INTRODUCTION

Reinforced concrete has wide applications globally. It is used to build bridges, car parks, quays and offshore structures like gravity base platforms and barges. Its application in these areas is as a result of its good compressive strength, low cost and low maintenance requirement. It is also widely used in the marine environment, subsea as a weight coat to increase the seabed or bottom stability of pipelines.

Most of the reinforced concrete structures continue to perform as designed offering a low maintenance solution. However, due to exposure to adverse conditions not anticipated at inception or inadequate specification and construction practices, concrete structures can fail prematurely. It is not uncommon, therefore, to see extensive corrosion of reinforcing steel in such diverse structures as industrial & residential buildings, car parks, ports and power & desalination plants which require some form of repairs.

In a reinforced concrete structure the alkaline nature of the hydrated cement phases leads to the formation of a passive oxide layer on the surface of the reinforcing steel that effectively reduces corrosion to negligible levels. However, the finite permeability of concrete allows the ingress of chemical agents which lead to a breakdown in the protective passive layer and subsequent corrosion of reinforcing steel. The two most commonly encountered processes leading to rebar corrosion are: (a) carbonation in which a pH reduction in the concrete pore solution is induced by the action of carbon dioxide and (b) chloride attack. These processes lead to breakdown of the passive oxide layer and subsequent formation of expansive corrosion products, which can lead to cracking and spalling of the concrete surface (Trend 2000 Ltd, 2002).

Corrosion of reinforced steel is one of the most important and prevalent mechanisms of deterioration for concrete structures in marine environments. High permeability and porous concrete, poor design detailing, and construction defects, such as inadequate depth of cover, are quality control problems, which allow the ingress of salt and moisture into the concrete. The higher concentrations of salt and moisture can result in accelerated corrosion of the reinforced steel and significant deterioration to the concrete structure. Conventional repair methods, which include the removal of damaged concrete and repair with cement patching materials, have proven to be ineffective in controlling corrosion under these conditions (Davison, N).

Over the last ten years, cathodic protection has increasingly been used to provide long term corrosion control for reinforced concrete structures in marine environments. Cathodic protection is an electrochemical method, which can

effectively stop further corrosion of the reinforcing steel regardless of the salt content in the concrete. Galvanic (sacrificial) anode and impressed current are the two types of cathodic protection. Systems using both sacrificial (galvanic) and impressed current anodes have been successfully applied to the splash, tidal and atmospheric zones of marine structures.

Thermally sprayed zinc and zinc anodes are widely used sacrificial anodes in cathodic protection. The work carried out in this thesis measures current requirement for cathodic protection and checks the effectiveness of Zinga, a coating consisting of 96% by weight of pure zinc in an organic and polar solvent, painted and sprayed on the concrete to form the sacrificial anode against the more convectional impressed current cathodic protection method.

1. USES AND ADVANTAGES

Concrete is an artificial material similar to stone that is used for many different structural purposes. It is made by mixing sand, gravels, with water and cement and then allowing it to harden by hydration. Hydration causes crystals to form that interlock and bind together. Its density lies between 1750-2400kg/m^3 and compressive strength from 20Mpa for low strength concrete and at least 70Mpa for high strength concrete (Neville, 1995).

According to the Brooklyn Public Library, concrete was first made in 500 BC and can last up to 50,000 years. Concrete is one of the most important building materials. From sidewalks to skyscrapers to offshore structures, we see concrete everyday, everywhere. There are many different kinds of concrete (Katrina Jones, 1999).

Reinforced concrete is strengthened by steel. This is done by casting concrete around steel rods or bars and most large structures such as bridges need this extra strong concrete. Prestressed concrete is made by casting concrete around steel cables stretched by hydraulic jacks. After the concrete hardens the jacks are released and the cables compress the concrete. Concrete when compressed is the strongest. This type of concrete is used for floors and roofs as well as other things. Precast concrete is cast and hardened before being used for construction. Precasting makes it possible to produce a mass number of concrete building materials (Katrina Jones, 1999).

Concrete blocks are made in various weights and sizes and they are used to make about two-thirds of masonry walls in the US. Engineers have designed different kinds of concrete for certain uses. Air-entrained concrete is good in harsh weather and is used for roads and airport runways. High-early-strength concrete is used in hurried jobs and cold weather because it hardens quicker than ordinary concrete (Katrina Jones, 1999).

Reinforced concrete is widely used in harsh environments like the marine environment and for offshore structures. Its advantages include:

- The design weight of the concrete hull produces a low center of gravity, which increases the structure's stability.
- Good compressive strength
- Reduced fabrication time than steel structures at a competitive cost.
- Good tensile strength, thanks to the reinforcing steels.
- Chemically inert and resistant to creep
- The large mass of the concrete structure aids in dampening the vibration produced by compressors, generators, etc.

- Low maintenance, no painting, fire-proof, non-corroding, and no vibration fatigue.
- Compartmented base serves as a double hull as well as provides storage for oil, produced water, and/or various condensates.
- Provides its own buoyancy and stability during towing to site.
- Transportable and reusable.
- Its weight increases the bottom stability on subsea pipelines

1.1. THE HEIDRUN TENSION LEG PLATFORM

This is a floating   tension-anchored leg concrete platform. The hull consists of four columns and pontoons in addition to concrete main deck girders   and extensive use of low weight aggregate concrete, totaling approximately 70 000 m^3. The four sea-bed anchors   are formed as the base section   and support the   topside   facilities. This is the first of its kind and is located in a water depth of 350meters in Norway (http://www.aas-akobsen.no/Marine/marine_e.htm# Referanser).

Figure 1 The Heidrun Tension Leg Platform
 (http://www.aas-jakobsen.no/Marine/marine_e.htm#Referanser)

1.2. THE HIBERNIA GRAND BANKS CANADA

The Hibernia's novel 450,000 ton gravity base structure design consists of a 105.5metre concrete caisson with a height; constructed using high strength concrete reinforced with steel rods and pre-stressed tendons. The caisson is surrounded by an ice wall, which consists of 16 concrete teeth. Slip-forming, a continuous process of placing rebar and pouring concrete, was utilized during construction of the gravity based structure.

This supports the Hibernia platform located near the Newfoundland's shelf of the North sea. This is the heaviest platform in the world.

Figure 2 Gravity Base of the Hibernia Platform
(www.hrc-usa.com/offshore_ oil_platforms.htm).

2. CONCRETE MIXTURE

In its simplest form, concrete is a mixture of paste, sand and aggregates. The paste, composed of cement and water coats the surface of the sand and coarse aggregates. Through a chemical reaction called hydration , the paste hardens and gains strength to form the rock-like mass known as concrete.

The physical properties of density and strength of concrete are determined, in part, by the proportions of the three key ingredients, water, cement, and aggregate.

The key to achieving a strong, durable concrete rests in the careful proportioning and mixing of the ingredients. A concrete mixture that does not have enough paste to fill all the voids between the aggregates will be difficult to place and will produce rough, honeycombed surfaces and porous concrete. A mixture with an excess of cement paste will be easy to place and will produce a smooth surface; however, the resulting concrete is likely to shrink more and be uneconomical. A properly designed concrete mixture will possess the desired workability for the fresh concrete and the required durability and strength for the hardened concrete.

The characteristics of the concrete are determined by quality of the paste. The strength of the paste, in turn, depends on the ratio of water to cement. The water-cement ratio is the weight of the mixing water divided by the weight of the cement. High quality concrete is produced by lowering the water-cement ratio as much as possible without sacrificing the workability of fresh concrete.

It is worth remembering that water is the key ingredient. Too much water results in weak concrete. Too little water results in a concrete that is unworkable and concrete has no theory which predicts its behavior and properties. Hence samples were made for testing to ensure quality.

2.1. FINE AND COARSE AGGREGATES

Aggregates are inert granular materials such as sand, gravel, or crushed stone that, along with water and cement, are an essential ingredient in concrete. The choice of the aggregates is a function of the required or expected physical/mechanical properties. Aggregates impact on properties such as density and strength of the concrete. Usually the density of concrete is about $2400kg/m^3$; light aggregates allow densities to reach $1750kg/m^3$.

For a good concrete mix, aggregates need to be clean, hard, strong particles free of absorbed chemicals or coatings of clay and other fine materials that could cause the deterioration of concrete. Aggregates, which account for 60 to 75 percent of the total volume of concrete, are divided into two distinct categories:- fines and coarse.

Fine aggregates generally consist of natural sand or crushed stone with most particles passing through a 3/8-inch (9.5mm) sieve. Coarse aggregates are any particles greater than 0.19 inch (4.75 mm), but generally range between 3/8 and 1.5 inches (9.5 mm to 37.5 mm) in diameter. Gravels constitute the majority of coarse aggregate used in concrete with crushed stone making up most of the remainder.

Natural gravel and sand are usually dug or dredged from a pit, river, lake, or seabed. Crushed aggregate is produced by crushing quarry rock, boulders, cobbles, or large-size gravel. Recycled concrete is a viable source of aggregate and has been satisfactorily used in soil-cement, and in new concrete. Aggregate processing consists of crushing, screening, and washing the aggregate to obtain proper cleanliness and gradation. If necessary, a benefaction process such as jigging or heavy media separation can be used to upgrade the quality. Once processed, the aggregates are handled and stored in a way that minimizes segregation and degradation and prevents contamination. Aggregates strongly influence concrete freshly mixed and hardened properties, mixture proportions, and economy. Consequently, selection of aggregates is an important process. Although some variations in aggregates properties are expected, characteristics that are considered when selecting aggregate include:

- Grading
- Durability
- Particle shape and Surface Texture
- Abrasion and Skid Resistance
- Unit Weight and Voids
- Absorption and Surface Moisture

Grading refers to the determination of the particle-size distribution for aggregate. Grading limit, and maximum aggregates sizes are specified because grading and size affect the amount of aggregates used as well as cement and water requirements, workability, pumpability, and durability of concrete. In general, if the water-cement ratio is chosen correctly, a wide range in grading can be used without a major effect on strength. When gap-graded aggregates are specified, certain particle sizes of aggregates are omitted from the size continuum. Gap-graded aggregates are used to obtain uniform textures in exposed aggregate concrete. Close control of mixture proportions is necessary to avoid segregation.

Particle shape and surface texture influence the properties of freshly mixed concrete more than the properties of hardened concrete. Rough-textured, angular, and elongated particles require more water to produce workable concrete than smooth, rounded compact aggregates. Consequently, the cement content must also be increased to maintain the water-cement ratio. Generally, flat and elongated particles are avoided or are limited to about 15 percent by weight of the total aggregates.

Unit-weight measures the volume that graded aggregates and the voids between them will occupy in concrete. The void content between particles affects the amount of cement paste required for the mixture. Angular aggregates increase the void content. Larger sizes of well-graded aggregates and improved grading decrease the void content.

Absorption and surface moisture of aggregates are measured when selecting aggregate because the internal structure of aggregates are made up of solid material and voids that may or may not contain water. The amount of water in the concrete mixture must be adjusted to include the moisture conditions of the aggregates.

Abrasion and skid resistance of aggregates are essential when the aggregate is to be used in concrete constantly subject to abrasion as in heavy-duty floors or pavements. Different minerals in the aggregates wear and polish at different rates. Harder aggregate can be selected in highly abrasive conditions to minimize wear (http://www.cement.org/basics/concretebasics_aggregate.asp).

2.2. CEMENT

The properties of concrete depend on the quantities and qualities of its components. Cement is the most active component of concrete and usually has the greatest unit cost, its selection and proper use are important in obtaining most economically the balance of properties desired for any particular concrete mixture. It is essential that engineers select the type of cement that will obtain the best performance from the concrete. This choice involves the correct knowledge of the relationship between cement and performance and, in particular, between type of cement and durability of concrete.

Table 1 Cement types and their uses.

Cement Type	Use
I[1]	General purpose cement, when there are no extenuating conditions
II[2]	Aids in providing moderate resistance to sulphate attack
III	When high-early strength is required
IV[3]	When a low heat of hydration is desired (in massive structures)
V[4]	When high sulphate resistance is required
IA[4]	A type I cement containing an integral air-entraining agent
IIA[4]	A type II cement containing an integral air-entraining agent
IIIA[4]	A type III cement containing an integral air-entraining agent

The composition of cements is what distinguishes one type of cement from another. The phase compositions in cement are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). However, it should be noted that these compositions would occur at a phase equilibrium of all components in the mix and do not reflect effects of burn temperatures, quenching, oxygen availability, and other real-world kiln conditions. The actual components are often complex chemical crystalline and amorphous structures, denoted by cement chemists as "elite" (C_3S), "belite" (C_2S), and various forms of aluminates. The behavior of each type of cement depends on the contents of these components. Different analytical techniques such as x-ray diffraction and analytical electron microscopy are used to understand fully the reaction of cement with water (hydration process) and to improve its properties.

Early hydration of cement is principally controlled by the amount and activity of C_3A, balanced by the amount and type of sulphate interground with the cement. C_3A hydrates very rapidly and will influence early bonding characteristics. Abnormal hydration of (C_3A) and poor control of this hydration by sulphate can

lead to such problems as flash set, false set, slump loss, and cement-admixture incompatibility

The microstructure of the cement hydrates will determine the mechanical behavior and durability of the concrete. In terms of cement composition, the C_3S and C_2S will have the primary influence on long term development of structure, although aluminates may contribute to formation of compounds such as ettringite (sulphoaluminate hydrate), which can cause expansive disruption of concrete. Cements high in C_3S (especially those that are finely ground) will hydrate more rapidly and lead to higher early strength. However, the hydration products formed will, in effect, make it more difficult for hydration to proceed at later ages, leading to an ultimate strength lower than desired in some cases. Cements high in C_2S will hydrate much more slowly, leading to a denser ultimate structure and a higher long-term strength (www.fhwa.dot.gov/infrastructure/materialsgrp/ cement. html).

2.3. WATER

Despite its simple chemical formula H_20, water plays a complex role in making concrete. Water chemically binds together sand, crushed stone or gravel and cement in a process called hydration, and makes it possible to work the mixture into the concrete slabs, columns and other forms used in construction.

Getting the right concrete mix is a matter of properly balancing the amounts of water and dry ingredients. The key ingredient in concrete workability is water. But water is also the element that combines with cement in a process called hydration, and the amount of water needed for hydration is less than that needed for workability.

Excess water makes concrete more porous, leaving voids as the water not needed for hydration slowly evaporates. Worse yet, excess water also causes shrinkage cracks which appear as the concrete cures.

Porosity can weaken concrete durability because salts and carbon dioxide can more easily penetrate the concrete and cause other chemical reactions, including reduced alkalinity. Alkalinity protects concrete reinforcing steel rods from rusting.

