure 4.17) where the chloride ingress was lower in PCDC than OPC at all depths of cover. The D_{app} for the PCDC at this w/c ratio was still lower than OPC's. Thus delayed active corrosion was expected at the 20 mm depth of cover but the opposite happened: PCDC's rebar attained active corrosion while OPC's rebars did not. This could perhaps have resulted from voids around the rebars due to poor compaction. This would thus have availed a high chloride ingress at the rebar that would have been sufficient enough to initiate corrosion and hence the observed behaviour. A more incisive study on the porosity and hence permeability would thus be required to provide information on the same for such low w/c ratio of PCDC.

Generally, increase in w/c ratio was observed to cause an increase in corrosion rates. This can be seen, for example, from a comparison of highest corrosion current densities between w/c 0.8 and 0.85 for OPC's rebars which were 0.08 and 0.64 $\mu A/cm^2$ respectively (figures 4.26 and 4.22). The T_{cal} values (OPC29/31GL, OPC29/31BL and OPC29/31YL which were 2.2, 3.18 and 5.14 respectively) were above T_{crit} of 2.14. This showed that there was significant difference in the corrosion rates between the rebars at these w/c mortar cubes. This was also observed in case of PCDC's rebars (T_{cal} values PCDC29/31GL, PCDC29/31BL and PCDC29/31YL which were 2.95, 3.61 and 2.34 respectively). Increased w/c ratio has the effect of increasing the porosity, lowering concrete resistivity, increasing chloride and oxygen diffusivity (Arya, *et al.*, 1990; Pech and Castro, 2002; Yiğiter, *et al.*, 2007), conditions which favour increased corrosion rates.

Apparent diffusion coefficients of PCDC mortars were lower than OPC (table 4.2). It would then have been expected that the PCDC's rebars would have exhibited delayed active corrosion than the OPC's in all the w/c ratios and depths. But as observed by many other workers (Ampadu and Torii, 2002; Bai, *et al.*, 2003; GjØrv and Vennesland, 1979; Hossain and Lachemi, 2004; Rasheeduzzafar Al-Saadoun, *et al.*, 1990), the concentration of chlorides at the surface is usually high, but there exists a significant drop in chloride ingress into the bulk of the blended mortar or concrete. Similar higher surface concentrations in PCDC profile than OPC were observed in this study (table 4.2). The researchers mainly point to a depth greater than 20 – 25 mm into the bulk which is when the blended cements exhibit observed resistance to chloride ingress. This study was carried out with the greatest depth being 20 mm for corrosion tests. At this depth of cover, the authors agree, it is not enough to appreciate the effect of blended cements. The depth was used as an accelerating factor as laboratory set-ups are mainly short-term studies.

Sagoe-Crentsil and Glasser (1993) observed that the reduction of the pore pH due to pozzolanic reaction, even at low chloride concentration, increases iron solubility due to formation of stable chlorocomplex (of $Fe^{2+/3+}$) corrosion products (mainly green rust). These products are easily oxidised and precipitated as β – FeOOH (Akagenite) by diffused oxygen thereby releasing the Cl^-. This regenerates the Cl^- that replenishes the cycle which in essence destabilises the passive layer. The effect of lowered Cl^-/OH^- ratio as a contributing factor to early corrosion initiation phenomenon in blended cements has been observed by other workers (Ampadu and Torii, 2002; Thomas, 1996).

Generally PCDC's rebars were observed to have higher corrosion rates and earlier attainment of active corrosion compared to OPC's. Perhaps this could be attributed to its high level of substitution. There was significant drop in chloride ingress as depths of cover increased and low apparent diffusion coefficients by PCDC compared to OPC. These suggest that the test cement (PCDC) might show better protection against rebar and resistance against chloride ingress compared to OPC at greater depths of cover.

4.7.1 Visual Examination of Rebars

Upon dismantling of the simulated reinforced mortar cubes, rusty surfaces were observed on rebars that exhibited active corrosion. This was as opposed to Thiong'o (1995) who observed visual corrosion of the rebars after some few days upon dismantling his simulated reinforced mortar cubes. The rusty surfaces had mixtures of brown and green rust on the rebars. Plate 4.1 shows one of the rebars after dismantling the simulated reinforced mortar cubes. Table 4.3 gives a summary of the observations made from the different rebars in each cement category.

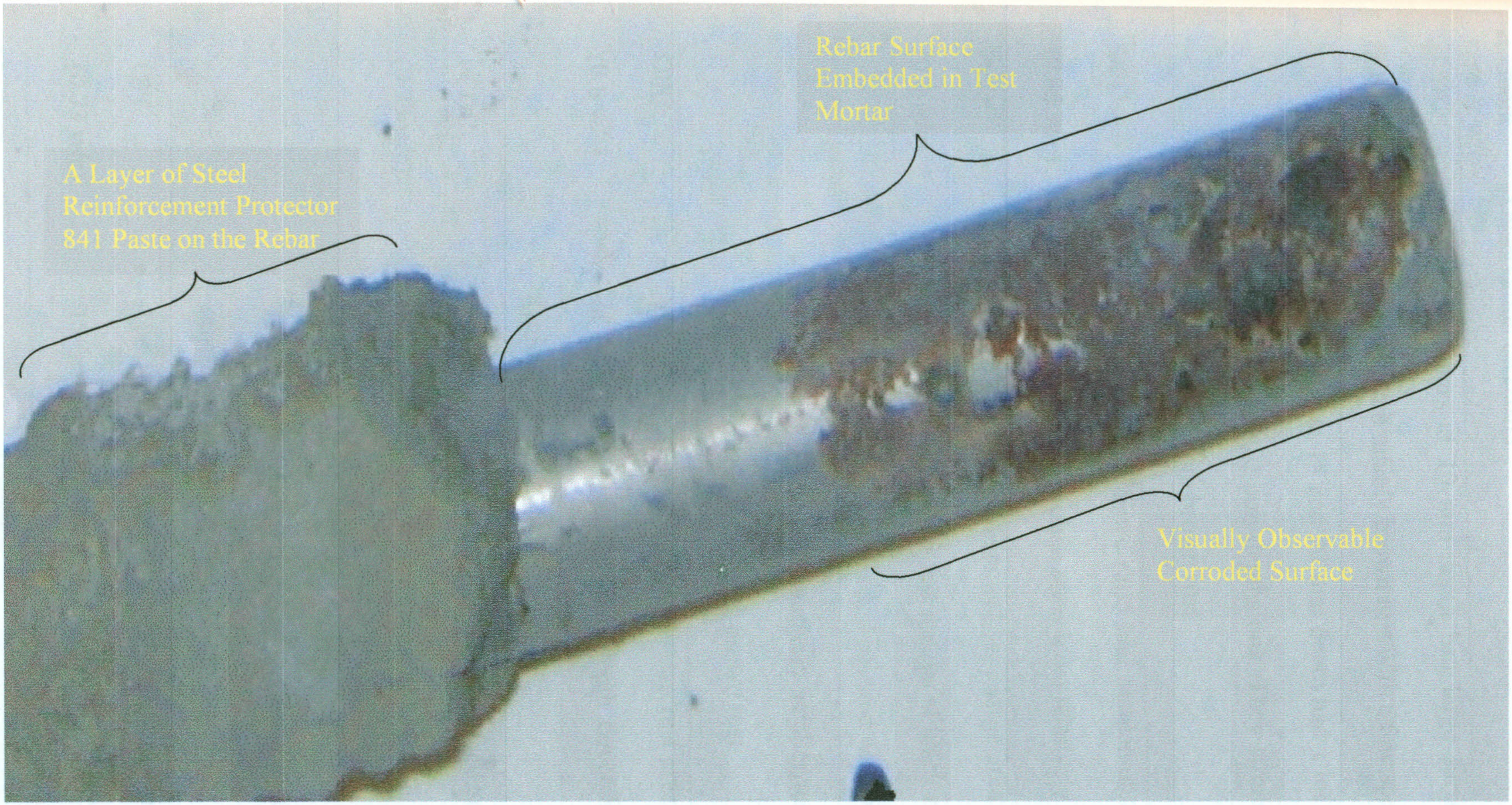

Plate 4.1: Picture of Rebar upon Dismantling of the Cement Mortar

Table 4.3: Observations made on Rebars after Dismantling

Cement type & w/c	Observation on rebars
PCDC (0.85 w/c)	• The rebars at 10 mm depth had large surface area of corrosion marked with mainly brown rust with a few specks of black rust. • The rebars at 15 and 20 mm depth had a lot more specks of black rust than the 10 mm depths one. They similarly had large surface area covered with brown rust.
OPC (0.85 w/c)	• The rebars in this w/c ratio had similar observations to PCDC at 0.85 w/c but the surface areas were relatively smaller
PCDC (0.8 w/c)	• The 10 mm depth rebars had very large area rusted mainly covered with brown rust with a few specks of black rust. The area of rust at 15 mm depth was smaller and covered with brown and black rust. • The 20 mm rebars had relatively smaller rust area mainly covered with black rust specked with brown rust
OPC (0.8 w/c)	• The 10 mm depth had large brown rust area with few black specks of rust. The 15 and 20 mm depth cover had no observable rust regions
PCDC (0.73 w/c)	• The 10 mm depth cover had large surface area of rust covered with mainly brown rust with a few black specks. The 15 mm rebars had small brown black brown rings. • The 20 mm depth showed no rusting surfaces in one rebar but the other two had slight corroded spots
OPC (0.73 w/c)	• The 10 and 15 mm rebar showed little corrosion regions with the 15 mm rebar having smaller corroded surface areas

It was observed that the visual corrosion surface areas were relatively larger for PCDC's rebars than their corresponding OPC's. This was in line with PCDC corrosion rates observed in the corrosion monitoring section where they were higher than their corresponding OPC rebars.

The visual corrosion surface areas were observed to be larger for higher w/c ratios. The corroded areas especially for the 0.85 w/c ratio for the two cements were extremely large. This again corresponded to the high corrosion rates that were observed. The rebars in this w/c ratio experienced early corrosion as compared to corresponding rebars in 0.8 w/c ratio. They were therefore as observed, expected to have corroded more.

An interesting phenomenon was observed again in the 0.73 w/c ratio cements where the 10 mm depth rebars had large visual surface areas of corrosion. The corroded surface decreased with increase in the depth of cover. This was again correspondent with the observed active corrosion initiation in which the rebars corroded earlier than expected.

It was also observed that the corroded areas of the rebars had a mixture of black and brown rusts. The black rust was normally in specks over large brown surface areas. The intensity of the black specks increased with increasing depth and decreased with increase in w/c ratio. Brown and black rusts are normally observed in concrete, with black rust observed with decreasing oxygen availability (Erdogdu, *et al.*, 2001). Erdogudu *et al.* (2001) observed black rust in oxygen deficient rebars and brown with green spots in oxygen sufficient rebars. Black rust, mainly Fe_3O_4 are mainly found as protective film on passivated steel film with brown rust, Fe^{3+} associated with corroded/ing surfaces. The brown and black rust are formed as given by equations 4.6 and 4.7 respectively (Ahmad, 2003)

$$2Fe + 3H_2O \longrightarrow \underset{\text{Brown Rust}}{Fe_2O_3} + 6H^+ + 6e \qquad 4.6$$

$$3Fe + 4H_2O \longrightarrow \underset{\text{Black Rust}}{Fe_3O_4} + 8e + 8H^+ \qquad 4.7$$

It was generally observed that the PCDC's rebar had larger corroded surface areas compared to corresponding OPC's rebars at all w/c ratios. It is therefore apparent to conclude that, PCDC did not offer protection of its rebars against corrosion at the tested depths of cover. There was significant drop in chloride ingress in PCDC's mortar compared to OPC from the chloride profile analyses as the depth of cover was increased. Further studies at greater depths of cover on PCDC's protection against rebar corrosion would therefore shed more light on chloride ingress and corrosion initiation of the reinforcement.