If a mix of concrete has more water than is needed for workability, it may not meet the strength specified, thus reducing its load carrying capacity. Similarly, too little water weakens the chemical bonding between the sand, aggregates and cement during hydration.

Whether the concrete is used for a parking structure, a high-rise building, or a slab-on grade, compromising its strength can be very costly, not only in terms of testing and rework but also in potential lawsuits. With concrete, it is important to keep the mix right from start to finish
(http://www.beyer.com/news_ fall 98_concretebasics.htm).

2.4. ADMIXTURES

Admixtures are materials other than sand, water, cement and reinforced fiber, used as ingredients of cement, and added to the batch immediately before or during mixing. They include: accelerators, retarders, water reducers, superplasticizers, air entrainers, pumping aiders, coloring admixtures, etc. Their uses depend on some factors which include the expected properties of the concrete, the environment in which the concrete is made, for example subsea pouring.

A proper use of admixtures offers certain beneficial effects to concrete, including improved quality, acceleration or retardation of setting time, enhanced frost and sulphate resistance, control of strength development, improved workability, and enhanced finishability. It is estimated that 80% of concrete produced in North America these days contains one or more types of admixtures. According to a survey by the National Ready Mix Concrete Association, 39% of all ready-mixed concrete producers use fly ash, and at least 70% of produced concrete contains a water-reducer admixture.

Admixtures vary widely in chemical composition, and many perform more than one function. Two basic types of admixtures are available: chemical and mineral. All admixtures to be used in concrete construction should meet specifications; tests should be made to evaluate how the admixture will affect the properties of the concrete to be made with the specified job materials, under the anticipated ambient conditions, and by the anticipated construction procedures.

Chemical admixtures are added to concrete in very small amounts mainly for the entrainment of air, reduction of water or cement content, plasticization of fresh concrete mixtures, or control of setting time.

Seven types of chemical admixtures are specified in ASTM C 494, and AASHTO M 194, depending on their purpose or purposes in PCC. Air entraining admixtures are specified in ASTM C 260 and AASHTO M 154. General and physical requirements for each type of admixture are included in the specifications (http://www.fhwa.dot.gov/infrastructure/materialsgrp/admixture.html).

2.5. FLY ASHES

Fly ashes are finely divided residue resulting from the combustion of ground or powdered coal. They are generally finer than cement and consist mainly of glassy-spherical particles as well as residues of hematite and magnetite, char, and some crystalline phases formed during cooling. Use of fly ash in concrete started in the United States in the early 1930's.The major breakthrough in using fly ash in concrete was the construction of Hungry Horse Dam in 1948, utilizing 120,000 metric tons of fly ash. This decision by the U.S. Bureau of Reclamation paved the way for using fly ash in concrete constructions.

In addition to economic and ecological benefits, the use of fly ash in concrete improves its workability, reduces segregation, bleeding, heat evolution and permeability, inhibits alkali-aggregate reaction, and enhances sulphate resistance.

The finer the material the higher the water demands due to the increase in surface area. The finer material requires more air-entraining agent to be added to achieve the mix desired air content. The important thing to remember is uniformity. If fly ash is uniform in size, the mixture design can be adjusted to give a good uniform mixture.

The carbon content, which is indicated by the loss of ignition, also affects the air entraining agents and reduces the entrained air for a given amount of air-entraining agent. An additional amount of air-entraining agent will need to be added to get the desired air content. The carbon content will also affect water demand since the carbon will absorb water. Again uniformity is important since the differences from non-fly ash concrete can be adjusted in the mixture design.

The use of fly ash increases the absolute volume of cement materials compared to non-fly ash concrete; therefore, the paste volume is increased, leading to a reduction in aggregate particle interference and enhancement in concrete workability. The spherical particle shape of fly ash also participates in improving workability of fly ash concrete because of the so-called "ball bearing" effect (http://www.fhwa.dot.gov/infrastructure/materialsgrp/flyash.htm).

3. CONCRETE PROPERTIES

3.1. WORKABILITY

This   is often referred to as the ease with which concrete   can be transported, placed and   consolidated   without excessive bleeding or segregation. It   includes properties such   as   flowability,   moldability, cohesiveness, and compatibility (http://www.engnetbase.com/books/844/0958%20ch40.pdf).

One of the main factors affecting the concrete workability is the water content in the concrete mix. A harsh concrete becomes workable by the addition of water. Workability can also be improved by the addition of plasticizers and air entraining agents. The factors that affect   workability includes quantities of paste and aggregates, plasticity of the   cement   paste,   maximum   size   and   grading   of aggregates, and shape and surface characteristics of the aggregates.

It   is   obvious   that   no   single   test can evaluate all these factors. In fact, most of these   cannot   be   easily   assessed   even though some standard tests have been established to evaluate   them   under   specific   conditions which   are not always similar   to   that   occurring   on site. Thus   it   is therefore   more useful comparing mixtures than accepting testing on site (http://www.engnetbase.com /books/844/0958%20ch40.pdf).

3.2. SETTING

The setting of concrete is determined by the cement contained in it. A penetrometer is used for determining the initial and final setting times of cement. A needle of approximate size has to be used. The force required to penetrate 1 inch (0.0254m) in depth is noted. The force divided by the area of the bearing surface of the needle yields the penetration resistance.

Concrete may exhibit flash set due to the reaction of C_3A, forming calcium aluminate hydrates and monosuphate hydrate .Workability will not be restored by remixing when flash set occurs(Ramachandran, and Beaudoin, 2001, p.38-39).

3.3. BLEEDING

In a freshly placed concrete which is still plastic, settlement of solids is followed by the formation of a layer of water on the surface. This is known as bleeding or water gain. In lean mixes, localised channels develop and the seepage of water transports some particles to the surface. Bleeding may thus give rise to laitance, a layer of weak, nondurable material containing dilute cement paste. If bleeding occurs by uniform seepage of water, no undesirable effects result and such a bleeding is known as normal bleeding. Bleeding is not necessarily harmful. If undisturbed, the water evaporates so that the effective water-cement ratio is lowered with a resultant increase in strength.

The amount of bleeding can be reduced by using proper amount of fines, high alkali or C_3A contents, increasing cement content, and admixtures such as pozzolans, calcium chloride, or air entraining admixtures. Bleeding characteristics are measured by bleeding rate or bleeding capacity, applying the ASTM C232 standard (Ramachandran and Beaudoin, 2001, p. 40).

3.4. SEGREGATION

During the handling of concrete mixture, there may be some separation of coarse aggregates from the mixture, resulting in a concrete mass that is not uniform. This is known as segregation. Segregation may lead to flaws in the final product and honeycombing may occur in some instances. The primary cause of segregation which may result during handling, placing, vibrating, or finishing operations is the differences in size of the particles and specific gravity of mix. The tendency to segregate increases with slump, reduction in cement content, or increase in the maximum size of the aggregate. By proper grading of the constituents and handling, this problem can be controlled (Ramachandran and Beaudoin, 2001, p. 40-41).

3.5. MECHANICAL PROPERTIES

Hardened concrete has to conform to certain requirements for mechanical properties. They include compressive strength, splitting tensile strength, flexural strength, static modulus of elasticity, Poisson's ratio, mechanical properties under triaxial loads, creep under compression, abrasion resistance, bond development with steel, penetration resistance, pull out strength ,etc(Ramachandran and Beaudoin, 2001).

The mechanical behaviour of concrete should be seen from the point of view of a composite material. A composite material is a three dimensional combination of at least two chemically or mechanically distinct material with a definite interface separating the components. The model of concrete is simplified by treating it as a matrix containing aggregates embedded in a matrix of cement paste (Ramachandran and Beaudoin, 2001, p. 41).

The factors that influence the mechanical behaviour of concrete include: shape of particles, size and distribution of particles, concentration, their orientation, topology, composition of the disperse and continuous phases, and that between the continuous disperse phase and the pore structure(Ramachandran and Beaudoin, 2001, p. 41)

Concrete is stronger in compression than in tension and the most important properties of concrete are its strength and rigidity. Rigidity or the modulus of elasticity of concrete is in a range of 30 to 80MPa and is frequently expressed in terms of compressive strength. While many empirical equations for predicting modulus of elasticity have been proposed by many investigators, few equations are considered to cover the whole data. The reason is considered to be that the mechanical properties of concrete are highly dependent on the properties and proportions of binders and aggregates.

When concrete is freshly produced, it is plastic in behavior and is often called plastic concrete. However, concrete is a brittle composite and its failure mode is dependent on its ultimate strain. Even under axial load, tensile strain is generated by Poisson's effect in the lateral direction (http://www.engnetbase.com /books/844/0958%20ch40.pdf).

Abrams in 1918 formulated the relation between water-cement ratio and the strength of concrete given by the equation: $S = A/B^w$. Where S is the strength of the concrete and w is the water-cement ratio. The law governing the equation is called Abram's law. The constants; A and B depend on the age, cure regime, type of cement, and the testing method. This law is valid provided the concrete is fully compacted. This is the reason why below a

certain minimum, further reduction in the water-cement ratio does not result in the expected strength gain. At such low water-cement ratios, concrete is not workable enough to allow full compaction. Air entrainment reduces concrete strength and this effect should be considered when applying the law (Ramachandran and Beaudoin, 2001, p.42).

3.6. THERMAL PROPERTIES

Concrete is a poor thermal conductor. This makes it a good insulator. Thermal conductivity is a property of a material that expresses the heat flux f (W/m^2) that will flow through the material if a certain temperature gradient δT (K/m) exists over the material. The thermal conductivity is usually expressed in W/m.K. and called l. The usual formula is:

f = l * δT

Thermal conductivity is a property that describes the semi static situation; the temperature gradient is assumed to be constant. As soon as the temperature starts changing, other parameters enter the equation. The thermal conductivity, volumetric heat capacity, and thermal diffusivity of concrete are about 1.28W/mK, $1.940*10^6 J/m^3$ $66*10^{-8} m^2$/s respectively at 20°C.

Although latent heat effects are primarily determined by the cement paste, the thermal conductivity of concrete is determined by the aggregates. The heat of hydration has to be limited so as to reduce the thermal gradient which limits the probability of cracking. This can be achieved by controlling the chemistry of the cement or cooling the mix or any other method that reduces or limits the heat of hydration (http://www.hukseflux.com/thermal%20conductivity/thermal.htm).

3.7. ELECTRICAL PROPERTIES

The electrical properties of concrete depend on the quality of the concrete. A porous concrete will be more conductive than a well compacted concrete. The electrical conductivity of concrete also depends on the type of cement and electrical nature of the aggregates.

Conductive concrete is a cement-based composite that contains a certain amount of electronically conductive components to attain stable and relatively high conductivity. In essence, the aggregates normally used in concrete can be largely replaced by a variety of carbon-based materials to achieve electrical conductivity in conductive concrete (Kelly Baldwin, 1998).

4. DURABILITY OF CONCRETE

Concrete is a composite with properties that change with time. During service, the quality of concrete provided by the initial curing can be improved by subsequent wetting as in the case of foundations or water retaining structures. However, concrete can also deteriorate with time due to physical and chemical attacks.

Durability of concrete depends on a lot of factors including physical and chemical properties, service environment and design life. Physical properties of concrete are mostly discussed in terms of permeation and the movement of mass aggressive agents in and out of the concrete, while chemical properties are discussed in terms of the quality and type of hydration products, mainly calcium silicate hydrate, and calcium hydroxide of the set cement. It is the nature of the reaction of the hydration products and the penetrating agents that control the severity of chemical attack. Physical damage can occur due to contraction and expansion under restraint, or resulting from exposure to abrasion, erosion or fire during service (http://www.engnetbase.com/books /844/0958%20ch41.pdf).

The surface layer or cover layer plays a major role in concrete durability as it serves as the first line of defence against physical and chemical attacks from the environment (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

4.1. PERMEATION THROUGH CONCRETE

Permeation defines the ease with which fluids, both liquids and gases, can enter into, or move through concrete. The ability of fluids to enter into concrete is sometimes referred to as penetrability of concrete. Three fluids are relevant to durability and they are water, carbon dioxide and oxygen. Water can be detrimental in either its pure (uncontaminated) form or if it is contaminated with aggressive ions such as chlorides and sulphate (http://www.engnetbase.com/books/844/0958% 20ch41.pdf).

Concrete is a porous medium with permeation properties controlled by the microstructure of its hardened cement paste, which in turn, is determined by the type of cement used, the water-cement ratio, the paste volume, and the extent of curing and compaction. Within this cement paste, the transition zone, which is the interface between the cement paste and the aggregate, is known to be more porous than the bulk of the cement paste. Thus, it is the microstructure of this transition zone that controls the permeation of concrete. As far as the ease of movement of fluids through concrete is concerned, three transport mechanisms should be distinguished and they are permeability, diffusion and absorption (http://www.engnetbase.com/books/844/0958%20ch41 .pdf).

Permeability refers to the flow of water through concrete under a pressure differential. The rate of flow follows Darcy's law for laminar flow through a porous medium. It depends on the pressure gradient and size of interconnected pores in the cement paste. For flow to occur, the concrete has to be in its saturated conditions with relevant pores being continuous and greater than 120 nm. Quantitatively, this property is discussed in terms of the coefficient of permeability, commonly expressed in meters per second (m/s). Permeability is a relevant property to be measured in assessing the durability and serviceability of structures like dams, foundations, and underground structures, where they are in constant contact with water (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Diffusion is the process whereby gases like carbon dioxide and oxygen or ions in solution like chlorides ions enter concrete under a differential in concentration. The diffusion of these species can be described by Fick's law. Diffusivity or diffusion coefficient, in m^2/s, is often used to refer to the rate at which these species enter or leave the concrete. In addition to concentration gradient and sizes of capillary pores, the rate of diffusion is influenced by the type of penetrating species and the chemical properties of the concrete. Diffusion of gases is very slow in saturated concrete and is, therefore, a property relevant to concrete in above ground structures such as buildings and bridges, where concrete is partially dry. For the durability of submerged or underground structures, the diffusion of chloride

and sulphate ions should be considered (http://www.engnetbase.com /books/844/0958% 20ch41.pdf).

Absorption is a result of capillary movement of liquids in the pores of the hardened cement paste under ambient conditions. Note that capillary suction occurs in dry or partially dry concrete, a condition which commonly occurs in practice for above ground structures. Absorption is relevant, particularly to coastal structures, where chloride salts carried by wind deposit on concrete surfaces. Once wetted by rain, water carrying chloride ions is absorbed into the concrete. The rate at which liquids, mainly water is absorbed into concrete is often referred to as absorptivity, in m/s$^{0.5}$. This parameter is highly dependent on the initial moisture content of the concrete and therefore, the test method used (http://www.engnetbase.com /books/844/0958%20ch41.pdf).