4.8 Results for Test Cements in Sulphate Solutions

4.8.1 Compressive Strength Development

Results for compressive strength gain for mortar cubes subjected to sulphate solutions are presented in figure 4.31. PCDC and PPC mortar cubes under this corrosive media registered a significant gain in compressive strength. The gain was even more pronounced with increase in sulphates concentration (T_{Cal} = 4.49 for PCDC SO2 verses PCDC SO1. T_{Cal} = 18.40 for PPC SO2 verses PPC SO1 way above T_{Crit} value of 4.30). The strength gain in OPC was also notable in the sulphate solution but there was a significant less gain when the solution concentration was doubled ($T_{Cal} = -5.59$ for OPC SO2 verses OPC SO1: The negative sign indicating a decline in strength gain).

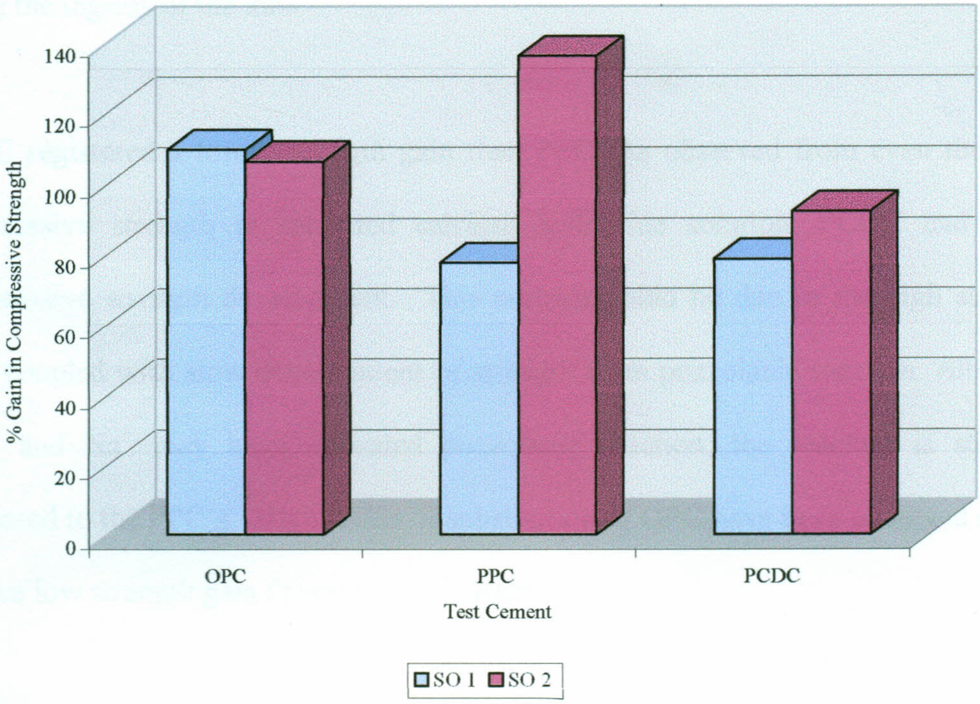

Figure 4.31: Percent Gain in Compressive Strength versus Test Cement

Sulphates have two main effects on cements; the activation of pozzolanic reaction (Aimin and Sarkar, 1991; Lorenzo, *et al.*, 2002) in pozzolana based cements and the formation of deleterious thaumisite, ettringite, gypsum, sodium sulphate or even magnesium sulphate (if Mg – ions are present) (Hime and Mather, 1999; Türker, *et al.*, 1997) in PPC and OPC. OPC is the most susceptible to the deleterious effects of sulphates. The two effects tend to give an increased then a decline in physical properties such as strength in mortars or concrete (Türker, *et al.*, 1997).

The appreciable gain in strength in blended cements can be explained by ingress of sulphate and sodium ions. The ions initiate pozzolanic reaction. This results to additional

CSH which improves the physical properties of the resultant mortar (Lorenzo, *et al.*, 2002). Such physical properties include compressive strength and density of the mortar. This in turn improves the resistance to sulphates attack by lowering the diffusivity and hence the ingress of the ions.

PCDC registered a lower strength gain than PPC. As observed from even the 28th day compressive strength in saturated calcium hydroxide solution, PCDC had the least compressive strength development. This perhaps could be due to the high substitution level coupled with slow development of strength from pozzolanic reaction. Although the SO_4^{2-} and Na^+ may have activated pozzolanic reaction, the reaction is still slower compared to the PPC's. High levels of substitution of OPC have been observed elsewhere to have low strength gain (Turanli, *et al.*, 2005).

The lower strength in OPC as the sulphates concentration was doubled could be inferred from the three stages of sulphate attack postulated by Türker *et al.* (1997). The worker (Türker, *et al.*, 1997) classified the attack to involve early, transition and later stages. At the early stage, densification of mortar or concrete due to sulphate products increased strength, but in transition and later stages, the deleterious effects of the sulphates were observed. The deleterious effects brought about decline in physical properties such as the compressive strength. An increase in sulphate concentration, in this study, may have caused an earlier lapse of the early stages compared to the lower sulphate concentration. This may be attributed to the observed decline in strength gain as the sulphate concentration was increased.

In general, the PPC had the highest strength gain, followed by PCDC in the sulphate solutions. This is expected of blended cements compared to OPC. This is mainly attributed to low permeability from the resultant secondary CSH from pozzolanic reaction. The packaging of pozzolana grains between the cement grains and aggregates also reduce permeability. The reduction in $Ca(OH)_2$ content through pozzolanic reaction reduces a phase that is most vulnerable to sulphates attack. These factors make blended cements to be less vulnerable to sulphates form of attack (Ampadu and Torii, 2002; Halse, *et al.*, 1984; Hossain and Lachemi, 2004; Page, *et al.*, 1986; Taylor, 1999).

4.8.2 Selected Ion Analyses in Sulphate Solutions

4.8.2.1 Sulphate Intake and Leaching

Figures 4.32 and 4.33 show the analyses of sulphate ions against monitoring period from the sulphates simulated solutions. PCDC showed a continuous intake of the ions up to about 103rd and 163rd day for the simulated solution 1 and 2 respectively. After these days, a subsequent leach was observed. Similar observations were made for the PPC (intake was observed up to about the 163rd day followed by leaching). OPC exhibited an intake up to about 103rd and 45th day for simulated solution 1 and 2 respectively, after which leaching was observed. An increased intake of the sulphates was observed when the concentration of the sulphates was doubled.

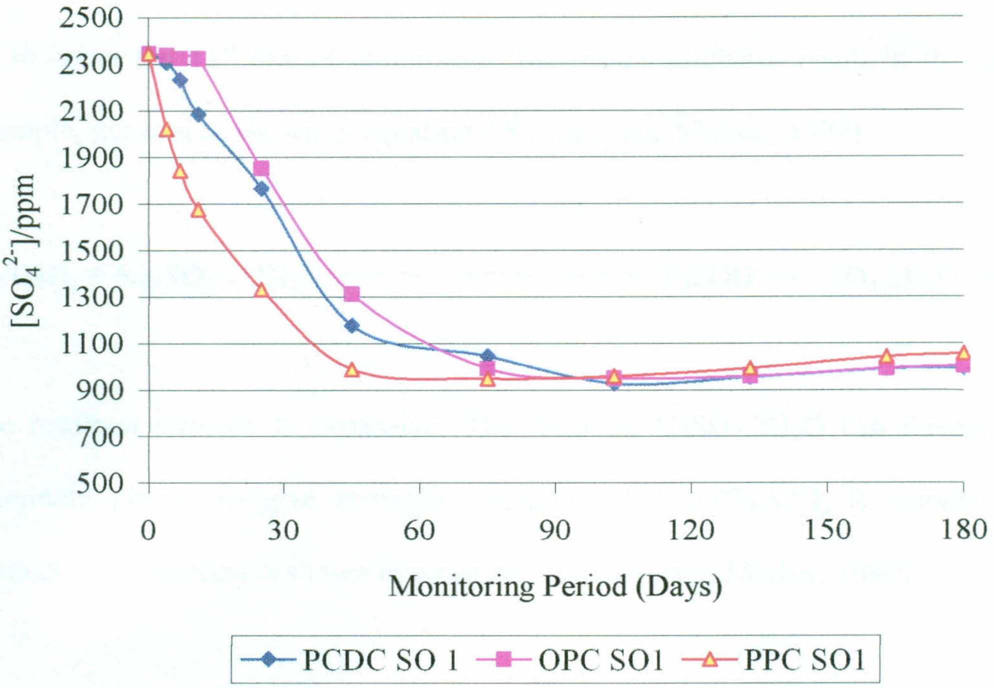

Figure 4.32: SO_4^{2-} Analyses in Sulphate Simulated Solution 1

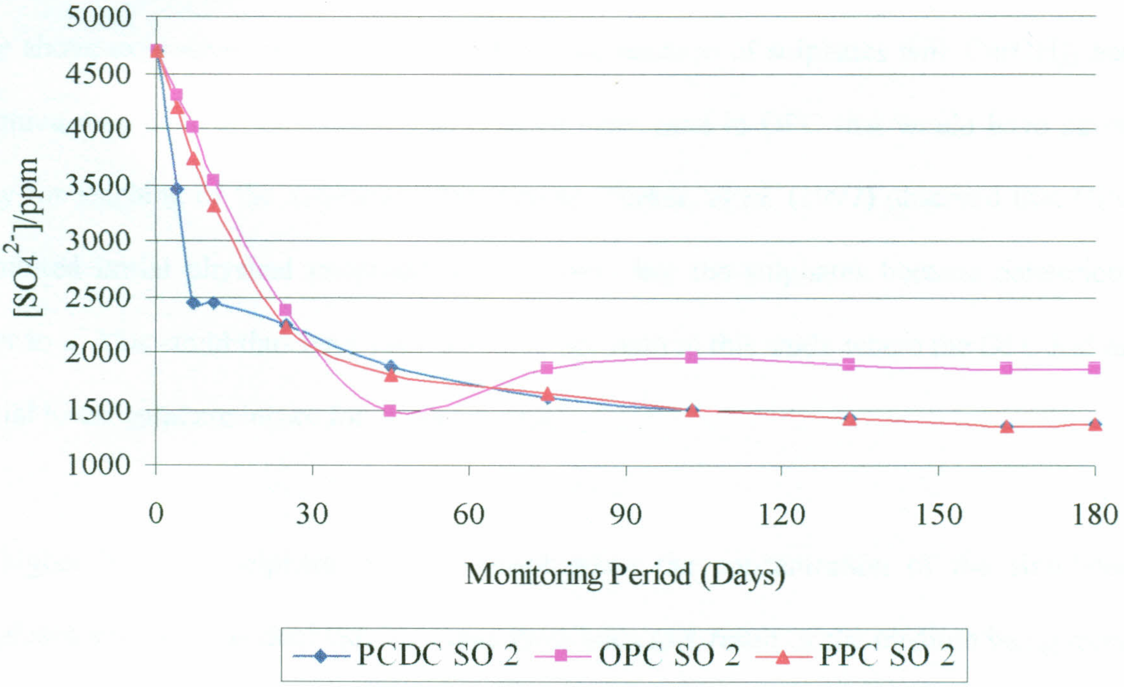

Figure 4.33: SO_4^{2-} Analyses in Sulphate Simulated Solution 2

OPC showed an initial reduced sulphates intake at the lower sulphates simulated solution up to about the 11th day of monitoring. Ingress of sulphates result in formation of for example, gypsum as shown in equation 4.8 (Hime and Mather, 1999)

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \xrightarrow{\hspace{4cm}} 2NaOH + CaSO_4.2H_2O \qquad 4.8$$

The resultant gypsum is expansive. The resultant $CaSO_4.2H_2O$ can further react with aluminate phases to give ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$), another expansive product. The reaction is shown in equation 4.9 (Hime and Mather, 1999)

$$3(CaSO_4.2H_2O) + 3CaO.Al_2O_3 + 26H_2O \longrightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O \quad 4.9$$

The above expansive products resulting from the reaction of sulphates with $Ca(OH)_2$ and alumina may have created micro-cracks at an early time in OPC that would have paved way for leaching of the sulphates after ingress. Türker, *et al.* (1997) observed that OPC exhibited initial physical properties development but the sulphates became deleterious later to it. This could thus have been a similar scenario in this study where the OPC had an initial lower sulphate intake for about 11 days.