It is important to specify concrete with low water-cement ratio, adequate initial curing and proper compaction so as to achieve good quality concrete with low permeation properties. In testing for permeation properties, it is important to recognize the type of structure under consideration and its service environment. This helps to identify the transport mechanism and the appropriate permeation property to be measured.
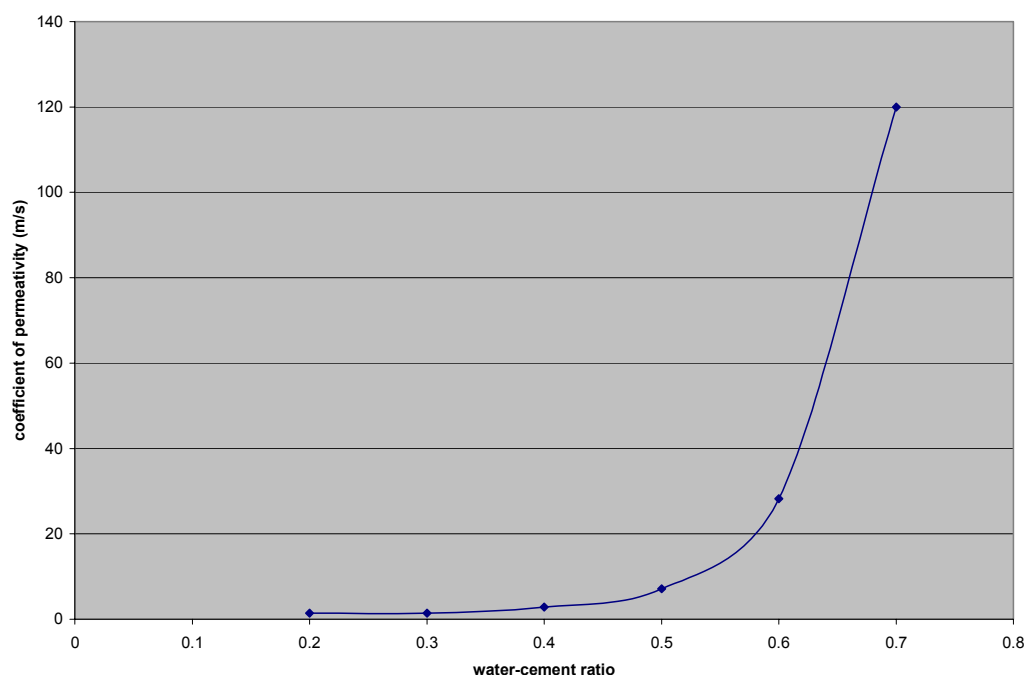
Graph 1 Relationship between permeability and water-cement ratio (Francois, 2000).

4.2. REINFORCED CONCRETE IN SEA WATER

Reinforcement corrosion and the subsequent spalling of the cover concrete have been major issues in construction industries for many years. In theory, embedded steel should not corrode. It is protected against corrosion because of the passivating film of ferric oxide, which is formed and maintained in the alkaline environment produced by cement hydration. Hydration products, mainly calcium hydroxide and small proportions of sodium and potassium hydroxides, give the pore solution of concrete a pH of around 13. However, aggressive agents such as carbon dioxide or chloride ions can destroy this passivating film. Once destroyed, corrosion proceeds with the formation of electrochemical cells on the steel surface. Finally, the corrosion product causes cracking and spalling of the concrete cover. Thus, the corrosion process of steel in concrete can be divided into two stages: Initiation and Propagation. The initiation stage is determined by the ingress of carbon dioxide or chloride ions into the concrete cover while the propagation stage, or corrosion rate, is dependent on the availability of water and oxygen in the vicinity of the steel reinforcement. The time before repair, often referred to as the service life of the reinforced concrete element, is determined by the total time of these two stages (http://www.engnetbase.com/books/844/0958%20ch41.pdf).
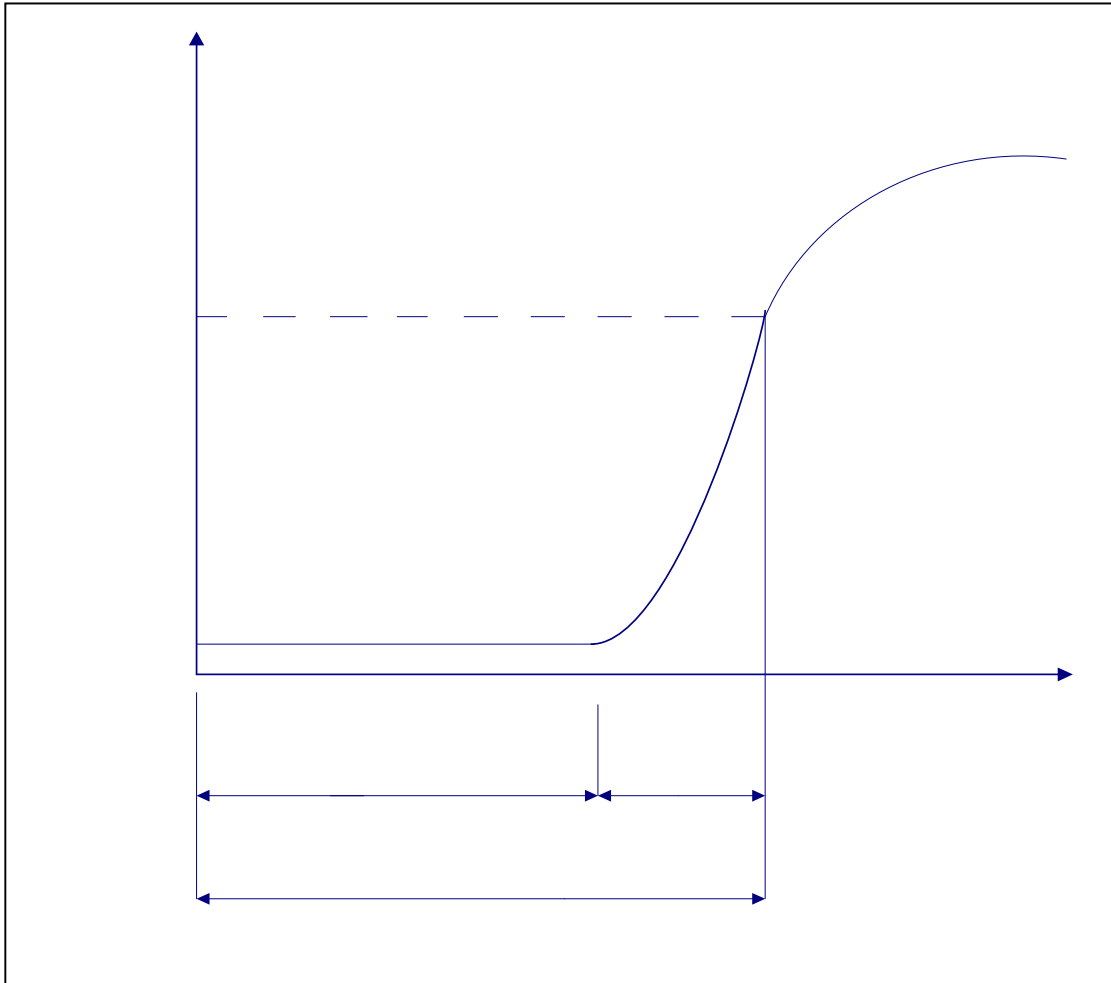
Figure 3   Schematic   diagram   of   corrosion   process   of   steel rebar in concrete (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

4.3. CARBONATION

Carbonation is defined as the process whereby carbon dioxide in air diffuses into concrete, dissolves in the pore solution, and then reacts with the hydroxides, converting them to carbonates with a consequent drop in pH to a value less than 9. Depassivation of steel occurs as pH of the pore solution approaches 11. Carbonation continues from the concrete surface, as a penetrating front, throughout the life of the structure, with depth, d, proportional to the square root of time, t, as follows:

$$d = C* t^{0.5},$$

Where C is referred to as carbonation coefficient or rate of carbonation, often expressed conveniently in mm/year. The reaction involved in the process of carbonation is:

$$Ca(OH)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2O$$
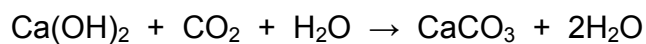
In practice, the depth of carbonation can be determined by spraying a phenolphthalein solution onto a freshly broken concrete sample. This colourless solution changes to pinkish purple at pH values greater than about 9.5, indicating un-carbonated concrete. The rate of carbonation is very much moisture dependent. Carbonation of concrete is known to be highest at relative humidity between 40% to 70%, but negligible in dry conditions (<25% relative humidity) due to insufficient water to promote the reaction. Negligible carbonation is also expected at high humidity (>90% relative humidity) because water in pores of cement paste inhibits diffusion. Compared with tropical environment, concrete exposed to temperate climate are expected to have higher carbonation rates. In practice, vertical surfaces such as building facades carbonate faster than horizontally exposed surfaces like top surface of roof slabs and balconies because horizontal surfaces have a higher frequency and longer duration of wetting (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Temperature can also influence the rate of carbonation with higher rates at higher temperatures, but the influence is less significant compared to the moisture content of concrete. Carbon dioxide content is another influencing factor. In rural areas, carbon dioxide content in air is about 0.03% by volume. However, in cities, the concentration is much higher and could be in the order of 0.3% in densely populated areas. In vehicular tunnels, the concentration could reach 1% giving very fast rate of carbonation (http://www.engnetbase.com/books /844/0958%20ch41.pdf).

Note that carbonation in itself does not cause the deterioration of concrete. In fact, compared to the original concrete, carbonated elements tend to have slightly higher compressive strength and improved permeation properties due to the formation of calcium carbonate with a consequent reduction in the porosity of concrete. This reaction product is not detrimental to the durability of concrete as it does not leach out and is not expansive. Carbonation is not a concern for un-reinforced concrete elements such as roofing tiles and masonry blocks (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Carbonation affects only the length of corrosion initiation stage. For internal structural elements and due to the lack of sufficient moisture to initiate corrosion, concrete remains durable even though carbonation can be substantial. For external elements exposed to the weather, corrosion will occur once the concrete is carbonated close to the reinforcement. Thus, the quality and quantity (thickness) of the concrete cover are important in controlling the time to initiate corrosion. In normal practice and for typical run-of-the-mill concrete, it may take some 20 years or more to carbonate the concrete cover. Note that carbonation is not critical for concrete with high cement content, low water-cement ratio (<0.4) and low permeation properties, because carbonation is extremely slow in good quality concrete(http://www.engnetbase.com/books /844/0958%20ch41.pdf).

4.4. EFFECTS OF CHLORIDE.

Soluble chlorides present in sea water, ground water or de-icing salts may enter concrete through capillary absorption or diffusion of ions in water. Chlorides may also be present in chemical admixtures and contaminated aggregates or mixing water in the production of concrete. The presence of chlorides in reinforced concrete can be very serious and depending on the quality of concrete and its exposure environment, the total time of initiation can be relatively short(http://www.engnetbase.com/books/844/0958% 20ch41.pdf).

Note that it is not the total chloride content that is responsible for corrosion. Part of the chlorides can be chemically bound to the hydrated cement paste, by reaction with C_3A to form calcium chloroaluminate, often referred to as Friedel's salt. Another proportion of chlorides is physically bound, being adsorbed on the surface of gel pores. The remaining part is the free chlorides, which are the only chlorides that are responsible for the initiation of steel corrosion. The distribution of these three forms of chlorides is not permanent and under special circumstances like carbonation or sulphate attack, some of the bound chlorides can be released as free chlorides. Due to various factors, the proportion of free chloride ions in concrete varies from 20% to more than 50% of the total chloride content (http://www.engnetbase.com/books/844/0958%20ch41 .pdf).

For corrosion to be initiated, there has to be a minimum level of free chloride concentration at the steel surface. However, threshold values for depassivation are uncertain, with commonly quoted values between 0.1 and 0.4% of free chloride ions by mass of cement. Due to the concern over the possibility of bound chlorides being released as free chlorides, the probability of corrosion has sometimes been expressed in terms of total chloride ion content. Buildings and bridges near the coast often suffer severe corrosion problems due to the co-existence of both carbonation and chloride penetration (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Once the embedded steel has lost passivity, corrosion proceeds with the formation of electrochemical cells comprising anodic and cathodic regions on the steel surface, with electric current flowing in a loop between the two. Corrosion occurs at the anode, where there is ionization and dissolution of the metallic iron to Fe^{2+}
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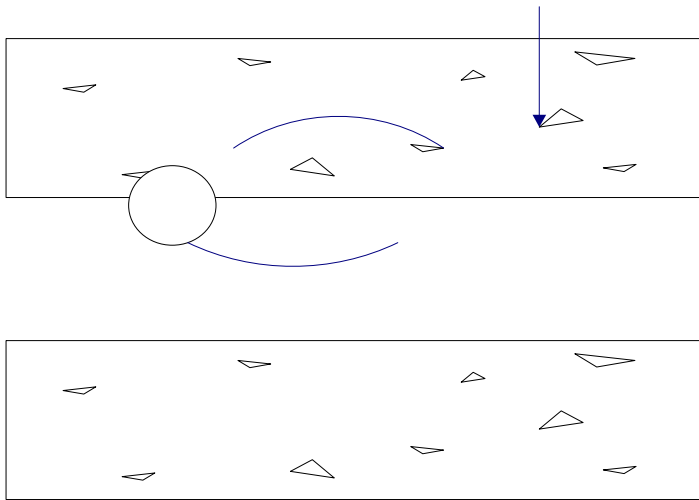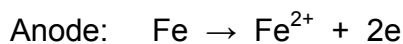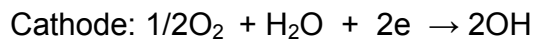
Figure 4 Schematic representation of electrochemical reaction.

Anode: $Fe \rightarrow Fe^{2+} + 2e$

At the cathode, reduction of   oxygen occurs. The cathodic   reaction consumes electrons and leads to the formation of the OH^-.

Cathode: $1/2O_2 + H_2O + 2e \rightarrow 2OH$

The ions formed at the cathode and anode move in the pore solution of the paste of the concrete and react chemically to produce an iron oxide near the anode, generally known as rust. It is obvious from above that for cathodic reaction, and thus corrosion, to occur; both oxygen and water are required. In dry concrete with relative humidity less than 60% as in the case of concrete exposed indoors or protected from rain, corrosion of reinforcement may be considered negligible even though carbonation can be substantial. Corrosion may also be negligible in water-saturated concrete because of the restriction in oxygen supply. Typical examples are   constantly   submerged elements of offshore structures, where concrete is subjected to severe chloride attack, and due to the limited supply of oxygen, corrosion rate can be very slow. On the contrary, high corrosion rate will occur in concrete elements located in splash or tidal zones, where concrete experiences periodic wetting and drying cycles (http://www.engnetbase.com/books/844/0958% 20ch41.pdf).