A higher leach in sulphates was observed when the concentration of the simulated sulphates solution was doubled. This may have been as a result of the medium being more aggressive when the concentration is doubled. This may have been a similar scenario to the strength development observed in figure 4.31 where as the concentration of the sulphates was increased, the strength gain decreased for OPC. Sulphates have the effects of initially improving the mortar by activation of pozzolanic reaction but later cause deterioration from expansive sulphates products. Perhaps the deterioration stage in sulphate attack was attained earlier as the solution concentration was doubled.

PCDC and PPC showed a similar intake of the sulphates in both solutions. PCDC had a higher substitution level than PPC. The pozzolanic reaction and cement hydration were therefore, expected to be slower in PCDC compared to PPC. Therefore, its resistivity to sulphates may not only have been due reduction in its permeability from secondary CSH from the pozzolanic reaction. This may also have been attributed to the packaging of the pozzolana particles in between the aggregates and cement grain which reduces permeability.

The results of this study suggested that PPC had the most resistance to sulphate attack followed by PCDC and least OPC. The lower resistance to sulphates attack by OPC has been observed by many workers (Al-Amoudi, 2002; Dongxue, *et al.*, 1997; O'Farrel, *et al.*, 2000; Türker, *et al.*, 1997). Blended cements are known to exhibit resistivity to sulphate attack especially to the sodium sulphate type but not the $MgSO_4$ (Mehta, 1993). The resistivity is due to their reduced alumina phase and $Ca(OH)_2$ because of less cement proportions. This could also be attributed to the production of more cementious CSH from pozzolanic reaction. This makes the resultant mortar less permeable to the sulphates and hence more durable (Ampadu and Torii, 2002; Halse, *et al.*, 1984; Hossain and Lachemi, 2004; Page, *et al.*, 1986; Taylor, 1999). Perhaps more in-depth of the sulphate profile and the type of internal reactions will help determine the extent of the sulphate effect on the test cement (PCDC).

4.8.2.2 K^+, Na^+ and pH Analyses in Sulphate Simulated Solutions

Figures 4.34 - 4.36 show the changes in K^+, Na^+ and pH in the simulated sulphate solutions. The simulated sulphate solutions were made from sodium sulphate. There was progressive increase in K^+ ions in the solutions. The pH rose from the near neutral to higher than 9.

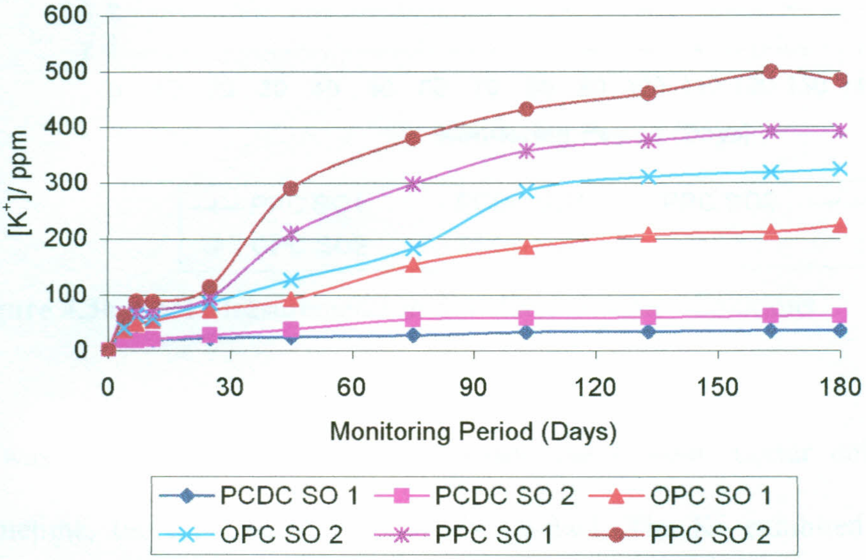

Figure 4.34: K^+ Analyses in Sulphate Simulated Solution

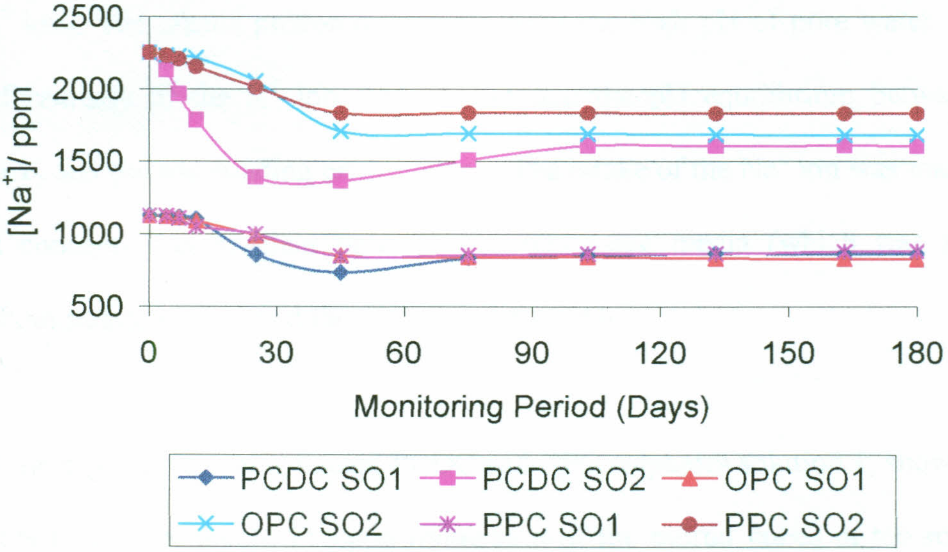

Figure 4.35: Na^+ Analyses from Simulated Sulphate Solutions

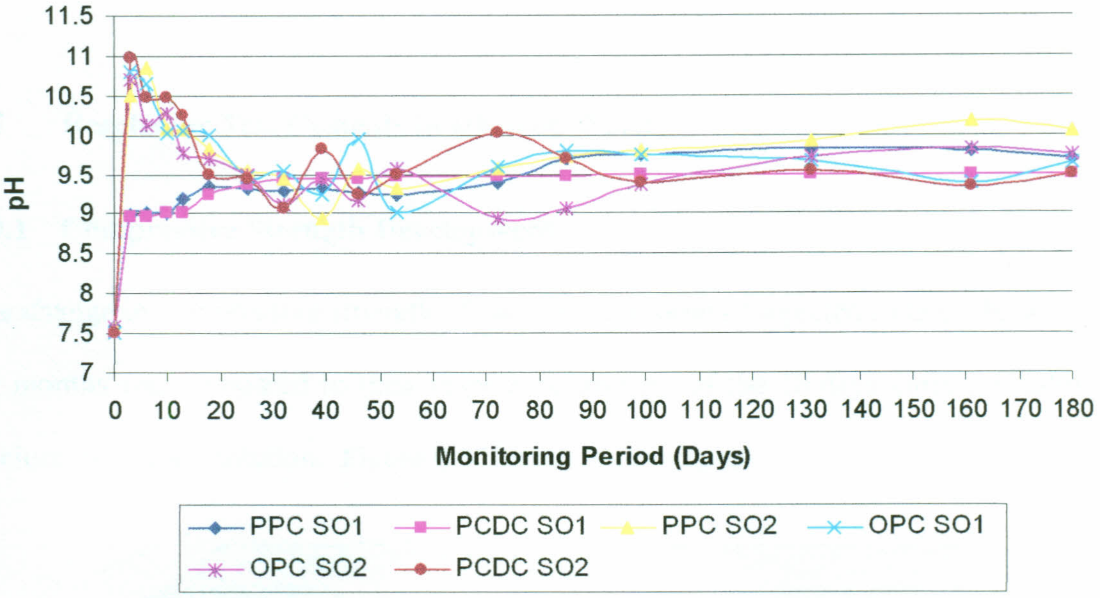

Figure 4.36: pH Measurements in Simulated Sulphate Solutions

It was observed that Na^+ ions ingressed the cement mortar cubes initially. After sometime, the ions were subsequently leached. The K^+ exhibited a continuous leach throughout the experimental period. Diamond (1981), while studying the effect of PFA on cement pore solution content and pH, observed a higher concentration of the K^+ than Na^+ ions. The alkalis predominantly maintain the high pH of pore water. The leaching preferentially of the K^+ ions helped maintain the pH equilibrium between the mortar matrix and the surrounding environment. The intake of the Na^+ ion was mainly due to the ion concentration gradient between the aggressive media (which was prepared from sodium sulphates salt) and the cement pore system.

All the aggressive media, except PCDC and OPC sulphates solution 1, showed an increase in pH to approximately 11 upon immersion of the mortar cubes in the solutions. There was a decline in these solutions' pH after some time but PPC's solutions maintained a

This leads to deterioration of such properties as the cement's strength, porosity, alkalinity of the pore solution among others.

4.9 Results for Test Cements in Distilled Water

4.9.1 Compressive Strength Development

The change in compressive strength of the cement mortars subjected to distilled water for six months was compared to their respective strength of the 28 days curing in saturated calcium hydroxide solution. Figure 4.37 shows these results.

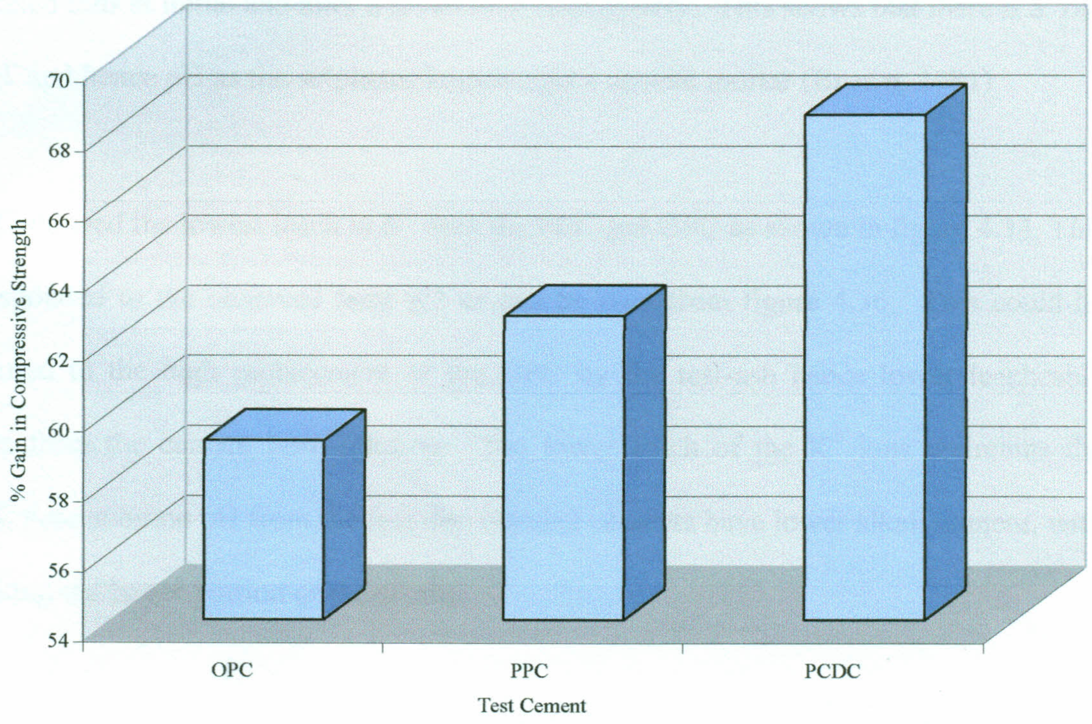

Figure 4.37: Percent Gain in Compressive Strength Verses Test Cement in distilled water

There was observed strength gain for all the test cements in water. The increase in compressive strength in distilled could be attributed mainly to a continued hydration of the higher pH to the end of the monitoring period. Some workers (Brown, 1981; Ferraris, *et al.*, 1995) observed a steady rise in pH of the corrosive media in few days, to about 12, due to release of the OH^- from the pore solution of the associated concrete. Brown (1981) observed the interdependence of sulphates intake and OH^- to be related as shown in equation 4.10

$$[SO_4^{2-}]_t = [SO_4^{2-}]_o - \tfrac{1}{2}[OH^-]_t \qquad 4.10$$

The subscripts o and t denote concentrations (in the solution under investigation) of the bracketed ions at initial and after a given time respectively. This shows that there is a rise in OH^- and hence pH as the sulphates ingress into a cement mortar (Brown, 1981).