The deterioration of concrete due to corrosion results because the corrosion product, rust, occupies a volume two to six times larger than the original steel it replaces. This increase in volume exerts substantial pressure   on   the surrounding   concrete,   causing   spalling   and delamination   of   the

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concrete cover. In practice, initial concerns are cracking and rust stains on the concrete surface. Rust from outer 0.1 to 0.5 mm of steel bar is sufficient to cause cracking. However, the reduction in this diameter is generally considered too small to have practical significance on the load-carrying capacity of the reinforced concrete element. Of serious concern is the falling concrete, which may pose as a safety hazard to pedestrians and vehicles traveling below deteriorated overpasses and buildings. As corrosion continues to an advanced stage, reduction in steel cross-section will lead to a decrease in load carrying capacity of the member (http://www.engnetbase.com/books/844/0958%20 ch41.pdf).

To improve the service life of reinforced concrete structures, it is important to have high quality, low permeable concrete with adequate cover. Other strategies can be more complex and may require advice from specialists. These include the use of corrosion inhibitors such as nitrites of sodium and calcium, and the specification of galvanized or epoxy-coated reinforcing bars. For prestigious structures or those that require high durability, expensive electrochemical protective system such as cathodic protection is sometimes employed. This involves the application of a low-voltage direct current via an anode system to inhibit corrosion by causing the steel reinforcement to act as a cathode rather than an anode as it does when it corrodes. Other electrochemical treatments, namely re-alkalization and chloride extraction, are sometimes used as rehabilitation strategies for deteriorated structures (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

4.5. ALKALI-AGGREGATE REACTION

Certain types of rock contain reactive silica, which can react with the hydroxides in pore water derived from the alkalis(Na_2O, K_2O) in the cement causing damage to concrete. The most common is the alkali silica reaction (ASR), which can be viewed simplistically as similar to etching of glass by strong hydroxide solutions. The visual signs of ASR damage are pop-outs or "map" cracking with gels coming through cracks on the concrete surface. Reaction rims around affected aggregate particles can also be identified from cores taken from damaged structures (http://www.engnetbase.com/books /844/0958%20ch41.pdf).
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The reaction starts with the attack on the siliceous minerals in the aggregate by the alkali ions released through cement hydration with the formation of an alkali-silica gel on the surface or in the pores of aggregate particles. Gel absorbs water and causes localized swelling and cracking, which could destroy the aggregates integrity or the bond between the aggregate and the hydrated cement paste. The gel goes from solid to liquid phases as water is taken up into the concrete. Some of the liquid gel is later leached out by water and deposited in the cracks(http://www.engnetbase.com/books/844/0958%20ch41 .pdf).

Damage due to ASR has caused much anxiety to property owners, particularly those from government authorities, who are responsible for the structural integrity of many civil engineering structures (dams, wharves and bridges). However, it must be emphasized that the extent to which ASR can be deleterious depends on certain critical conditions such as the nature and size of aggregates, amount of reactive silica, alkali concentration and the availability of moisture(http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Reaction between some dolomitic limestone and the alkalis in cement, known as alkali-carbonate reaction, can also cause damage to concrete. However, reactive carbonate rocks are not very common and can usually be avoided.

ASR takes place only at high pH because the solubility of the siliceous minerals increases as pH increases. The use of low alkali cement controls the alkali content and thus, the pH of the pore solution. The reactive alkali content is generally expressed in terms of soda equivalent ($Na_2O + 0.65 K_2O$) with a maximum level often quoted as 0.6% by mass of cement or 3.0 kg/m^3 of concrete. The control of alkali-silica reaction can also be taken by avoiding reactive aggregates (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

The swelling of silica gel occurs only in the presence of water. However, in practice, it is practically impossible to keep water away from exposed concrete, particularly for water-retaining structures. Due to the presence of water under service conditions, structures like dams and wharves are more vulnerable than buildings to ASR attack (http://www.engnetbase.com/books/844/0958%20ch41 .pdf).

4.6. SULPHATE ATTACK

Naturally occurring sulphates of sodium, potassium, calcium, or magnesium can be found in soils, seawater or ground water. Sulphates are also used extensively in industry and as fertilizers. These may cause contamination of the soil and ground water. Sources of sulphate can also be internal, released from the cement during service. Sulphate attack is generally considered not a serious or common problem or sole contributor to damage and can take one of the following forms:

1. Physical attack due to salt crystallization;

2. External chemical sulfate attack involving reactions between sulphate ions from external sources with compounds from set cement;

3. Internal chemical sulphates attack due to late release of sulphate within the concrete.

Physical attack is likely to occur in permeable concrete with top surface exposed to the dry environment, while the bottom surface is in contact with the ground with salt bearing solutions. Under these conditions, solutions rise to the surface by capillary action. Due to surface evaporation, and if the rate of evaporation is faster than the migration of salt solution to the surface, salt crystallization occurs beneath the top surface. The transformation of anhydrous Na_2SO_4 to its hydrated form, $Na_2SO_4 \cdot H_2O$, involves significant volume expansion. This generates pressure in the pores causing flaking, spalling and cracking. The damage is often in the form of surface scaling and loss of mass from the surface which can be substantial. This damage should not generally lead to structural failure unless there is a significant reduction in the cross section of the member. Damage of this type results in white crystalline deposits at the crack sites and should not be confused with efflorescence, where salt crystallization takes place on the concrete surface (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Cement is the most vulnerable to chemical sulfate attack. The extent of damage depends on the quality of the concrete, the type of sulphate compounds involved and their concentrations. In permeable concrete, sulphate ions migrate from external sources and react with the products of cement hydration. The use of concrete with low permeation properties would seem to be an essential first step in limiting the penetration of sulphate ions into concrete. With sodium sulphate, it attacks $Ca(OH)_2$ to form gypsum and NaOH. Gypsum then reacts with calcium aluminate hydrate forming ettringite (CaO.Al2O3·3CaSO4·32H2O). The formation of NaOH ensures high alkalinity in the cement system. As for calcium sulphate, it only attacks the calcium aluminate hydrate to form ettringite. The

formation of ettringite is accompanied by volume expansion, which causes internal stresses and cracking. For concrete in contact with magnesium sulphate, the deterioration can be more serious than the damage caused by other sulphates. Magnesium sulphate attacks $Ca(OH)_2$ as well as calcium silicate hydrate and calcium aluminate hydrate. The critical consequence of magnesium sulphate attack is the destruction of calcium silicate hydrate resulting in loss of cohesiveness and reduction in strength. Due to the lime $(Ca(OH)_2)$ consuming pozzolanic reaction, the incorporation of mineral admixtures into the concrete mix would be beneficial in reducing the amount of calcium hydroxide and suppressing the formation of gypsum. The use of sulphate resisting cement with a low C_3A content will minimize the damaging formation of the ettringite. Underground structures or elements such as tunnels, foundations, pipes, and piles are vulnerable to sulphate attack (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Internal sulphate attack is a case of chemical attack where the source of sulphates is internal. Due to late sulphate release, ettringite is formed in the hardened concrete causing expansion and cracking. This phenomenon is often referred to as delayed ettringite formation (DEF). It has been reported in steam cured products using cements of high sulphate content. Ettringite is not stable at temperatures above $65^{o}C$. Therefore, ettringite formed during the early hydration of cement decomposes when the curing temperatures exceed 65C. The sulphate ions released are absorbed by the calcium silicate hydrate. During service, these ions are desorbed under ambient conditions with the reformation of ettringite. In a holistic approach mechanism three conditions must be satisfied for DEF to occur and they are (a) presence of micro cracks, (b) late sulphate release and (c) exposure to water (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Highly permeable concrete exposed to sulphate rich soils or ground water can deteriorate resulting from physical and chemical attacks. In the control of sulphate attack, it is therefore important to use high quality, low permeable concrete. The use of sulphate resisting or blended cement is an added advantage. Prestressed products produced by steam curing process are more prone to DEF related problems. Irrespective of the source of sulphate, the presence of interconnected micro cracks and water is a necessary condition of any sulphate related concrete. In view of the above, care should be taken in the manufacturing process of precast products to minimize the development of micro cracks. During service, a good drainage or waterproofing system may be necessary to keep concrete in a relatively dry state (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

4.7. ACID ATTACK

As with sulphates, acids can be found in soils and ground water. These may be organic in nature resulting from plant decay like humic acid or dissolved carbon dioxide, or may be derived from industrial wastes, effluents and oxidative weathering of sulphide minerals. Liquids with pH less than 6.5 can attack concrete. The attack is considered severe at pH of 5.5 and very severe at pH of 4.5. Concrete is held together by alkaline compounds and is therefore not resistant to attack by strong acids. They do not go into complex chemical reactions similar to those in sulphate attack, but simply dissolve the hydrated compounds of the set cement. The ultimate result of sustained attack is the disintegration and destruction of the concrete. The mechanism of attack is the reaction between cement hydrates, mainly the calcium hydroxide and calcium silicate hydrate, and the acid, resulting in the formation of calcium salts associated with the acid. The dissolution of these salts lead to further exposure of cement hydrates to attack. The rate of damage is controlled by the solubility of the calcium salt. That means more rapid deterioration occurs under conditions of flowing water, rather than static. Acid rain, which consists of mainly sulphuric acid and nitric acid, may cause surface weathering of the exposed concrete. The reduced content of calcium hydroxide of concrete incorporating fly ash or ground granulated blast furnace slag is generally considered to be beneficial in reducing the rate of attack. However, it appears that the permeation property of concrete is of less importance in acid attack (http://www.engnetbase.com/books/844/0958%20ch41.pdf).
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Action on sewers is a special case of acid attack with sulphuric acid produced by the activities of micro-organisms. Domestic sewage by itself is alkaline and does not attack concrete, but severe damage can occur above the level of flow. This occurs when anaerobic bacteria, found in the slime layer of sewer walls, convert sulphates in the sewage to hydrogen sulphide. Anaerobic bacteria become more active at higher temperatures and at slightly alkaline solutions. At   high   enough concentrations or due to turbulence, H_2S volatiles from the effluent and accumulates on the roof or upper part of the sewer. It then dissolves in the moisture films on the exposed concrete surfaces and undergoes oxidation by aerobic bacteria, finally producing sulphuric acid. It is this acid that attacks concrete. In localized areas, pH values can be as low as 2. Since damage occurs only on exposed surfaces, sewers running full are not attacked. Chlorination and the injection of compressed air into rising mains have been used successfully to extend the life of sewers. Other effective measures include the removal of slime deposits, increase in flow velocities, and forced ventilation of sewers. It has also been found that the   use of limestone, instead of silicate aggregates could greatly improve the durability of sewers (http://www.engnetbase.com/books/844/0958% 20ch41.pdf).

4.8. SEA WATER

Concrete exposed to seawater can be subjected to both physical and chemical attacks. Seawater contains a number of dissolved salts with a total salinity of around 3.5% and pH values ranging from 7.5 to 8.4. Typical composition of seawater is sodium chloride (2.8%), magnesium chloride (0.3%), calcium chloride (0.1%), magnesium sulphate (0.2%), calcium sulphate (0.1%) and some dissolved carbon dioxide. In terms of chemical attack, the damage from sulphates is not significant because in seawater, the deleterious expansion resulting from ettringite formation does not occur. The ettringite as well as gypsum are soluble in the presence of chlorides and can be leached out by seawater. Frost damage, abrasion due to wave actions, salt crystallization, and biological attack are other factors that may lead to the deterioration of concrete. However, the main durability concern for marine structures is the corrosion of the reinforcement resulting from chloride ingress. Of particular interest is the splash and tidal zones (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

To be durable under seawater exposure conditions, concrete must have an adequate cover and low permeation properties with the appropriate choice of cement materials. Seawater should never be used as mixing water for the production of reinforced or prestressed concrete structures (http://www.engnetbase.com/books/844/0958%20ch41.pdf).
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4.9. PHYSICAL ATTRITION OF CONCRETE

Under many circumstances, concrete surfaces are subject to wear with progressive loss of mass from the concrete surface. Abrasion is a major concern to the durability of pavements or industrial floors with damage resulting from impact or wearing action by vehicular traffic. Damage may also occur due to erosion on spillways of hydraulic structures caused by water borne solids moving at high speed, or offshore structures subjected to wave action. Another possible damage to hydraulic structures is by cavitation, which relates to the formation of vapour bubbles and their subsequent collapse due to sudden change of direction in rapidly flowing water (http://www.engnetbase.com/books/844 /0958%20ch41.pdf).

Set cement paste does not have a good resistance to attrition, especially when it has a high porosity and low strength. Hard wearing aggregates should be used for improved abrasion resistance. Heavy duty industrial floors or pavements could be designed to have a 25 to 75 mm thick topping of low water-cement ratio. Small aggregates of 12.5 mm maximum size should be used to minimize the effect of aggregates pull out. To reduce the formation of a laitance or weak surface, it is often recommended to delay floating and finishing until the concrete has lost its surface bled water. In contrast to abrasion and erosion, the use of high quality concrete may not be effective in reducing damage from cavitation. The best solution appears to lie in the design by removing the causes of cavitation (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

4.10. FROST ACTION

In cold climates, physical damage to concrete structures resulting from frost action or freeze-thaw cycles is a major concern requiring expensive repair and maintenance. The problem is common to all porous materials but the degree of damage depends on the pore system. Set cement paste, which has large pore system and small pore diameter, represents the worst situation.