PCDC showed the lowest leach in K^+ than the PPC and OPC as shown in figure 4.34. This corresponded to the observed least pH as can be seen from figure 4.36. This could be attributed to the high replacement of the OPC by the test-ash hence lower leacheable alkalis from the cement pore solution. The lower leach of the K^+ ions maintains the PCDC pore solution pH from the fact that blended cements have lower alkali content, with K^+ taking the larger portion of the alkalis.

Generally, OPC exhibited lower strength gain and resistivity to sulphates intake and subsequent leach compared to the blended cements. PPC exhibited higher strength gain than PCDC. The alkalis leach, which was most pronounced in PPC and least in PCDC, leads to disruption of the media through which cement reactions take place. This in essence affects the microstructure of the resulting cement mortar and hence its properties.

cement. Distilled water did not have Na^+, Cl^- and SO_4^{2-} ions which activate pozzolanic reaction or residual cement hydration as was the case with other aggressive media. Strength development was therefore, as observed expected to be low.

PCDC had the highest strength gain which is significantly higher than OPC (T_{Cal} =5.17 against T_{Crit} = 4.30). There was no significant difference in strength gain between PCDC and PPC (T_{Cal} = 2.17). Pozzolana based cements have slow development in strength as compared to OPC (Blanks and Kennedy, 1955) if aggressive ions are not encountered. This is attributed to lower pozzolanic reaction. With time, due to continued pozzolanic reaction, blended cements are expected to exhibit higher gain in compressive strength than OPC (Neville and Brook, 1987) as observed in this case.

4.9.2 Selected Ion Analyses in Distilled Water

4.9.2.1 Sulphates Analyses

Figure 4.38 shows the analyses of sulphate ions versus the monitoring period. The sulphate ions were analysed from the corrosion media.

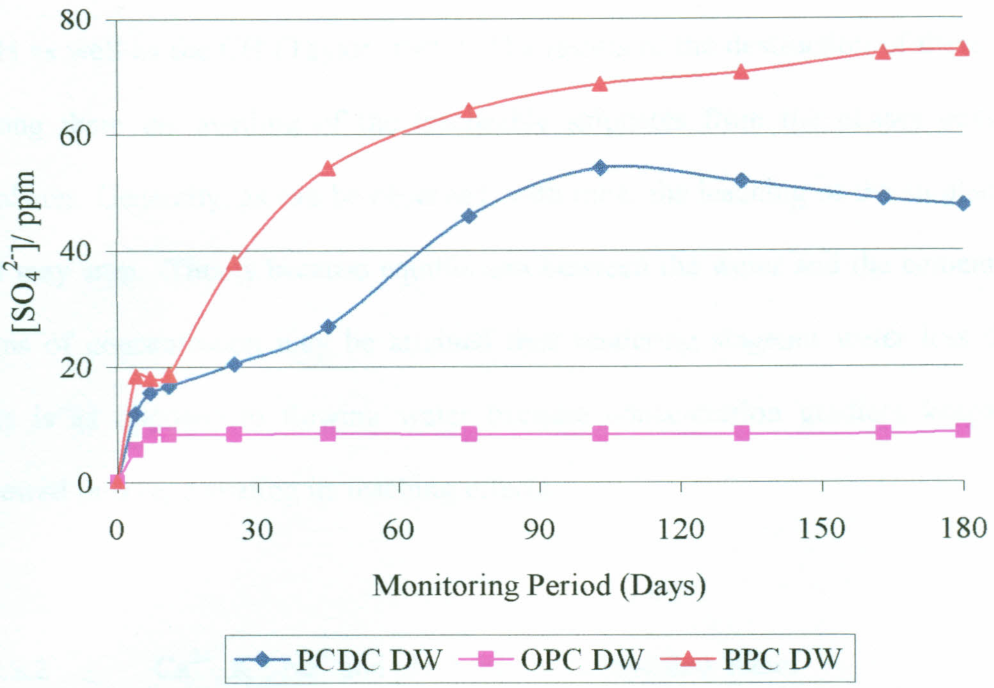

Figure 4.38: SO_4^{2-} Analyses in Distilled Water

Leaching of the sulphates was noted in all the test cements. With time, the amount of leached sulphates got to a constant level. This could be compared to a scenario observed by Herold (1995) of a protective layer development on cement mortar and a concentration build up in the solution. This is accompanied by a decline in the diffusion in and out of the cement mortar. As the protective layer develops, in this case, a $CaSO_4$ or $Ca(OH)_2$, the dissolution of the sulphates reduces.

PPC and PCDC exhibited a continued leaching with PPC showing a higher leach. PCDC had a higher substitution level than PPC. It was therefore expected, as observed, that PPC would exhibit a higher sulphates leach. This is because of its initial higher amount of sulphates, added as gypsum to control flash set. Perhaps, OPC was less permeable to distilled water by virtue of its higher compressive strength than the blended cements observed at the 28th day.

Leaching as a result of water has been shown to destroy the monosulphates, ettringites, CSH as well as the CH (Taylor, 1997). The results of the destruction of these phases are among them the availing of the leacheable sulphates from the phases containing the sulphates. Generally, as can be observed, with time, the leaching of the sulphates reduces and may stop. This is because equilibrium between the water and the cement system in terms of concentration may be attained thus rendering stagnant water less deleterious. This is as opposed to flowing water because concentration gradient keeps on being renewed thus regenerating its leaching effects.

4.9.2.2 Ca^{2+}, K^+, Na^+ and pH Analyses in Distilled Water

Figure 4.39 – 4.42 show the analyses of Ca^{2+}, K^+, Na^+ and pH from distilled water versus monitoring period. The Ca^{2+} ions were only detectable for a few days in OPC and PPC corrosion media. Ca^{2+} levels in PCDC varied from one testing day to the other.

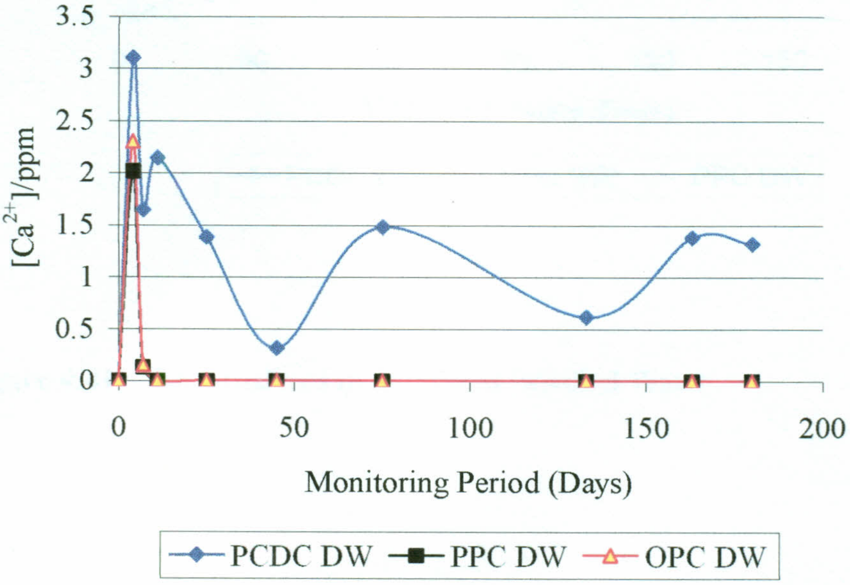

Figure 4.39: Ca^{2+} Analyses in Simulated Distilled Water

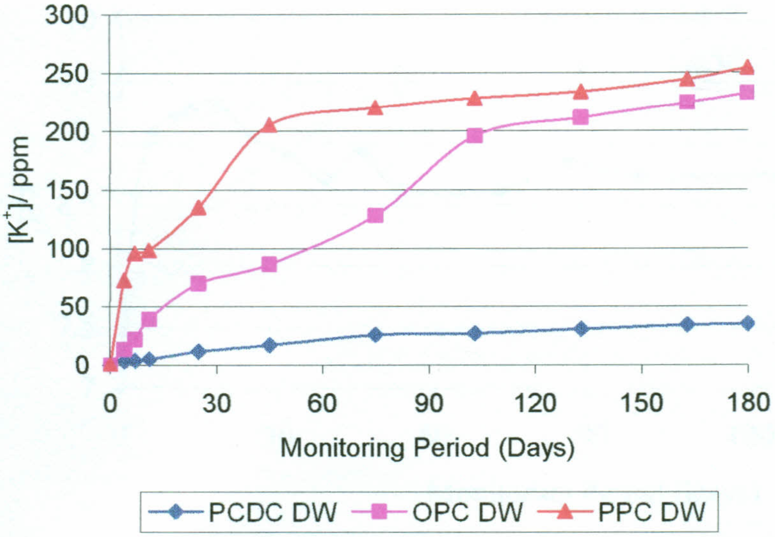

Figure 4.40: K$^+$ Analyses in Simulated Distilled Water

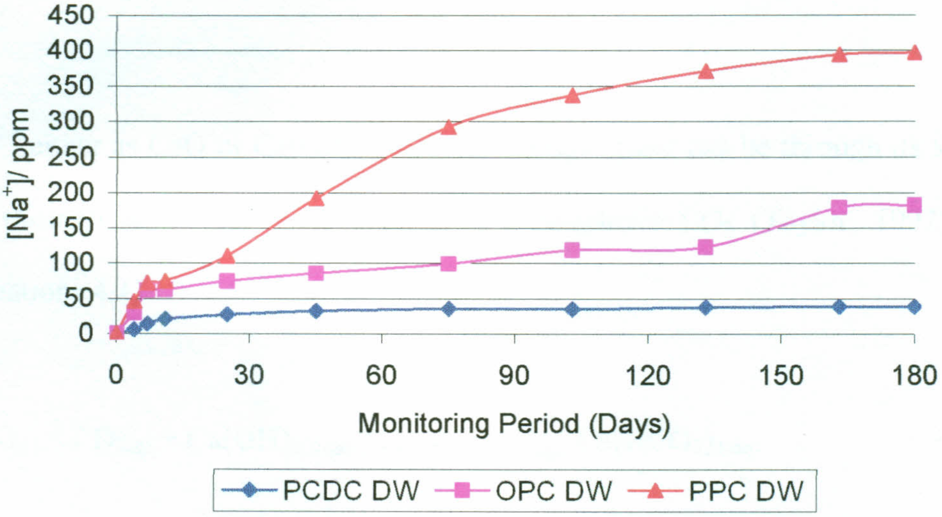

Figure 4.41: Na$^+$ Analyses in Simulated Distilled Water

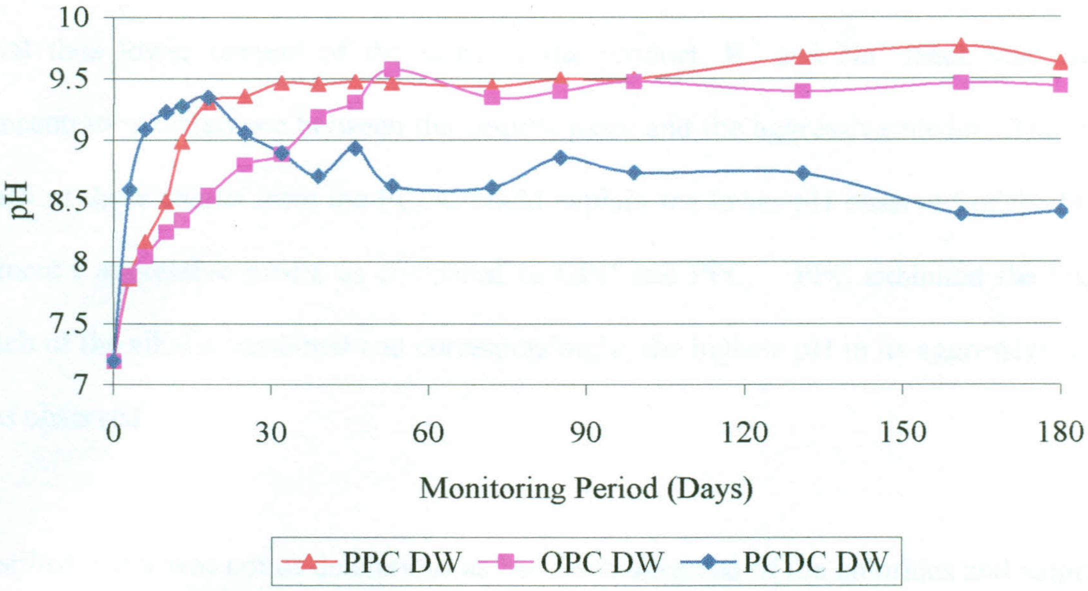

Figure 4.42: pH Measurements in Simulated Distilled Water

Ca^{2+} either as CaO or $Ca(OH)_2$ leaching through water can be through its slight solubility or through attack via solubilization of atmospheric CO_2 (Taylor, 1997) as shown in equations 4.11

$$H_2O_{(l)} + CO_{2(g)} + Ca(OH)_{2(\text{slightly soluble})} \longrightarrow Ca(HCO_3)_{2(aq)} \qquad 4.11$$

The leaching of Ca^{2+} from OPC and PPC declined immediately after the first few days. This could not be inferred from formation of protective layer on the surfaces of the mortar. This would have as well affected PCDC in a similar manner. The lower Ca^{2+} leach could probably be explained from a pH point of view. As discussed earlier, Ca^{2+} solubility decreases with increase in pH, thus with higher leach in K^+ and Na^+ from OPC and PPC would have inhibited its leach.

The lower leach in Na^+ and K^+ from PCDC could be attributed to a higher substitution level thus lower content of the same in the product. K^+ and Na^+ leach was due to concentration difference between the cement paste and the aggressive media. The lower leach of these alkalis from the PCDC could explain the lower pH observed of the PCDC cement's aggressive media as compared to OPC and PPC. PPC exhibited the highest leach of the alkalis combined and correspondingly, the highest pH in its aggressive media was observed.

Distilled water was not as deleterious as had been observed of the chlorides and sulphates especially in the leaching of the main cement constituents for example Ca^{2+}, Na^+, K^+ among others. The leach of these constituents in distilled water could mainly have been due to concentration difference as well as for attaining equilibrium between the cement matrix and corrosive environment as opposed to chemical attack. More so, with time, hydration of the cement mortar progresses, thus making the mortar less permeable and hence less vulnerable to attack.

4.10 Results for Test Cements in Simulated Sea Water

4.10.1 Compressive Strength Analyses

Figure 4.43 shows the percent gain in compressive strength versus test cement in sea water.

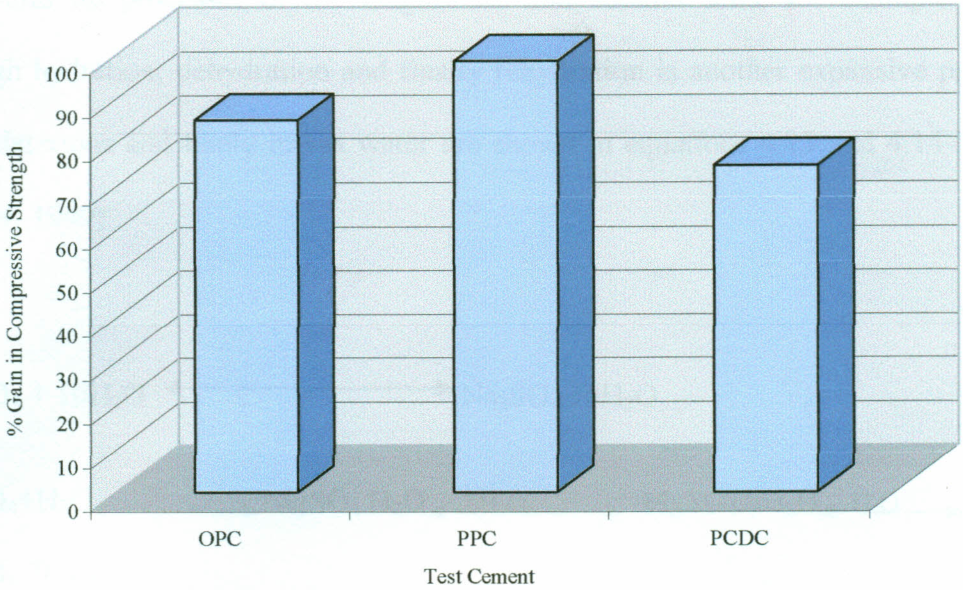

Figure 4.43: Percent Gain in Compressive Strength versus Test Cement in Sea Water

PPC had significant higher strength gain than OPC and PCDC in sea water. (T_{Cal} = 7.14 for PPC against OPC, 9.85 for PPC against PCDC, and 4.03 for OPC against PCDC [T_{Crit} = 4.30]). This could be attributed to the activation of pozzolanic reaction and rehydration of residual cements due to ingress of the sulphates, chlorides and sodium ions. This improves the compressive strength of the resultant mortar.

In sea water, deleterious products, for example magnesium silicate hydrates, calcium sulphates and ettringite, are expected to be formed as shown in equations 4.4, 4.7 and 4.8 respectively. Brucite [$Mg(OH)_2$], an expansive product, is formed via the magnesium ion attack (Al-Amoudi, 2002) as shown in equation 4.12

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+} \qquad 4.12$$

The build up processes of the magnesium and sodium salts, for example sulphates, through hydration, dehydration and finally rehydration is another expansive process that are deleterious and likely in sea water are shown in equations 4.13 and 4.14 (Hime and Mather, 1999).

$$Na_2SO_4 + 10H_2O \longleftrightarrow Na_2SO_4.10H_2O \qquad 4.13$$

$$MgSO_4 + H_2O \longleftrightarrow MgSO_4.H_2O \xleftrightarrow{5H_2O} MgSO_4.6H_2O \xleftrightarrow{H_2O} MgSO_4.7H_2O \qquad 4.14$$

A combination of the above products would be expected to exhibit higher deleterious effects by sea water compared to separate aggressive media of sulphates and chlorides. Elsewhere a decreased effect of sulphate attack in presence of chlorides and decreased chlorides effect in presence of sulphates have been observed (Zuquan, *et al.*, 2007). Santhanam *et al.* (2006) observed that the reduced effect of sea water was due to competition between the chloride and sulphates.

Kumar (2000) observed significant strength development for blended cements in marine environment compared to OPC. The author (Kumar, 2000) attributed this to greater resistance of blended cements. Similar observations were made by Lorenzo *et al.* (2003) while studying the effect of simulated sea water on Spanish fly ashes. They observed that the diffusion of SO_4^{2-}, Na^+ and Cl^- through the pore solution activated the pozzolanic reactivity of the fly ashes causing the corresponding microstructure changes. As a result, the strength of the fly ash based cements increased. The comparatively low percent gain in strength for PCDC could be attributed to the high substitution level.

4.10.2 Selected Ions Analyses

4.10.2.1 Chlorides Analyses in Sea Water

Figure 4.44 shows the analyses of chlorides against monitoring period in sea water.

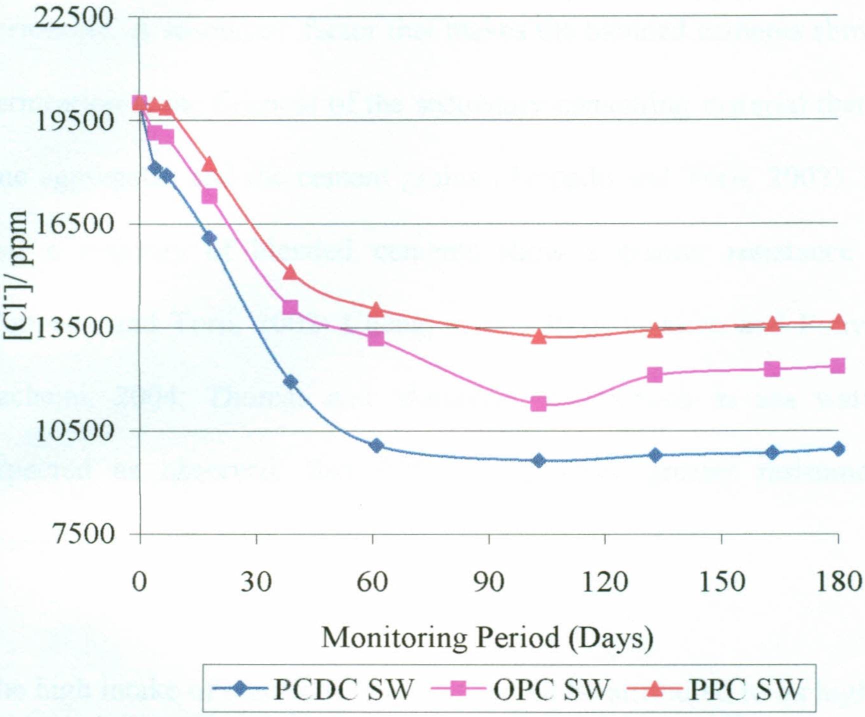

Figure 4.44: Cl^- Analyses in Sea Water

It was observed that the test cements showed an intake of Cl^- that was continued up to the 103th day. After this, the test samples showed an increase in the chloride content in the corrosive media. The leaching could be attributed to the saturation of the chlorides in the mortar cubes. Some workers (Arya, *et al.*, 1990) attributed the decline in $Ca(OH)_2$, due to pozzolanic reaction, to increase in solubility of the chloroaluminate. This may lead to formation of soluble salts of the chlorides of calcium, aluminium and iron from decomposition of the same (Hussain and Al-Gahtani, 1991). The salts may leach from the concrete mass. Thiong'o (1987) observed a similar trend of intake and subsequent leaching. The author (Thiong'o, 1987) attributed this to saturation of the chlorides in the mortar.

PPC showed the lowest intake of the Cl^-. PPC is known to cure over a long time compared to OPC. Pozzolanic reaction introduces more C-S-H, which makes the concrete less permeable. A secondary factor that makes the blended cements show greater resistance to permeation is the fineness of the secondary cementing material that packs in between the fine aggregates and the cement grains (Ampadu and Torii, 2002). It is well documented that a majority of blended cements show a greater resistance to aggressive media (Ampadu and Torii, 2002; Cheng, *et al.*, 2005; Ganjian and Pouya, 2005; Hossain and Lachemi, 2004; Thomas and Matthews, 2004) such as sea water. It was therefore expected as observed, that PPC would show greater resistance to ingress in the constituents of the sea water.

The high intake of chlorides by PCDC could be attributed to its high level of substitution. This was evident by the low compressive strength at the 28th day as well as the percent strength gain after being subjected to sea water. This could be attributed to a lower hydration rate of cement. Thus the cement showed a higher permeability than OPC and PPC.

4.10.2.2 Sulphates Analyses in Sea Water

Figure 4.45 shows the results of analyses of sulphates in sea water media against monitoring period. OPC showed the highest intake of the sulphates after which the cement mortar showed leaching of the same evidenced by increase in the sulphates in its aggressive media.