As temperature drops, some of the water in the pore system begins to freeze at about -5°C. Water expands upon freezing and the associated 9% increase in volume generates hydraulic pressure, causing localized fracture within the cement paste. Damage can be avoided if pressure can be released by allowing the water to move out of the paste or to adjacent pores, where there is plenty of space (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Resistance of concrete to frost action can be improved by air entrainment, with air content between 3% and 6% of the volume of concrete being appropriate for most applications. The incorporation of air entraining agent in a concrete mixture allows the distribution of free space throughout the entire cement paste in the form of tiny air bubbles. The addition of this admixture will obviously increase the yield of the fresh concrete and reduce the strength of the hardened concrete. Note that frost damage occurs mainly in saturated concrete. For partially dry concrete, many of the pores are empty and can play the role as air entrained bubbles(http://www.engnetbase.com/books/844/0958%20ch41 .pdf).
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4.11. ACTION OF HEAT AND FIRE

In the design of residential buildings and public facilities, human safety is one of the major considerations. In general, concrete is considered to have good properties with respect to fire safety. Unlike timber, concrete is noncombustible and does not release toxic fumes on exposure to high temperatures. In practice, structural components are required to maintain their integrity over a desired length of time, often referred to as fire rating. Unlike steel, concrete is able to maintain sufficient strength at temperatures about 700^oC to 800^oC over several hours. This is important in terms of safety because materials with a high fire rating allow rescue operations to proceed with reduced risk of structural collapse(http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Fire creates high temperature gradients and because of this, the hot surface layer tends to craze, followed by spalling from the cooler interior of the concrete member. The reinforcement may become exposed and the action of fire accelerates. The extent of damage depends on the temperature reached, loading conditions under fire, and characteristics of the concrete, which includes the quality of concrete and type of aggregates used. In general, concrete heated while under load retains a higher proportion of its original strength compared to unload concrete. Concrete of low permeability may suffer serious spalling. This occurs when vapor pressure or steam inside the concrete increases at a faster rate than the pressure relief by the release of steam to the atmosphere(http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Under exposure to high temperatures, concrete made with limestone or light weight aggregates performs better than concrete with siliceous aggregates. This could be due to the lesser difference in the coefficient of thermal expansion between the cement paste and these aggregates compared to siliceous aggregates, resulting in a stronger transition zone. In addition, at about 570^oC, siliceous aggregates containing quartz undergo deleterious expansion due to phase transformation. Concrete made with siliceous or limestone aggregates show a color change with temperature. This provides useful information in estimating the maximum temperature reached in a fire. The colour of concrete remains unchanged up to about 300^oC. Between 300^oC and 600^oC, it is pink to red. Then the concrete changes to grey between 600^oC and 900^oC, and buff above 900^oC. As for the cement paste, when temperature reaches about 300^oC, the interlayer water and some chemically bound water from the cement hydrates are lost. At about 500^oC, decomposition of the calcium hydroxide begins. Complete decomposition of calcium silicate hydrate occurs at temperatures around 900^oC. For practical purposes, approximately 600^oC is

considered the limiting temperature for structural concrete (http://www.engnetbase.com/books/844/0958%20ch41.pdf).
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4.12. DESIGN FOR DURABILITY

There are two approaches in the specification of concrete for durable structures and these are prescriptive and performance based specifications. Current prescriptive method focuses on important factors including service life, exposure environment, quality of concrete, and other interdependent considerations such as cover thickness, strength, curing and workmanship. An alternative approach based on performance tests and fitness for purpose has occasionally been suggested and used. However, there are difficulties in its implementation. One difficulty lies in developing a commonly accepted test, which directly assesses the resistance of concrete to a particular deterioration process. Others include the establishment of relationship between the test and real performance, availability of standard sampling and test procedure, and guidance on the level of performance required under various exposure conditions. These difficulties have to be overcome before the performance approach can be implemented in general practice (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

Concrete structures and members are usually designed for a service life of 40 to 60 years. Within this design life, concrete is expected to meet all essential properties or exceed minimum acceptable values, when routinely maintained. Guidance for durability criteria for this design life is usually provided by national standards. More stringent requirements should be considered for structures requiring longer service life such as monumental or civil engineering structures (power stations, tunnels, dams, etc). For temporary structures with short service life, some relaxation of requirements may be acceptable. It is emphasized that durability is a complex topic and compliance with requirements stated in local standards may not necessarily be sufficient to ensure a durable structure for an intended service life. If in doubt, specialist advice should be sought (http://www.engnetbase.com/ books/844/0958%20ch41.pdf).
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Exposure environment classifications are generally based on climatic conditions under which the concrete surfaces are exposed. Important factors include temperature, humidity, and frequency of wet-dry cycles. Compared to arid or temperate climates, tropical environment is generally considered to be more aggressive to exposed concrete. The presence of aggressive ions (sulphates and chlorides) is discussed in terms of surfaces in contact with the soil and sea water, or proximity of the structure to the coast and industrial areas. Correct interpretation of classifications and subsequent decision on the exposure class for a structure or member under consideration cannot be overemphasized (http://www.engnetbase.com/books/844/0958%20ch41.pdf).
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In the prescriptive approach, quality of concrete is specified in terms of materials selection and production process. No matter how well a mixture is selected and proportioned, inferior concrete will result from poor workmanship.

The initial step is to determine the type of cement material, its content, and the water-cement ratio, as these are critical material properties for durability. Other factors such as aggregates and chemical admixtures are interacting factors, which must be considered collectively in mixture design. For the materials and proportions required for durability, a corresponding strength will be achieved. This should be compared with the strength required for load bearing capacity of the structure under consideration with the higher value adopted.

The next step is the specification of production process, which includes workmanship and curing. Workmanship relates to the degree of compaction and surface finish that can be achieved. The use of rigid formwork and intense vibration in the manufacture of precast products often gives better quality concrete compared to that obtained with standard consolidation (poker vibrators) on site. Curing promotes cement hydration. The duration and type of curing techniques are critical parameters and must be clearly defined. More importantly, the curing process specified has to be appropriate and can be achieved in practice for the concrete member under consideration. Note that the quality of concrete achieved with water adding technique (e.g., water spray, wet hessian) is considered more effective than curing with water retaining techniques like curing compound. However, water adding curing techniques can be difficult to implement in many construction sites, without substantial increase in cost or delay in construction progress (http://www.engnetbase.com/books/844/0958%20ch41.pdf.

Besides quality, the quantity (thickness) of the cover determines the level of protection afforded by the concrete to the steel reinforcement against corrosion. The cover also acts as the first defense against other physical and chemical attacks. For durability, the cover thickness should be as large as possible, but this should be kept to a minimum for structural efficiency and the control of surface crack widths. The quantity and quality of the cover should be considered collectively because many codes of practice allow the reduction of cover thickness with increase in concrete quality (http://www.engnetbase.com/books/844/0958%20ch41.pdf).

5.   ELECTROCHEMISTRY OF CORROSION

5.1. NERNST EQUATION

The potential of a half cell reaction under non-standard conditions may be calculated as follows:

$M \rightarrow M^{n+} + ne^{-}$

$E = E_o + R*T/(n*F)*\ln([Ox]/[Red])$

Where   E = Potential under non-standard conditions
          E_o = Standard Electrode Potential
          R = Gas constant
          F = Faraday's constant
          n = Number of transferred electrons
   [Ox], [Red] = Concentration of the oxidized and reduced species

Electrode potential is the potential difference set up when a pure metal is in contact with a solution of its salt. While the standard electrode potential is the potential difference set up when a pure metal is in contact with 1mole/dm^3 of a solution of its salt under normal atmospheric pressure and 25°C temperature. In practice electrode potential is measured with the aid of a reference electrode. In water the commonly used reference electrode is hydrogen or the calomel electrode. Whereas in soil, the copper/copper sulphate, and in sea water, the silver/silver chloride electrode. All metals have different potentials which describe their tendency to be displaced in a reaction or a solution. In practice the electrode potential involve mixtures and not pure samples and also the environment is not normally a standard environment. Hence it is more practical to use the galvanic series (table 3) rather than the electrochemical series (table 2) which indicates the standard electrode potential of pure metals with hydrogen as the reference electrode.

Table 2 Electrochemical series of metals
(http://www.chemguide.co.uk/physical/redoxeqia/ecs.html)

Metal	Reaction	Potential (V)
Gold	$Au^+ + e^- \leftrightarrow Au$	1.6920
Platinum	$Pt^{2+} + 2e^- \leftrightarrow Pt$	1.1800
Palladium	$Pd^{2+} + 2e^- \leftrightarrow Pd$	0.9510
Silver	$Ag^+ + e^- \leftrightarrow Ag$	0.7996
Copper	$Cu^{2+} + 2e^- \leftrightarrow Cu$	0.3419
Hydrogen	$H^+ + e^- \leftrightarrow H$	0.0000
Lead	$Pb^{2+} + 2e^- \leftrightarrow Pb$	-0.1262
Tin	$Sn^{2+} + 2e^- \leftrightarrow Sn$	-0.1375
Nickel	$Ni^{2+} + 2e^- \leftrightarrow Ni$	-0.2570
Cobalt	$Co^{2+} + 2e^- \leftrightarrow Co$	-0.2800
Cadmium	$Cd^{2+} + 2e^- \leftrightarrow Cd$	-0.4030
Iron	$Fe^{2+} + 2e^- \leftrightarrow Fe$	-0.4470
Chromium	$Cr^{3+} + 3e^- \leftrightarrow Cr$	-0.7440
Zinc	$Zn^{2+} + 2e^- \leftrightarrow Zn$	-0.7618
Manganese	$Mn^{2+} + 2e^- \leftrightarrow Mn$	-1.1850
Titanium	$Ti^{3+} + 3e^- \leftrightarrow Ti$	-1.3700
Aluminum	$Al^{3+} + 3e^- \leftrightarrow Al$	-1.6620
Magnesium	$Mg^{2+} + 2e^- \leftrightarrow Mg$	-2.3720
Sodium	$Na^+ + 2e^- \leftrightarrow Na$	-2.7100
Calcium	$Ca^{2+} + 2e^- \leftrightarrow Ca$	-2.8680
Potassium	$K^+ + e^- \leftrightarrow K$	-2.9310
Lithium	$Li^+ + e^- \leftrightarrow Li$	-3.0401

This series is based on the following conditions:
1. One mole of the samples in one cubic decimeter (dm^3)
2. One atmosphere as the pressure
3. Temperature of 25 ^{o} C
4. Samples are all pure samples of metals
5. The reference electrode is Hydrogen.

Metals lower in the series will corrode preferentially to those above them. The activity of the metals   increases down the table as nobility decreases.

Table 3   The Galvanic Series: Corrosion Potentials in Flowing Seawater. (V vs SCE Half-Cell Reference Electrode)

RANGE	ALLOYS
+0.3 +0.2	Graphite
+0.26 +0.18	Platinum
+0.09 0.03	Ni-Cr-Mo alloy C
+0.06 0.04	Titanium
+0.04 0.02	Nickel-Iron-Chromium alloy 825
+0.06 0.04	Alloy "20" Stainless Steels, cast & wrought
0 -0.1	*Stainless Steel - Type 316, 317 (passive)
-0.03 -0.14	Nickel-Copper alloys 400, K-500
-0.10 -0.15	Silver
-0.04 -0.10	*Stainless Steel -Types 302 304 321 347(passive)
-0.10 -0.2	Nickel 200
-0.09 -0.2	Silver Braze Alloys
-0.13 -0.18	*Nickel-Chromium alloy 600 (passive)
-0.14 -0.22	Nickel-Aluminium Bronze
-0.17 -0.24 70-30	Copper-Nickel
-0.19 -0.25	Lead
-0.20 -0.28	*Stainless Steel - Type 430 (passive)
-0.21 -0.27	80-20 Copper-Nickel
-0.22 -0.28	90-10 Copper-Nickel
-0.24 -0.28	Nickel Silver
-0.23 -0.35	*Stainless Steel - Type 410 416 (passive)
-0.24 -0.32	Tin Bronzes (G&M)
-0.25 -0.29	Silicon Bronze
-0.26 -0.34	Manganese Bronze
-0.26 -0.36	Admiralty Brass, Aluminium Brass
-0.27 -0.36	Pb-Sn Solder (50/50)
-0.30 -0.37	Copper
-0.30 -0.33	Tin
-0.31 -0.40	Naval Brass, Yellow Brass, Red Brass
-0.31 -0.40	Aluminium Bronze
-0.33 -0.46	*Stainless Steel - Type 316 317 (active)
-0.34 -0.46	*Nickel-Chromium alloy 600 (active)
-0.43 -0.54	Austentic Nickel Cast Iron
-0.44 -0.58	*Stainless Steel - Type 302 304 321 347 (active)
-0.45 -0.57	*Stainless Steel - Type 410 416 430 (active)
-0.57 -0.63	Low Alloy Steel
-0.60 -0.72	Mild Steel, Cast Iron
-0.70 -0.74	Cadmium
-0.76 -1.00	Aluminium Alloys
-0.98 -1.03	Zinc
-1.60 -1.63	Magnesium

Alloys are listed in order of the potential they exhibit in flowing seawater. The alloys marked * may become active and exhibit a potential near -0.5 volts in low-velocity or poorly aerated water and at shielded areas. The activity of the alloys increases down the table. Hence the alloys down the table will corrode preferentially to those above them (http://www.corrprev.org.au/Galvanic.htm)

5.2. CORROSION OF STEEL IN CONCRETE

Like masonry and brick, reinforced concrete structures deteriorate under attack from external elements such as freeze-thaw damage (the expansion of frozen moisture within the structure as it thaws), and erosion. In a composite man-made material such as concrete, there are additional mechanisms caused by the greater complexity of its composition. Of particular concern today is the alkali silica reaction in the concrete and the corrosion of the reinforcing steel, both of which are affected by the alkalinity of cement concrete. Cement is made by burning constituents which include lime in a kiln and grinding the result to a fine powder. This produces a highly alkaline material which reacts with water and hardens. When it is added to coarse and fine aggregate and mixed with water, the cement combines with the aggregate and hardens to form concrete. The hardening process (hydration reaction) is complex and continues over many months if not years, depending on the amount of water in the mix. There must be excess water for workability and a pore network therefore develops as it dries out. Excess calcium hydroxide and other alkaline hydroxides are present in the pores and a solution of pH 12.0 to 14.0 develops (pH 7.0 is neutral; values below indicate acidity, and alkalinity above). It is this pore network and the solutions it contains that are critical to the durability of the concrete (Broomfield, 1996).

Although the alkalinity within the concrete pore structure can lead to alkali silica reactivity, the high pH value also provides a protective coating of oxides and hydroxides on the surface of the steel reinforcement. Without this layer, which is known as a 'passive' film, the steel would be exposed to the air and moisture in the pores, leading to rapid corrosion. It is the main chemical reason why reinforced concrete is a durable construction material. The layer is durable and self repairing, and it can last for hundreds of years if the alkalinity is maintained. However, the passive layer itself can be attacked by chlorides in salt and the alkalinity of the concrete can be reduced by reaction with atmospheric carbon dioxide, a process known as carbonation (Broomfield, 1996).

Carbon dioxide, which is present in the air in proportions of around 0.3 per cent by volume, dissolves in water to form a mildly acidic solution. Unlike other acids that may chemically attack and etch the surface of the concrete, this acid forms within the pores of the concrete itself where the carbon dioxide dissolves in any moisture present. Here it reacts with the alkaline calcium hydroxide forming insoluble calcium carbonate. The pH value then drops from more than 12.5 to about 8.5. The carbonation process moves as a front through the concrete, with a pH drop across the front. When it reaches the reinforcing steel, the passive layer decays when the pH value drops below 10.5. The steel is then exposed to moisture and oxygen and is susceptible to corrosion (Broomfield, 1996).

Concrete inside the building frequently carbonates totally without any sign of deterioration as the concrete dries out, leaving the steel exposed to air but not moisture. Problems are seen externally where concrete is exposed to the elements and in certain situations internally, such as kitchens and bathrooms, where the concrete is susceptible to condensation or water-leakage. External facades are particularly vulnerable, especially where cladding panels have poorly placed handling steel that is near the surface. Carbonation does not have to penetrate far and the concrete quality may be of poor quality. (Broomfield, 1996).

Salt causes corrosion by a different mechanism. When dissolved in water sodium chloride forms a versatile, highly corrosive solution of sodium ions ($Na+$) and chloride ions ($Cl-$). Salt is used for de-icing roads and its presence in sea water is a major problem for reinforced concrete structures. The very mobile chloride ions disperse through concrete pores in solution and where they come into contact with the reinforcing steel they attack the passive layer. Steel oxidises in the presence of air and water to form rust which has a volume of up to 10 times that of the steel consumed. As concrete has a low tensile strength it will crack when as little as a tenth of a millimetre of steel has been consumed. Horizontal cracks form, causing corners to 'spall' and surfaces to 'delaminate' as the reinforcement's concrete cover becomes detached and falls away in sheets. The consequence can be seen on the underside of road bridges and many buildings and structures beside the sea. Chloride ions can penetrate the passive film, cause the steel potential to shift, and result in corrosion. The nature of the chloride ion affects the severity of the corrosion problem. Chloride ion, which diffuses into hardened concrete, will initiate corrosion at a smaller amount than that required to initiate corrosion with chloride ions mixed in the concrete matrix (Broomfield, 1996).

Corrosion of steel in concrete occurs when these conditions are present. The diffusion of oxygen or availability of oxygen, presence of moisture and the breakdown of the passive oxide film.
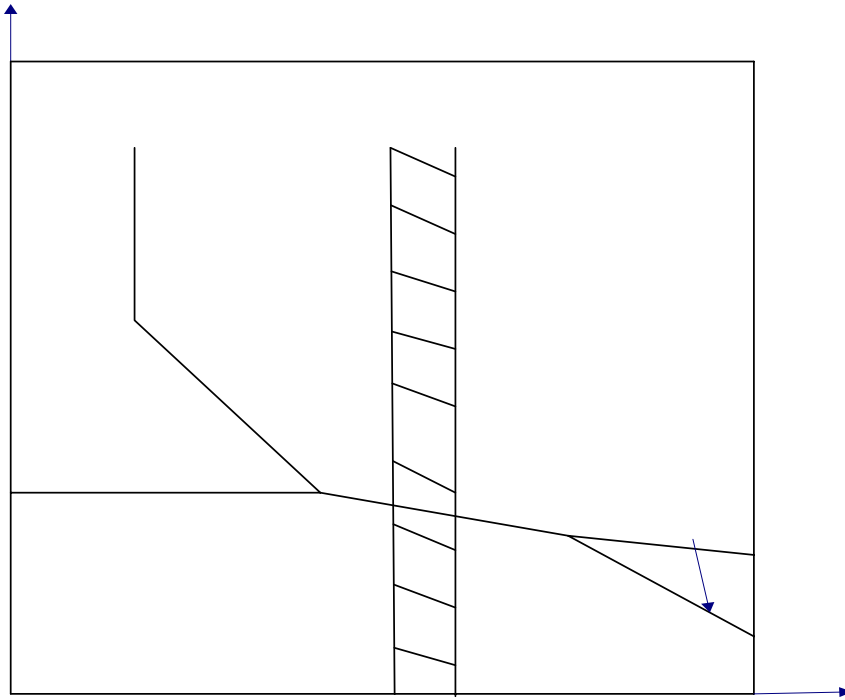
Figure 5 Simplified Pourbaix diagram of steel in concrete

Corrosion of steel reinforcement occurs by an electrochemical process which involves exchanges of electrons similar to that which occurs in a battery. The important part of the mechanism is the separation of negatively charged areas of metal or 'anodes' where corrosion occurs and positively charged areas or 'cathodes' where a harmless charge balancing reaction occurs (figure 6). At the anode the iron dissolves and then reacts to form the solid corrosion product, rust. The rust is formed at the metal/oxide interface, forcing previously formed oxide away from the steel and compressing the concrete, causing it to spall (Broomfield, 1996).

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Pass

al E (mV) .
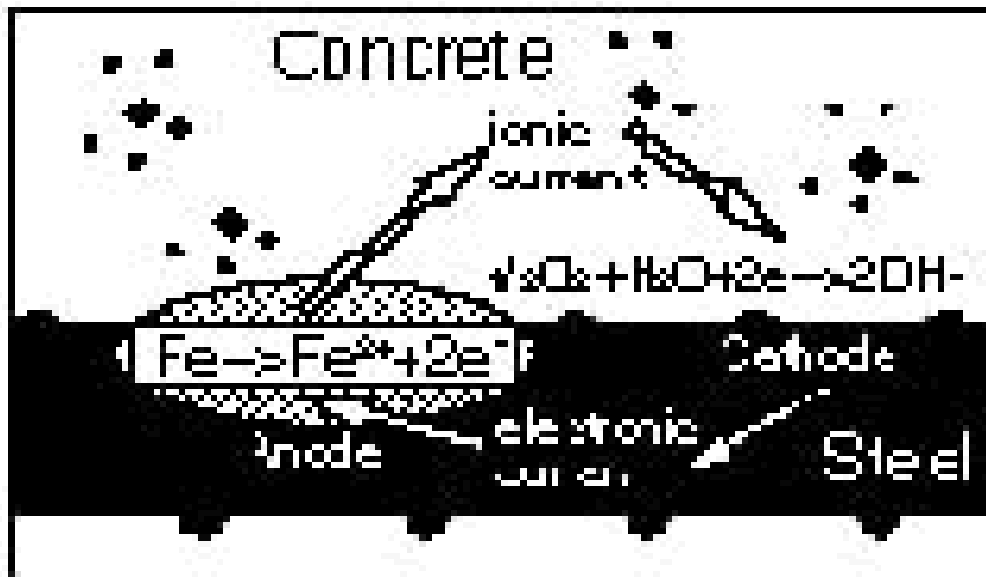
Figure 6 Anodic and cathodic reactions of steel in concrete (Broomfield, 1996).

Corrosion of steel in concrete can be seen to be a significant problem for many reinforced concrete structures if moisture is present. If there is no salt to cause corrosion in the short term, carbonation will affect most structures over the centuries. If the structure cannot be kept dry then there is a range of techniques that can be used depending on the structure, its condition and the cause and extent of the problem (Broomfield, 1996).

Electrochemical techniques can reduce the amount and extent of patch repairs, and leave the appearance unchanged with probes embedded in the concrete or a surface coating, depending on requirements and conditions. Alkali silica reaction (ASR) is a chemical attack of the aggregates in the presence of the alkalinity of the concrete and moisture. If the concrete can be kept dry then ASR will be minimised. Most ASR damage is unsightly rather than structurally dangerous (Broomfield, 1996).

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5.3. REDUCTION AND OXIDATION IN CONCRETE

In a chemical reaction, reduction is a decrease in electro-positivity, an increase in electro-negativity or gain in electrons, while oxidation is an increase in electro-positivity, a decrease in electro-negativity or a loss of electrons. A chemical reaction is characterized by both oxidation and reduction reactions, each of which forms a half cell reaction.

Corrosion is an electro-chemical process which involves both oxidation and reduction. The oxidation reaction occurs at the anode, where the metal Iron loses two electrons in a solution to have an oxidation number of +2, which is an increase in electro-positivity from 0 (zero) to +2 .

$$Fe \rightarrow Fe^{2+} + 2e^-$$
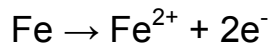
This is the anodic reaction in a corrosion process and the electrons flow to the cathodic site where a reduction reaction takes place.

Reduction reaction occurs at the cathode and the product formed depends on the environment. In an aerated environment, the likely reduction reaction results in the formation of a hydroxide ion (OH^-)..

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$
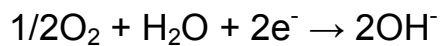
The two half cell reactions (oxidation and reduction reactions) will form a redox reaction.

$$Fe + 1/2O_2 + H_2O \rightarrow Fe\,(OH)_2$$
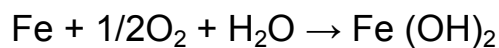
The pH of the solution increases becoming more alkali due to the alkalinity of the product formed. On further oxidation the, the Iron II hydroxide (Fe $(OH)_2$)forms a reddish Iron III hydroxide (Fe $(OH)_3$)which later becomes rust (Fe_2O_3).

$$2Fe\,(OH)_2 + 1/2O_2 + H_2O \rightarrow 2Fe\,(OH)_3$$
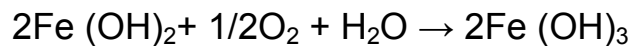
In an acid environment, the most likely cathodic reaction is the ionization of the acid to liberate hydrogen. Depending on the nature of the acid, the ionization may be complete in the case of a strong acid, or partial in the case of a weak acid. The reaction is indicated bellow.

$$2H^+ + 2e^- \rightarrow H_2\uparrow$$

$$Fe \rightarrow Fe^{2+} + 2e$$

Potential E(V)

Passive range

$$1/2O_2 + H_2O + 2e \rightarrow 2OH^-$$
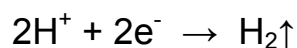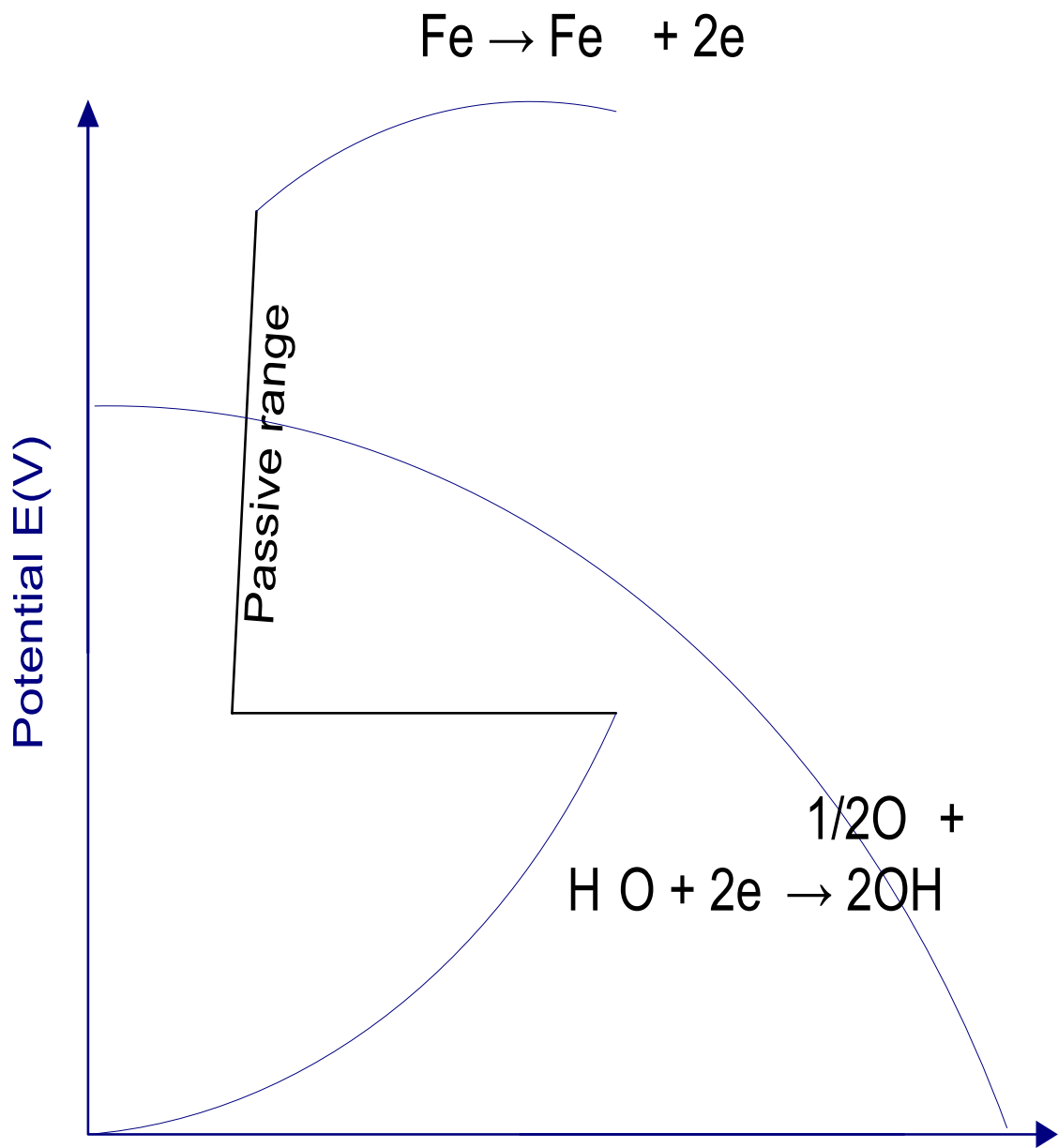
Figure 7 Evan's diagram of steel corrosion.

# 6. CATHODIC PROTECTION

6.1. THE PRINCIPLE

Any metal that has been extracted from a naturally combined state has a tendency to revert to that state under the action of oxygen and water. This action is called corrosion, the commonest example being the rusting of steel. Corrosion is an electro-chemical process that involves the passage of electric currents on a micro or macro scale. The change from the metallic to the combined form occurs by an anodic reaction (Cathodic protection, 1981).

$$M \quad \rightarrow \quad M^- \quad + \quad e^-$$

(Metal)   (Soluble metal)   (Electron)
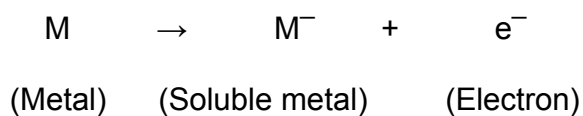
The reaction produces a free electron which passes through the metal to another site on the surface, the cathode, where it is consumed by the cathodic reaction.
In acid environment, the cathodic reaction is:

$$2H^+ \quad + \quad 2e^- \quad \rightarrow H_{2\,(gas)}$$
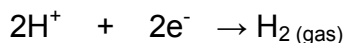
In neutral environment, the cathodic reaction involves the consumption of oxygen dissolved in the solution:

$$1/2O_2 \quad + \quad H_2O \quad + \quad 2e- \quad \rightarrow \quad 2OH^-_{\,(alkali)}$$
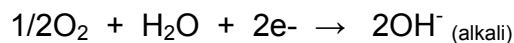
Corrosion thus occurs at the anode but not at the cathode. The anode and cathode of a corrosion process may be of two different metals connected together, forming a bimetallic couple, or they may be close together on a common surface. This corrosion process may also be the result of variations in the state of the metal at different points, or a result of the local difference in the environment, such as variations in the supply of oxygen at the surface (Cathodic protection, 1981).