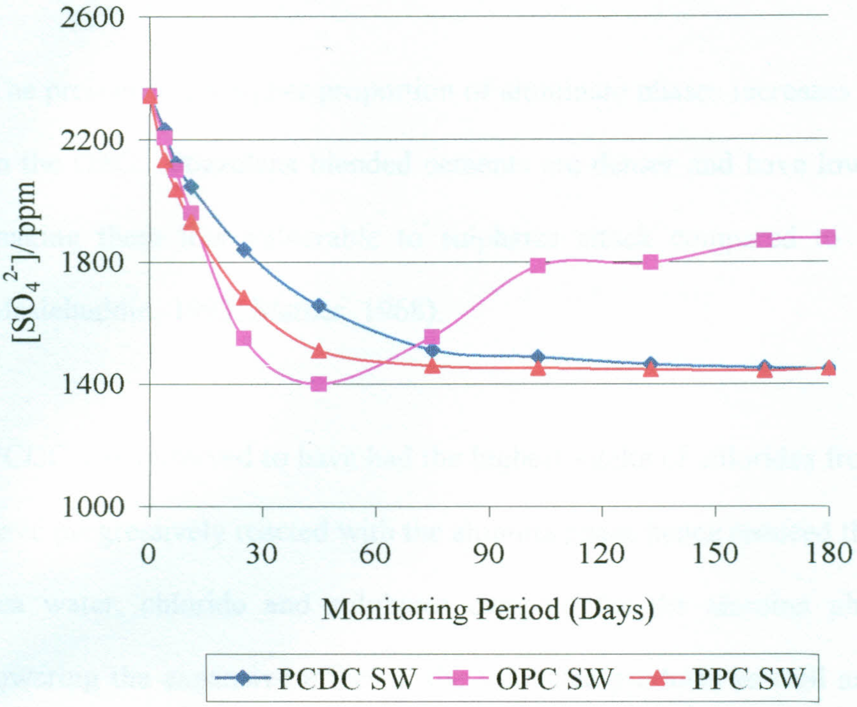

Figure 4.45: SO$_4^{2-}$ Analyses in Sea Water

All the cement mortars showed intake of sulphates. OPC showed an intake up to about the 45th day after which it showed subsequent leaching. OPC is known to be easily attacked by sulphates (Al-Amoudi and Maslehuddin, 1993; Mather, 1968; Taylor, 1999; Zuquan, *et al.*, 2007). In sulphates simulated solutions, OPC showed higher intake especially at higher concentrations of the sulphates solutions (figure 4.33). It was observed that at the higher sulphates concentration, the OPC exhibited leach after intake of the sulphates (figure 4.33). In simulated chloride solution, OPC showed the highest leach in the sulphates especially at the higher chloride concentration (figure 4.7). It would then appear that the combined effect of the two ions (sulphates and chlorides in sea water) exhibited the same trend where they were more aggressive to OPC than the blended cements. But the severity of attack in the separate aggressive solutions was noted to be higher compared to sea water. This could be observed, for example from figure 4.33 and

4.45 where the amounts of sulphates intake and subsequent leach were higher in simulated sulphates solution than sea water.

The presence of a higher proportion of aluminate phases increases the uptake of the SO_4^{2-} in the OPC. Pozzolana blended cements are denser and have lower $Ca(OH)_2$ than OPC making them less vulnerable to sulphates attack compared to OPC (Al-Amoudi and Maslehuddin, 1993; Mather, 1968).

PCDC was observed to have had the highest intake of chlorides from sea water. This may have progressively reacted with the alumina phase hence reduced the sulphate ingress. In sea water, chloride and sulphates compete for the alumina phase in cement, hence lowering the expansive effect of the sulphates products as well as the chlorides binding ability of cements.

A subsequent leaching from the OPC after about the 45th day may have been due to early micro-cracking which is associated with mixed salts (Hime and Marusin, 2001) for example, found in sea water. This may have been caused by the expansive sulphate products and brucite. Disintegration of the alumina-sulphate phases due to chloride ingress may have resulted in formation of soluble sulphates salts that are leachable. A concentration gradient may have also played a key role in the leaching of the sulphates from the cement mortar.

There was no significant difference between PCDC and PPC in terms of sulphates intake in sea water. This was despite the high intake of chlorides by PCDC from the same solution. This could be accounted for by the pozzolana included which makes them less permeable to aggressive agents or intake of chlorides suppressing the intake of the sulphates.

4.10.2.3 Ca^{2+}, K^+, Na^+ and pH Analyses in Sea Water

Figures 4.46 – 49 show the results for analyses of Ca^{2+}, K^+, Na^+ and pH in sea water against monitoring period.

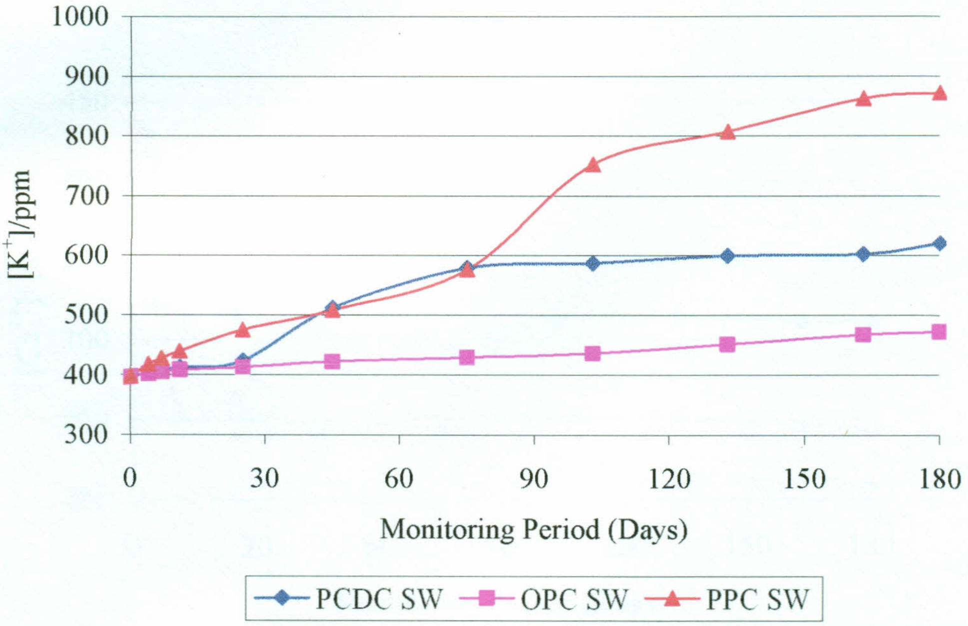

Figure 4.46: K^+ Analyses in Sea Water

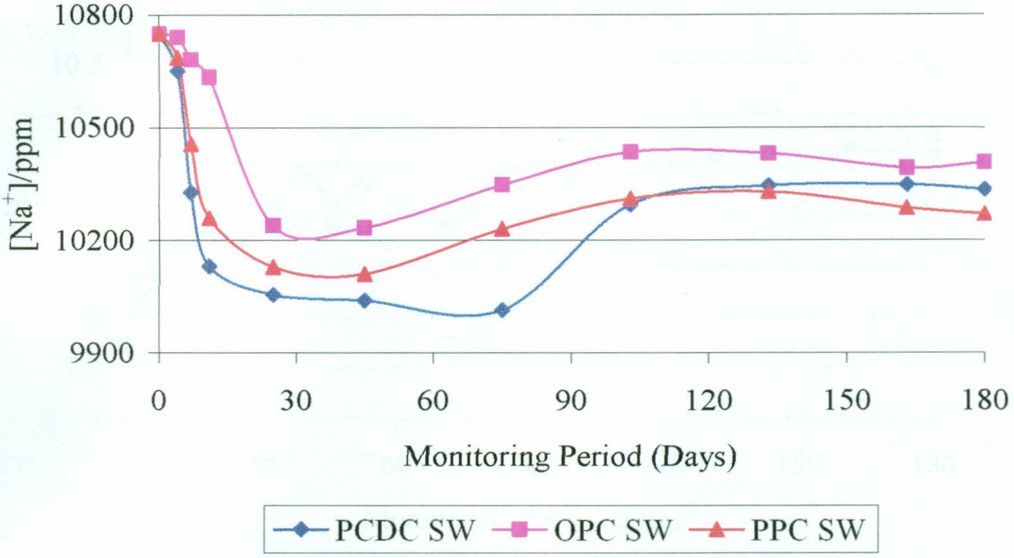

Figure 4.47: Na^+ Analyses in Sea Water

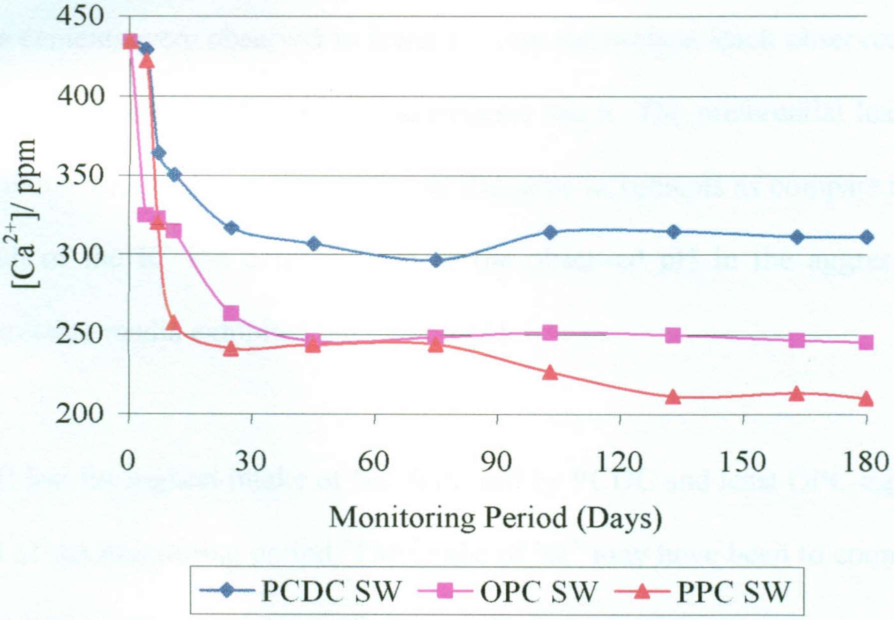

Figure 4.48: Ca^{2+} Analyses in Sea Water

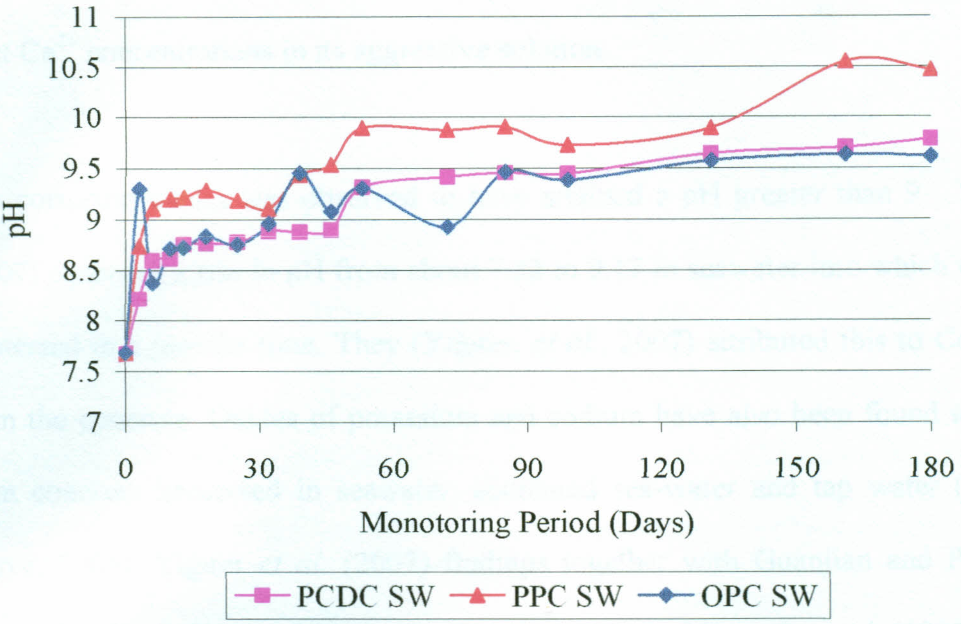

Figure 4.49: pH Measurements in Sea Water

The cements were observed to leach K^+ with the highest leach observed from PPC. There was initial intake of Na^+ then a subsequent leach. The preferential leach of K^+ could be attributed to a higher concentration of the same in cements as compared to Na^+. The high leach of the K^+ ion corresponded to the observed pH in the aggressive media. PPC aggressive media exhibited the highest pH.

PPC had the highest intake of Na^+ followed by PCDC and least OPC especially toward the end of the monitoring period. The intake of Na^+ may have been to counter for the leached K^+ on an ion exchange point of view.

The corrosive media was shown to exhibit a decline in Ca^{2+} ions. This could be most probable from precipitation of the same through salts of sulphates and/or hydroxides. PCDC maintained a higher amount of the ions in its corrosion media. Ca^{2+} ion solubility decreases with increase in pH. Thus the observed least pH in PCDC media favoured a higher concentration of the same as opposed to PPC which exhibited the highest pH with least Ca^{2+} concentrations in its aggressive solution.

The corrosion media was observed to have attained a pH greater than 9. Yiğiter *et al.* (2007) observed a rise in pH from about 7.52 to 9.17 in seawater into which concrete was immersed in a months time. They (Yiğiter, *et al.*, 2007) attributed this to $Ca(OH)_2$ leach from the concrete. Oxides of potassium and sodium have also been found to be leached from concrete immersed in seawater, simulated sea-water and tap water (Ganjian and Pouya, 2005). Yiğiter *et al.* (2007) findings together with Guanjian and Pouya (2005) agree with the findings of this study. Brown (1981) and Ferraris *et al.* (1995) observed a steady rise in pH of the corrosive media in few days, to about 12, due to release of the OH^- from the pore solution of the associated concrete.

There were dirty white precipitates observed in all cement mortar containers after pouring off the aggressive media at the end of the monitoring period. The precipitates may have resulted from scaling off of temporary protective coating formed on mortar cubes due to the presence of a combination of many ions (Taylor, 1997). The layers include, for example, of calcium sulphate and calcium hydroxides. These temporarily protective layers may have protected the mortar against aggressive ions. Thus, the attack by sea water, especially stagnant waters like in this study, was not expected to be as aggressive as pure chlorides or sulphates.

4.11 A Comparative Overview of the performance of cements in different test media

The intake rate of chlorides in their simulated solutions was faster than from the sea water both at lower and higher concentrations of the simulated solutions. Generally, there was a dirty white coating on the cubes subjected to sea water (which was also the case in sulphate solution, but few in chloride simulated solutions) that may have occasionally been scaled off during stirring at the time of sampling thus accounting for the dirty white precipitate observed in the aggressive solution sample holders. This could have acted as a 'temporarily' insoluble and thus impervious layers of, for example, $CaSO_4$, $Mg(OH)_2$ and aragonite [$(CaCO_3)n$] (Taylor, 1997). Evidence of temporally protective layer have also been found by Kurdowski (2004) that persisted over long periods in case of high alumina cements and alkali activated slag but very temporary for Portland cements and slag cements.

There was also higher intake of the chlorides in the simulated solutions as compared to the sea water. Arya *et al.* (1990) found more chloride being bound when solutions of magnesium (as well as calcium and sodium) were used compared to sea-water. The most probable reason given was the high diffusivity of the chlorides when associated with the magnesium ion in the case of simulated chloride solution.

Simulated sulphate solutions were more aggressive than the sea water. There was more intake of sulphates in the simulated solutions. This could be attributed to the presence of the chlorides in the sea water which may have provided competition for the aluminate phase with the sulphates (Santhanam, *et al.*, 2006). This is beneficial in the case of the sea water attack as it also lower the expansive potential associated with the ettringite (Santhanam, *et al.*, 2006).

In sea-water and sulphates simulated solutions, where the concentration of Na^+ was higher than the K^+. The Na^+ ingressed the cement mortar cubes initially. This could be due to the ionic difference as well as counter ion to maintain ionic.

All sulphates solutions except PCDC and OPC sulphates 1 (lower sulphates concentration) showed an increase in pH to approximately 11 upon immersion in sulphates simulated solution. Although there was a decline in their pH, the sulphates solution maintained a higher pH in the case of these cements. The observation could be linked to the high sulphates intake from the aggressive media that is counterbalanced by leach of the OH^- ions (Brown, 1981).

PCDC showed the lowest leach in K^+ from all the solutions than the PPC and OPC, except in sea water where it was higher than OPC. The leaching of Na^+ from PCDC was also noted to be least in distilled water. This could be attributed to the high replacement of the OPC by the test-ash hence lower leacheable alkalis.

It was clear that the degradation of the cement mortars was severer in chloride simulated solutions as can be seen by the large amounts of the Na^+, K^+ and Ca^{2+} leached from the mortar cubes. The source of these ions is the pore solution of concrete as well as from the disintegration of the CSH to replenish the $Ca(OH)_2$. This represents a major effect on the cement mortar properties. These include the passivation of the reinforcement as well as maintaining the media through which concrete phases and reactions are held. Leaching of these ions disturbs the equilibrium of the cement system and therefore its properties.

SO_4^{2-}, Cl^- and Na^+ ions are known to activate pozzolanic reaction as well as hydration of residual cements (Aimin and Sarkar, 1991; Barberon, *et al.*, 2005; Guerrero, *et al.*, 2000; Guerrero, 2000; Lorenzo, *et al.*, 2002; Lorenzo, 2003; Shi and Day, 2000). The percent gain of compressive strength in the sulphates was in line with the increased uptake of the SO_4^{2-}. Chlorides are known to enhance pozzolanic reaction than the SO_4^{2-} (Lorenzo, 2003). It was therefore expected that the Cl^- should have exhibited a higher percent gain in strength as compared to SO_4^{2-}. But the accompanying ion, Mg^{2+}, ingress is very destructive due to attack on CSH to form MSH that are spongy and of no cementitious value (Hime and Mather, 1999). The formed $Mg(OH)_2$, more so, is expansive and therefore deleterious to cement. This was in line with the observations in this study where the test cements had a higher strength gain in the sulphates than in chlorides simulated solutions.

It was generally observed that the test blended cements exhibited higher strength gain and reduced selected ion leach and/or intake in sulphates solutions than OPC. The opposite happened in simulated chloride solutions. In sea water and distilled water, the analysis can better be illustrated if a continued survey is done but it was observed that the PPC exhibited the highest strength gain in sea water while PCDC did so in distilled water. This was also evidenced from the selected ions analyses from the corrosive media.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

In view of the results and analyses, the following conclusions could be drawn

1. PCDC can be applicable in aggressive media and other conditions where commercial PPC (KS EAS 18-1 2001) is applicable. These include the environments with aggressive ions of sulphates, chlorides and sea water.
2. Where PCDC is used in reinforced concrete, the depth of cover should be high enough to offer protection of the reinforcement against corrosion.
3. PCDC can be used in masonry works just like commercial PPC. PCDC however, should be cured for a longer period before being subjected to the natural environment. This improves on its resistivity to aggressive media.
4. PCDC should be used with a w/c ratio that is just sufficient to allow for workability of the concrete or mortar paste.

5.2 RECOMMENDATIONS

The following are recommendations for further work:

1. The analyses of the PCDC in the aggressive media over a longer time in terms of strength development, permeability, shrinkage, expansive tests, corrosion of simulated reinforcement, chloride ingress, porosity changes, and other durability tests. These should be done with varied levels of replacement of the OPC with the test ash. The aggressive media should also include real life scenario for example, dipping the test concrete/mortar in ocean or salty water bodies. Different levels of the components of the test ash should also be considered.
2. The micro-structural changes of the cement pastes due to calcium, magnesium, chloride and sulphate ions ingress or leach into the PCDC vis a vis OPC and PPC mortar when subjected to the corrosive media.
3. A research that would involve determination of the changes in the diffusion coefficients, binding abilities, chloride profiles and corrosion extends of simulated reinforcements of the PCDC verses OPC and PPC over a long period of time, for example ten years or more. Such a survey would shed more light on the effect of the test ash on diffusivity of chloride over a long term. This would help in establishing the durability of rebar and hence the reinforced concrete where PCDC may find application.

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7.0 Appendix A

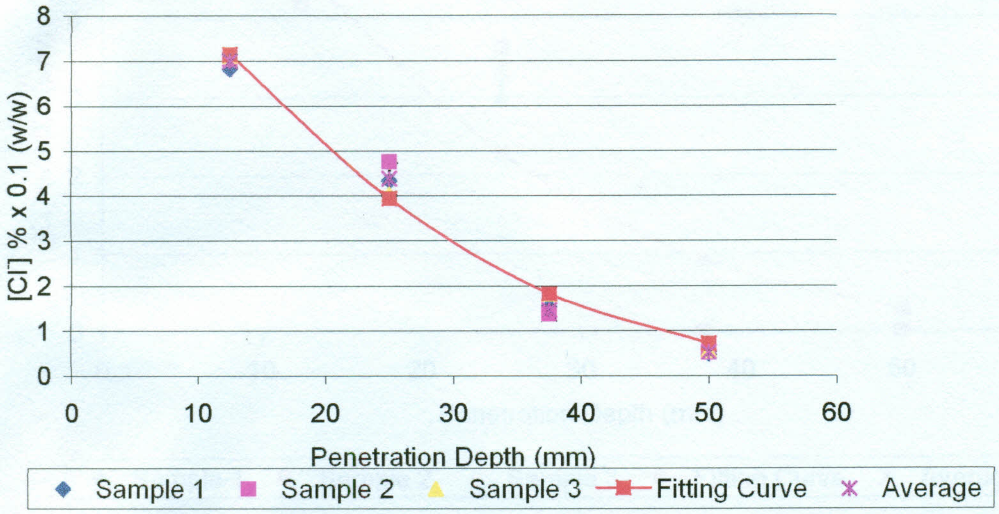

Figure 7.1: Error Function fitting for OPC (w/c 0.8), D_{app}= 2.5 x 10^{-11} m^2/s, and C_s = 1.111 % (r^2 = 0.9864)

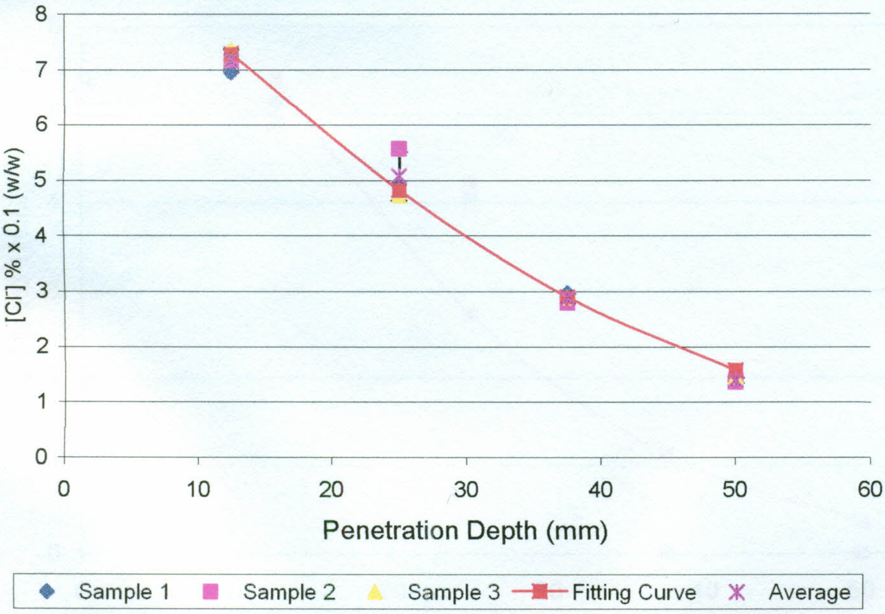

Figure 7.2: Error Function fitting for OPC (w/c ratio 0.85), D_{app}= 4.27 x 10^{-11} m^2/s, and C_s = 1.008 % (r^2 = 0.9945)

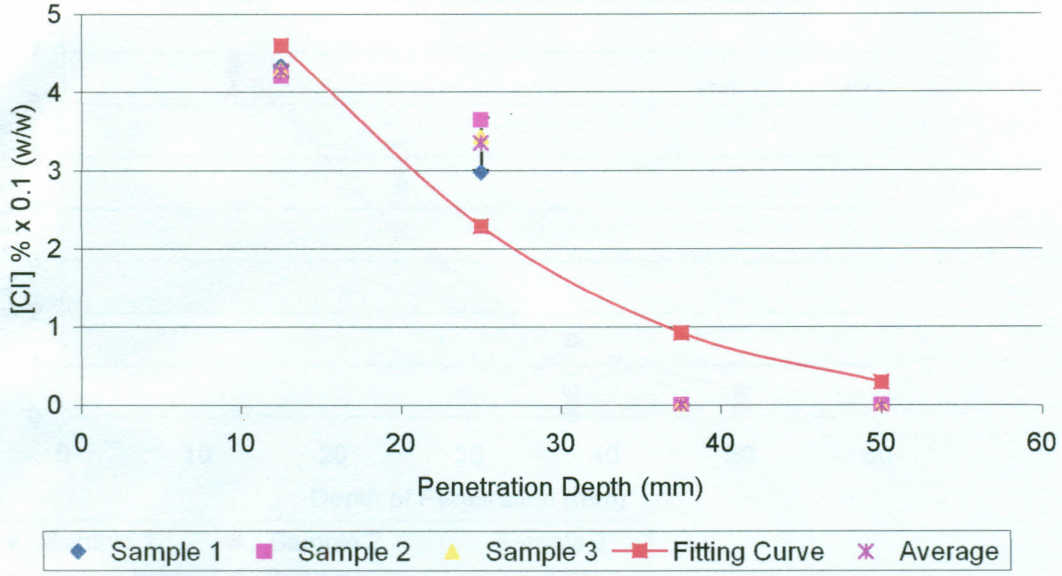

Figure 7.3: Error Function fitting for OPC-25 % PFA(w/c ratio 0.73), D_{app}= 2.01 x 10^{-11} m^2/s, and C_s = 0.76 % (r^2 = 0.87)