The principle of cathodic protection consists in the connection of an external anode to the metal to be protected and the passing of an electric current so that all areas of the metal becomes cathodic and therefore do not corrode. In electrochemical terms, the electrical potential between the metal and the electrolyte with which it is in contact is lowered to a value at which corroding anode reactions are stifled and only cathodic reactions can take place.Cathodic protection can be achieved in either of two ways: by the use of galvanic (sacrificial) anode, or by impressed current. Galvanic anode systems employ reactive metals as auxiliary anodes electrically connected to the steel to be protected. The difference in the natural potentials between the anode and the steel, as indicated by their relative position

in the electro-chemical series, causes a positive current to flow in the electrolyte from the anode to the steel, so that the whole surface of the steel becomes cathodic. The three metals commonly used as sacrificial anode are aluminium, zinc and magnesium. Impressed current systems employ inert or non-galvanic anodes with an external source of direct current power to impress a current from the anode to the cathode (Cathodic protection, 1981).

6.2. SACRIFICIAL ANODE

A sacrificial or galvanic anode system for reinforced concrete uses a more reactive metal (anode) such as zinc or aluminum-zinc-indium (Al-Zn-In), to create a current flow. Sacrificial or galvanic cathodic protection is based on the principle of dissimilar metal corrosion and the relative position of specific metals in the galvanic series. The direct current is generated by the potential difference between the anode and reinforcing steel. Sacrificial cathodic protection systems have the advantage of no auxiliary power supply, and the advantage of being used for prestressed or post tensioned concrete without the risk of elevated potential levels which can lead to hydrogen embrittlement of the steel .The sacrificial anode will corrode during the process and is consumed. Current will flow from the anode, through the concrete, to the corroding reinforcing steel. Galvanic anodes may be installed as cast anodes in soil or thermally sprayed or painted onto atmospherically exposed concrete to form a sacrificial coating (http://www.cathodicprotection.com/concrete/daily.htm).

The commonly used anodes for sacrificial systems are alloys based on zinc, magnesium or aluminium. For sea water applications zinc alloy anodes are most popular. As the open circuit potential of zinc anode is around -1.05 volts with reference to an Ag/AgCl electrode. Over protection of suitably painted steel structures is most unlikely to occur, as such a system is known to be self regulating (Rowland J. C. et al, 1976, p.3).

The current generated from a sacrificial anode is directly related to the environment that it is placed. Anodes in wet/humid environments will typically produce higher levels of current. Due to their low driving voltage, sacrificial anodes are appropriate on structures that have single mats of steel, such as bridge substructure components. Also, since the sacrificial anode is connected directly to the reinforcement, shorting of the anode is not a concern.

Cathodic protection systems for concrete structures in marine environments fall into three categories: surface-applied, encapsulated and non-encapsulated immersed. The surface applied systems may involve the application of the anode material over the entire surface or to selected areas where cathodic protection is most needed. A condition survey of the structure will assist in determining the extent of protection required. The encapsulated system may involve a concrete encasement, spray applied concrete overlays, saw cutting for ribbon mesh in slots, or drilling to insert discrete anodes (http://www.corrpro.com/Concrete/cp-49.pdf).

It is particularly difficult to apply cathodic protection to the splash and tidal zones of concrete structures because of the constant wetting and drying, marine growth,

and possible abrasion and impact from floating debris. Furthermore, any anode installed in the splash and tidal zone will experience high levels of current discharge if allowed to directly contact the seawater. This phenomenon occurs because of the tendency of the anode to "leak" high levels of current into the seawater due to the path of least resistance to the steel in portions of the structure below water. Many corrosion engineers have recognized this effect, and designers have developed methods to deal with the problem. Current leakage may be reduced by using an electrical insulator over the anode, or by applying a supplemental current from a cathodic protection system installed below the water line (http://www.corrpro.com/ Concrete/cp-49.pdf).

The anode life, however, may be relatively short as compared to the inert anodes, which are used with impressed current systems. Also, the current that is produced by a galvanic anode is a function of its environment (i.e. moisture and temperature conditions) and the output cannot be easily adjusted or controlled as with the impressed current method. Reference electrodes are used to evaluate cathodic protection levels. They may be portable devices or permanently embedded probes in the concrete structure. The most commonly used embedded reference electrodes are silver/silver chloride (Ag/AgCl). Reference electrodes should have a separate ground connection to the reinforcing steel (http://www.cathodicprotection.com/ concrete/daily.htm).

Energy for the sacrificial anode system is provided by the difference in energy level between the anode and the structure being protected. Typically, magnesium anodes are utilized to protect steel structures in fresh water. Referring back to the galvanic series table (table 3), it is indicated that the magnesium anode would corrode preferentially when connected to steel. There is approximately a 1.0 volts difference between these two materials.

A sacrificial anode installation is also a direct current circuit with positive current supplied from the anodes and a return negative current supplied from the structure. Again, Ohms law applies: E=IR, where E is the driving voltage of the circuit or approximately 1.0 volts, difference between magnesium and steel, I is the current magnitude that results from the resistance of the circuit R. Proper system design seeks to minimize the resistance of the circuit through anode groundbeds design.

Sacrificial anode systems do not provide as much energy output as the impressed current design. Therefore, they would not function properly in many applications where cathodic protection would be required. Sacrificial systems require that the structure is coated with a tightly adhered coating system, and is electrically isolated from all other metallic structures and system components (http://www.corrtech-inc.com/technicalpapers.html).

6.3. IMPRESSED CURRENT

This method requires inert anodes, a direct current power source, well insulated conductors between anodes and the power source, and a well secured connection between the power source and the structure. The inert anode is to be cast with the steel mesh in the concrete and a direct current supplied to it through well secured conductors. The anode is kept close to the mesh without direct contact.

Impressed current method of cathodic protection permits voltage and current regulations. A rectifier is used to convert alternating current (AC) to direct current (DC). A rectifier works on the same principle as an AC adapter for a computer or a battery charger. In an impressed current cathodic protection system, the rectifier provides the power (i.e. low voltage direct current) and controls the amount of power to each zone. Rectifiers are available in many types and operating outputs. Mainly, they are designed to provide either constant current or constant voltage to the anode system.

The anode is one of the most critical components for a cathodic protection system. It is used to distribute protective current to the reinforcing steel and provides locations for anodic reactions to take place in lieu of the reinforcing steel. By using relatively inert materials, such as catalyzed titanium, anode consumption is minimized. One of the main benefits of catalyzed titanium is that its life expectancy can be determined through accelerated life testing (http://www.cathodicprotection.com/concrete/ daily.htm).

Impressed current cathodic protection system has the ability to repel chloride ions from the concrete. As conventional current flow into the concrete, electron such as ions flow out to complete the circle. This helps to establish equilibrium between the migration due to the electrical field and the ingress of ions into the concrete. The inert anode is never consumed as in the case of the sacrificial anode, where the anode is a consumable. Hence the service life is not predetermined as in the case of the sacrificial anode. Impressed current Systems with consumable anodes are known as hybrid systems (http://www.cathodicprotection.com/concrete /daily.htm).

Energy for an impressed current system is provided by a power supply or rectifier. The rectifier provides a positive current supply to the anodes and a negative current return from the structure. For this circuit, Ohms law applies: E=IR, where E is the driving voltage of the rectifier output voltage, I is the current magnitude that results from the resistance of the circuit R. Proper system design seeks to minimize the resistance of the circuit through anode groundbeds design. Impressed current systems are capable of small to very large energy output levels through proper design. This range of ability allows protection possibilities for poorly coated pipe, large structures, automatic control and other options in design and operation.

Anode size, quantity, location and other operating parameters need to be designed to ensure proper operation. Much of the field data obtained in the earlier investigations would be used in the system design. These include soil resistivity, structure electrical continuity and stray current exposure (http://www.corrtech-inc.com/technicalpapers.html).
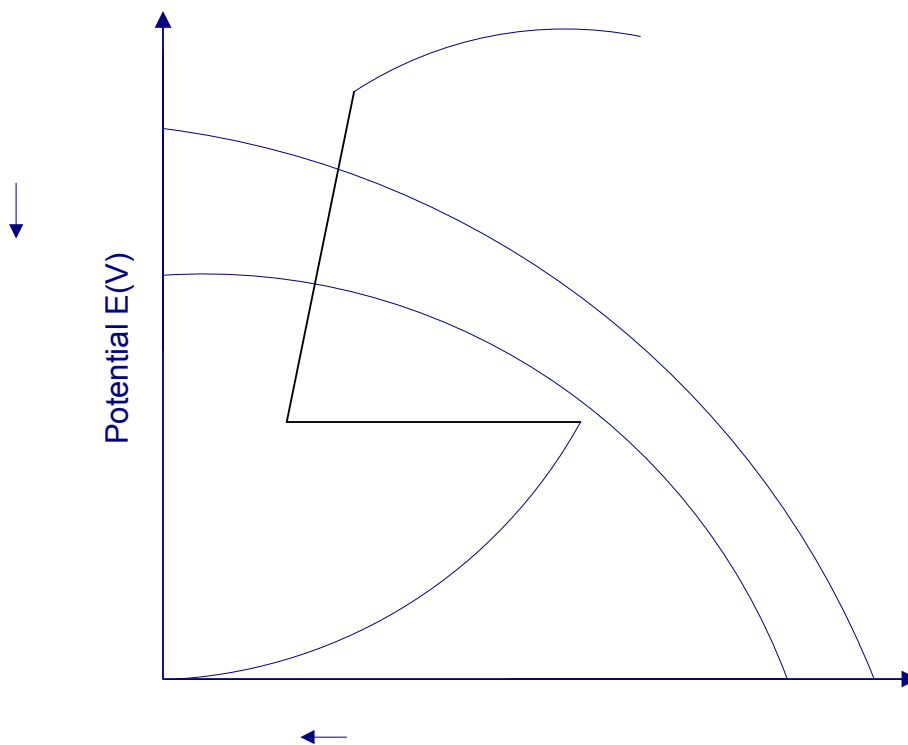

Figure 8. Evans diagram of steel with cathodic protection.

6.4. CATHODIC PROTECTION AS A METHOD OF REHABILITATION

Application of cathodic protection is a proven electro-chemical method for arresting corrosion on metallic structures. Cathodic protection converts all active anode sites on the structure, the areas that corrode, into cathode sites that do not corrode. New anode sites are provided through the installation of anode groundbeds.

The movement of charged ions and the separation of anodes and cathodes along the steel offer us some solutions to the corrosion of steel in concrete, as corrosion can be stopped by making all the steel a cathode. This is done by putting an external anode on the surface or embedding it in the concrete. This electro-chemical rehabilitation approach can be used in three different ways: cathodic protection; electrochemical chloride migration or 'desalination'; and re-alkalization (Broomfield, 1996).

In cathodic protection, the anodes, power supply and control systems are permanent, and a range of anodes can be used. The aggressive anodic reaction is isolated to a corrosion resistant anode while the harmless cathodic reaction occurs at the surface of the steel reinforcement. This process creates additional hydroxyl ions, rebuilds the passive alkaline layer and repels chloride ions. Cathodic protection has been used on hundreds of reinforced concrete structures around the world and has potential for the conservation of historic brick and stone masonry, terracotta and statuary where steel and iron has been used to provide reinforcement or a structural frame (Broomfield, 1996).

Re-alkalisation is the equivalent of desalination for carbonated structures. It relies on the principle that the hydroxyl ions produced at the cathode re-alkalise the concrete from the reinforcement outwards. This is linked with a wet anode at the surface that contains calcium carbonate, which moves under electro-osmotic pressure and re-alkalises the concrete from the surface inwards(Broomfield, 1996).

There are more than one hundred re-alkalisation projects completed in the UK and on the continent. One of the earliest was the renovation of the Hoover Factory beside the M40 at Perivale, NW London (Broomfield, 1996).

These specialist treatments require expert advice to check that the structure is suitable and that the best system is applied. There must be steel continuity, separation between steel and anodes and reasonable concrete quality before these techniques can be considered as cost effective and technically sound for a particular structure (Broomfield, 1996).

Corrosion of steel in concrete can be seen to be a significant problem for many reinforced concrete structures if moisture is present. If there is no salt to cause

corrosion in the short term, carbonation will affect most structures over the centuries. If the structure cannot be kept dry then there is a range of techniques that can be used depending on the structure, its condition and the cause and extent of the problem.

Electrochemical techniques can reduce the amount and extent of patch repairs, and leave the appearance unchanged with probes embedded in the concrete or a surface coating, depending on requirements and conditions.

Alkali silica reaction is a chemical attack of the aggregates in the presence of the alkalinity of the concrete and moisture. If the concrete can be kept dry then ASR will be minimised. Most ASR damage is unsightly rather than structurally dangerous (Broomfield, 1996).

7. CORROSION MONITORING IN CONCRETE

Corrosion of steel reinforced concrete structures is a major global problem. Chloride induced rebar corrosion damage results mainly from the use of de-icing salts in cold climates and/or exposure to marine environments. Carbonation damage is a further important degradation mechanism.

In view of the large scale and cost associated with the deteriorating reinforced concrete infrastructure, corrosion monitoring is becoming increasingly important for maintenance scheduling and life prediction purposes. The uses of corrosion monitoring of steel in concrete has been outlined to include the following:

- Ensuring that structures remain safe and fully operational.
- Information for timely and cost-effective intervention to prevent unacceptable damage and also service life extension.
- Durability modeling and related predictive elements.
- Enhanced understanding of micro and macro corrosion environments.

Corrosion monitoring of reinforcing steel poses many challenges such as:

- Direct inspection of the rebar or corrosion coupons, sensors is almost impossible as these are embedded in concrete.
- Retrofitting of corrosion probes/sensors is difficult.
- Concrete is actually a complex composite material, whose structure and properties tend to change with time. It does not "behave" like simple aqueous corrosion systems.
- Cracks in the concrete may represent a major factor in the severity of corrosion damage.
- Chloride induced rebar corrosion tends to be of the localized variety.
- Corrosion damage is typically manifested over many years of exposure.