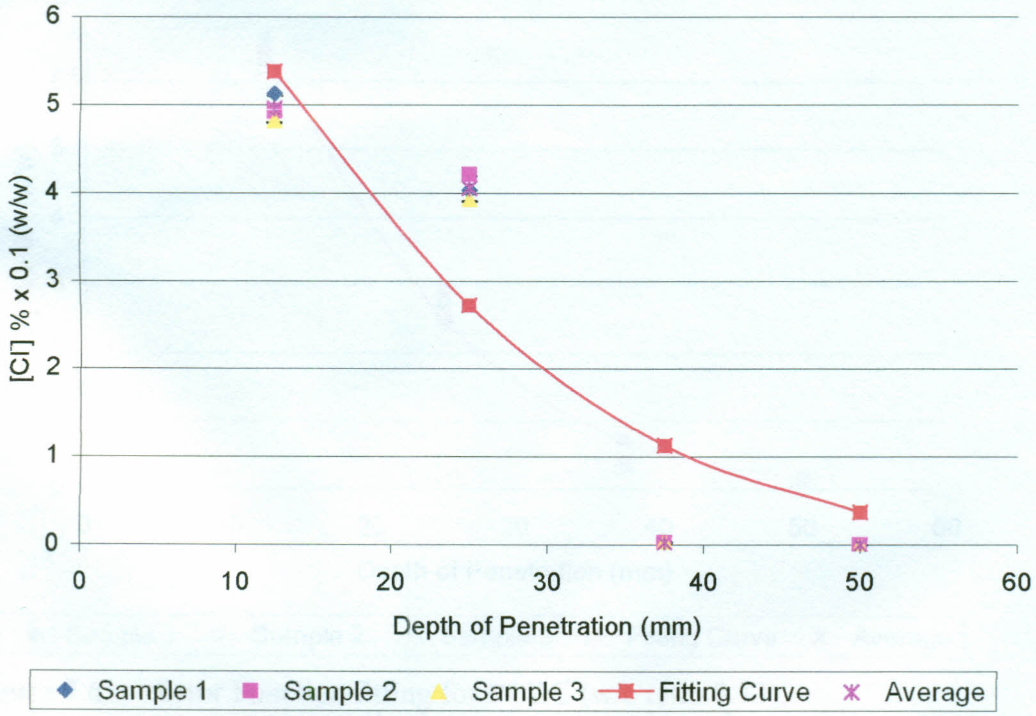

Figure 7.4: Error Function fitting for OPC-25 % PFA(w/c ratio 0.80), D_{app}= 2.09 x 10^{-11} m^2/s, and C_s = 0.879 % (r^2 = 0.8505)

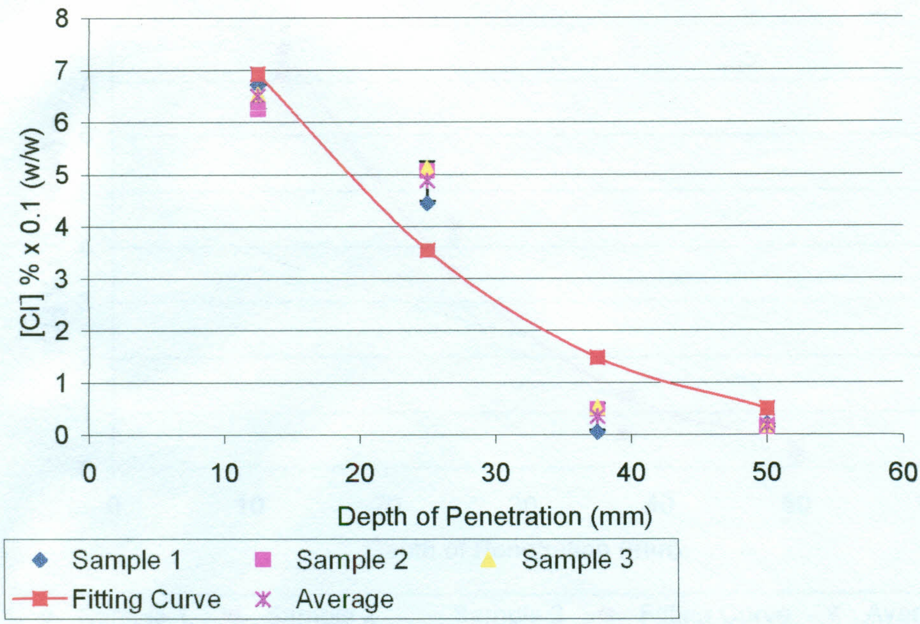

Figure 7.5: Error Function fitting for OPC-25 % PFA(w/c ratio 0.85), D_{app}= 2.12 x 10^{-11} m^2/s, and C_s = 1.124 % (r^2 = 0.8969)

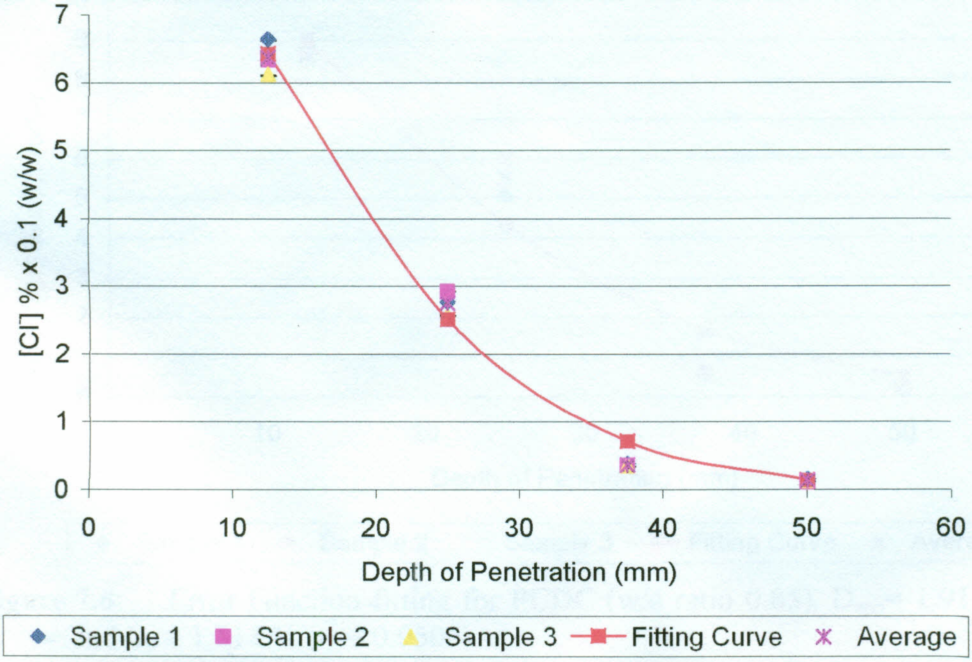

Figure 7.6: Error Function fitting for PCDC (w/c ratio 0.73), D_{app}= 1.34 x 10^{-11} m^2/s, and C_s = 1.219 % (r^2 = 0.9934)

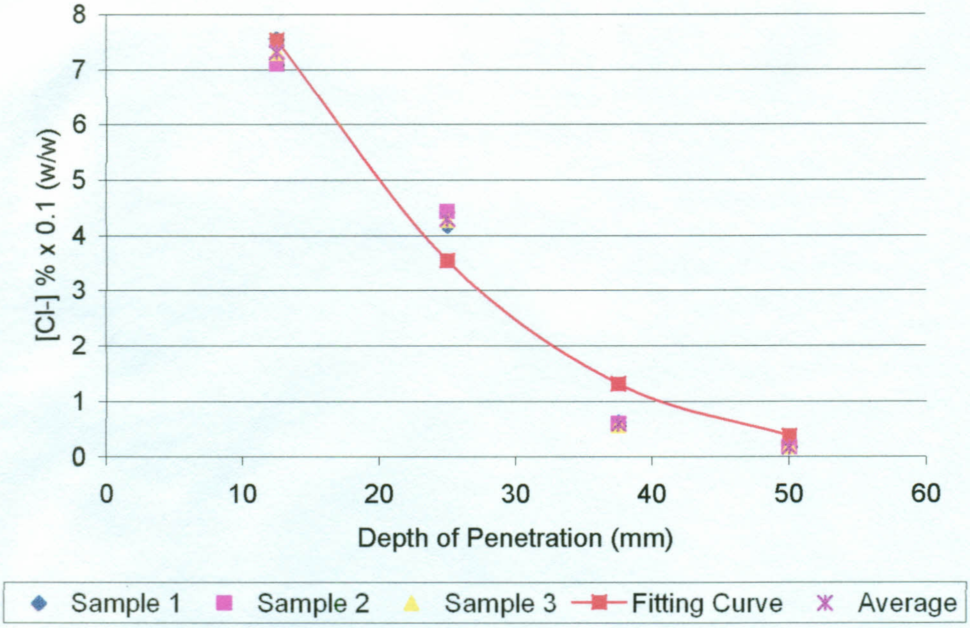

Figure 7.7: Error Function fitting for PCDC (w/c ratio 0.8), D_{app}= 1.81 x 10^{-11} m^2/s, and C_s = 1.285 % (r^2 = 0.968)

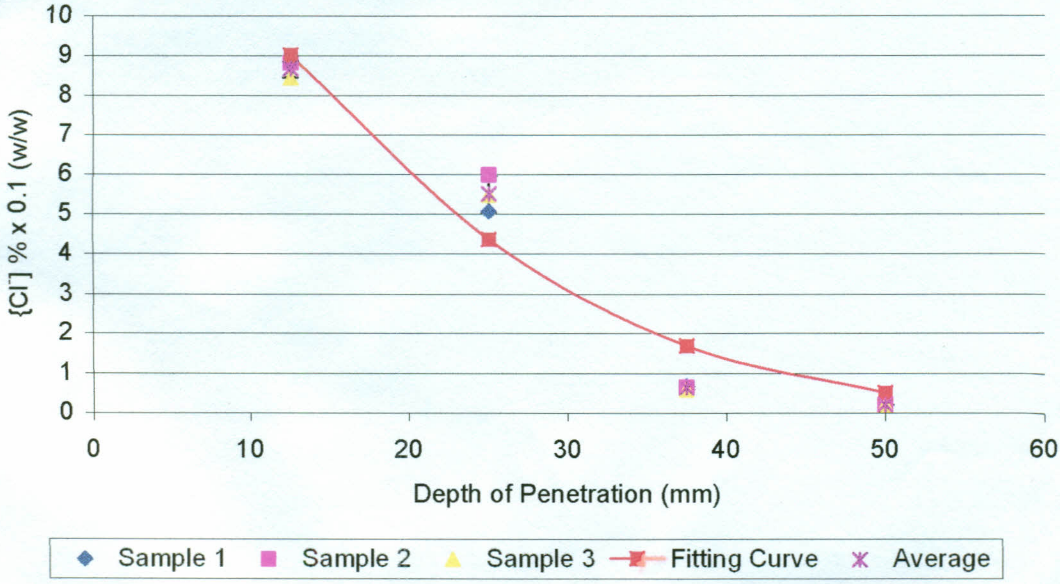

Figure 7.8: Error Function fitting for PCDC (w/c ratio 0.85), D_{app}= 1.91 x 10^{-11} m^2/s, and C_s = 1.513 % (r^2 = 0.9506)