Existing corrosion monitoring and assessment methods include electrochemical techniques, probes, examination of extracted core samples, measurement of chloride concentration profiles in the concrete and carbonation depths, tests for the "soundness" and permeability of concrete, and visual inspection (http://www.corrosion-club.com/concrete.htm).

Corrosion monitoring methods may be direct or indirect methods. Direct methods include:

- Coupons, they are weighted to determine the metal loss due to corrosion
- Electric resistance technique, the cross sectional area changes because of corrosion so also does the resistance of the bar.

- Linear polarization technique, utilizes the potential current relationship for a corroding electrode.

While the indirect methods include:

- Ultrasonic
- Radiography

The above methods are not easily set up for concrete measurement. Hence the following methods are currently used for concrete measure and often require embedded probes in the concrete. They include:

- Bar potential measurements
- Galvanic pulse technique which gives a potential versus time curve, where the slope gives information on the corrosion rate.
- Guard ring device directly gives weight losses due to corrosion.
- Potentiodynamic polarization with three electrodes system provides potential and current data.
- Zero resistance ammeters display micro cell current between bars.
- Electrochemical noise is measurement of natural fluctuations in the corrosion potential.

8. ZINGA

Zinga is a one-component cold applied anti-corrosion zinc coating system. Its unique formula provides environmentally safe cathodic protection to steel comparable with hot-dip galvanizing, with the added advantage that it can be applied as though it were paint (http://www.zinga-uk.com/how.html).

Zinga exhibits the properties of a galvanic zinc coating and a zinc paint. This combination provides benefits not provided by either system alone. Under the continuous immersion conditions studied, Zinga coated mild steel specimens corroded at a lower rate than galvanized zinc coated specimens (http://www.zinga-uk.com/how.html).

Zinga is a unique form of corrosion protection because it provides both Active and Passive protection in a form that is as easy to apply as a paint. But Zinga is not paint (http://www.zinga-uk.com/how.html).

Zinga is an active zinc performance coating which works in conjunction with the metal beneath whereas paints are only passive barriers. Regardless of how thick paints are applied, they remain as barriers. Once they are breached, corrosion sets in immediately. Despite this significant difference, Zinga is still often mistaken for paint simply because it is liquid and it comes in a tin. But there are other, more subtle differences. For example it does not "skin over" in the tin because Zinga has an unlimited pot-life, it doesn't go "tacky" like paint and also the thickness of a Zinga coat cannot be measured wet because it flattens off and dries too quickly (http://www.zinga-uk.com/how.html).
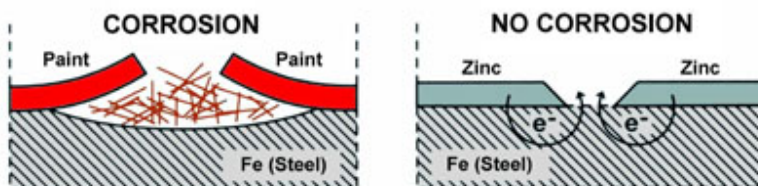
Figure 9 Schematic diagram of Zinga and paint.

Cathodic protection, or Active protection, arises from the zinc (the anode) sacrificing itself in favour of the base metal (the cathode) with the resulting flow of electrons preventing corrosion. In this way the protection of the metal is guaranteed, even when the zinc layer is slightly damaged. Other well established methods of cathodic protection include hot-dip galvanizing (HDG) and zinc thermal spraying both of which exhibits a constant sacrificial rate of the zinc layer (http://www.zinga-uk.com/how.html).

Within Zinga though this sacrificial rate reduces dramatically after the zinc layer has oxidized and the natural porosity has been filled with zinc salts. Additionally each zinc particle within the Zinga layer is encased and protected by the organic binder without adversely affecting the electrical conductivity. This enables Zinga to create nearly the same galvanic potential between the zinc and the steel as hot dip galvanizing but with a lower rate of zinc loss because, put simply, the binder acts as a "corrosion inhibitor" to the zinc (http://www.zinga-uk.com/how.html).

9. METHODS AND EXPERIMENTS

9.1. PREPARATION OF SAMPLES.

Table 4 Concrete blocks composition.

Ingredients	Weight (Kg)
Cement	1.2
Sand	2.4
Aggregates	3.6
Water	0.6

The water-cement ratio was chosen to be 0.5 so as to have a good quality concrete, with good workability and low porosity.

The specification for the solid ingredients was 1:2:3 for cement, sand and aggregates respectively. Thus the over all ratio of the mix became 1:2:4:6 for water, cement, sand and aggregates respectively.

The steel bars are carbon steel with a diameter of 5mm. This has been chosen in line with those used in the industry. A steel mesh was achieved by connecting all the steel rods together with the aid of electrical connectors. This forms a network with a mean potential.

All the samples were bathed in fresh water between 10 to 15 days for curing with the top above the water level to avoid direct contact with the steel rods and the connection.
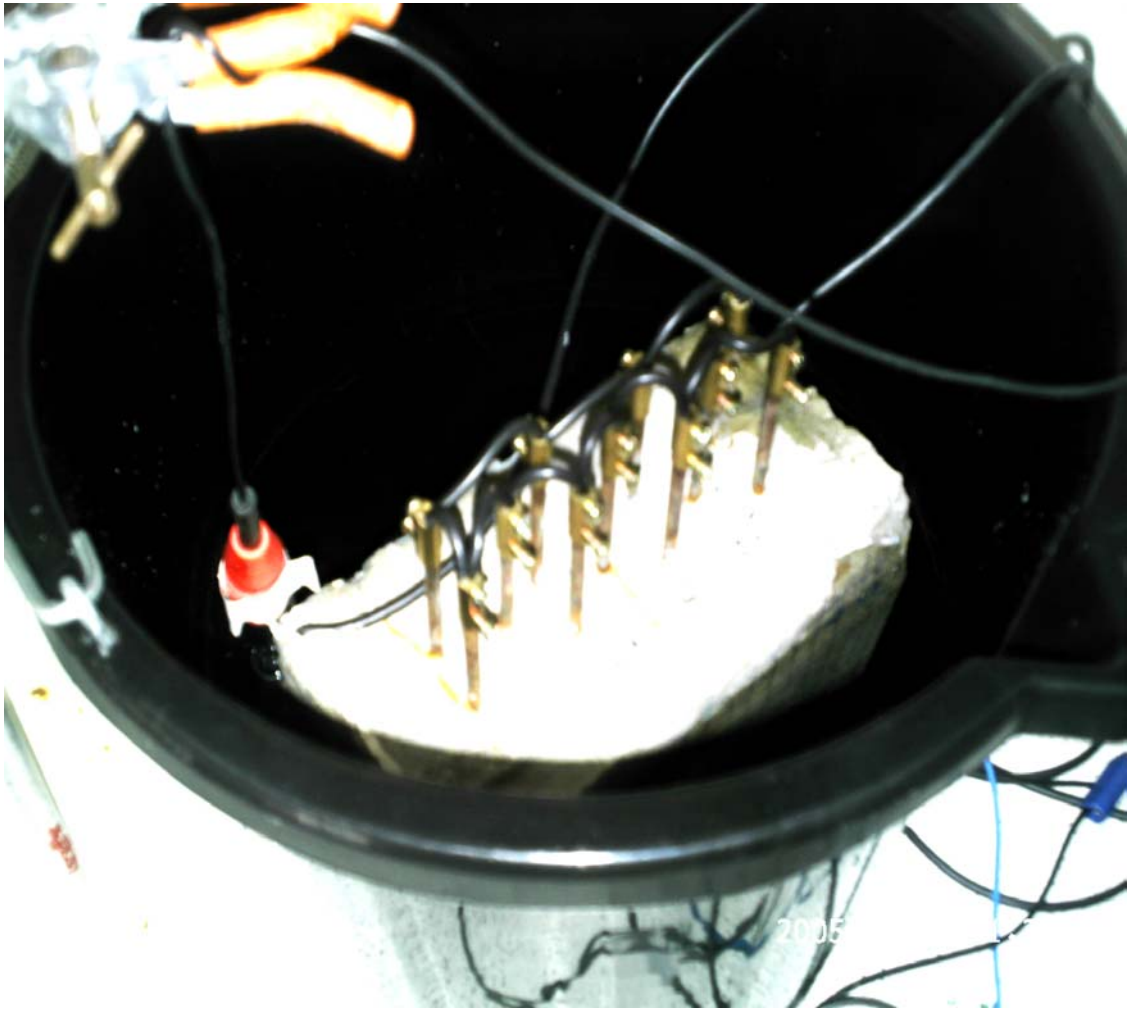
Figure 10 Steel rods connected together to form a mesh.

9.2. DESIGN OF THE CONCRETE BLOCK

The dimensions of the sample are:

Height: 15cm

Width: 10cm

Length: 20cm

A mould was made, varnished and each concrete block was cast in it, and then left for two days to set. After which it was removed from the mould.
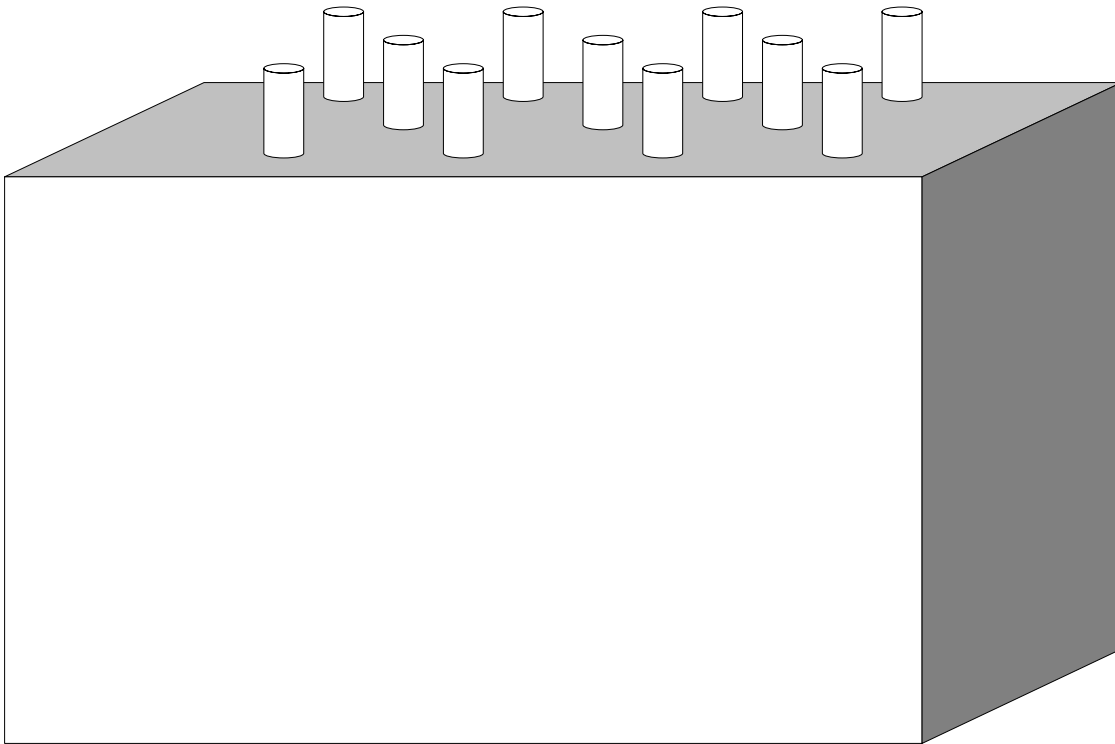
Figure 11 Diagram of concrete block and the steel rods arrangement

The steel rods were located in the middle of the concrete. The first row is made of four steel rods which are 4 cm apart and 4 cm away from the right and left ends of the row and 4 cm away from the inside end of the block. The second row is 1 cm away from the first row and is made of three rods which are 4 cm apart and 2 cm of horizontal distance apart from the neighboring first row rods. The third row is 1cm away from the second row and is made of four rods which are 4cm apart from each other and 4cm away from both ends of the row and the outer end of the concrete block.

4cm
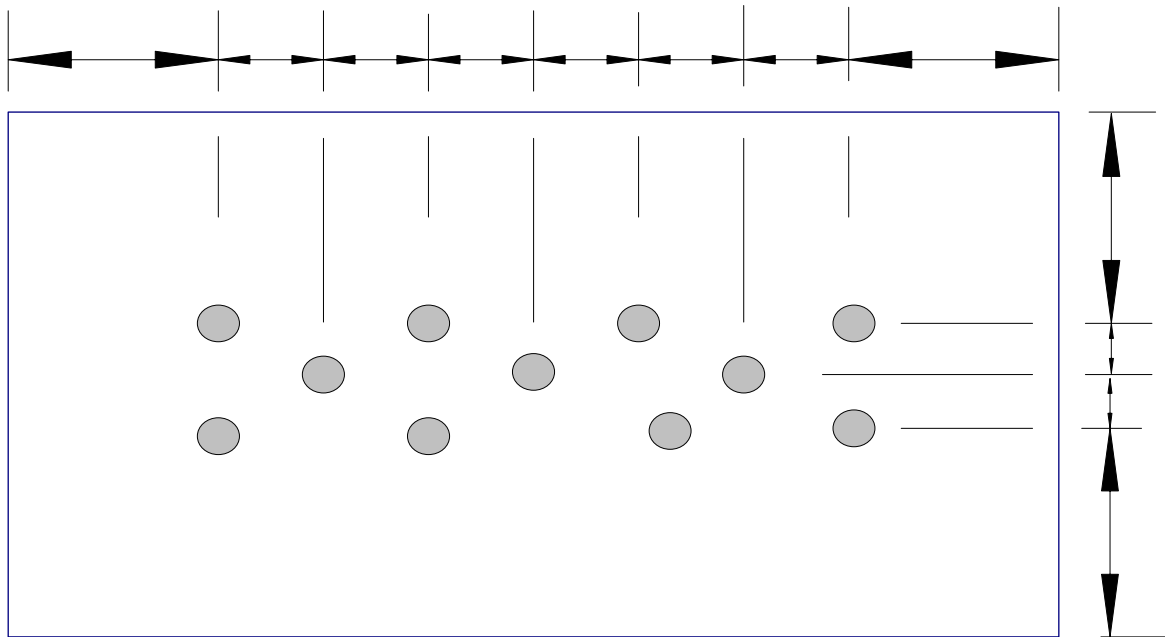
Figure 12 The geometry of the steel reinforcement in the concrete block.   2cm

The four samples are similar in their geometry and the arrangement of the steel rods to form a network, but one had additional features. This was the addition of a steel mesh, 2 centimetres from one end of the concrete. Four rods were contaminated with lithium chloride for each sample and in the same configuration.

Figure 13 Concrete sample removed from the mould.

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Figure 14 Concrete samples in fresh water during curing
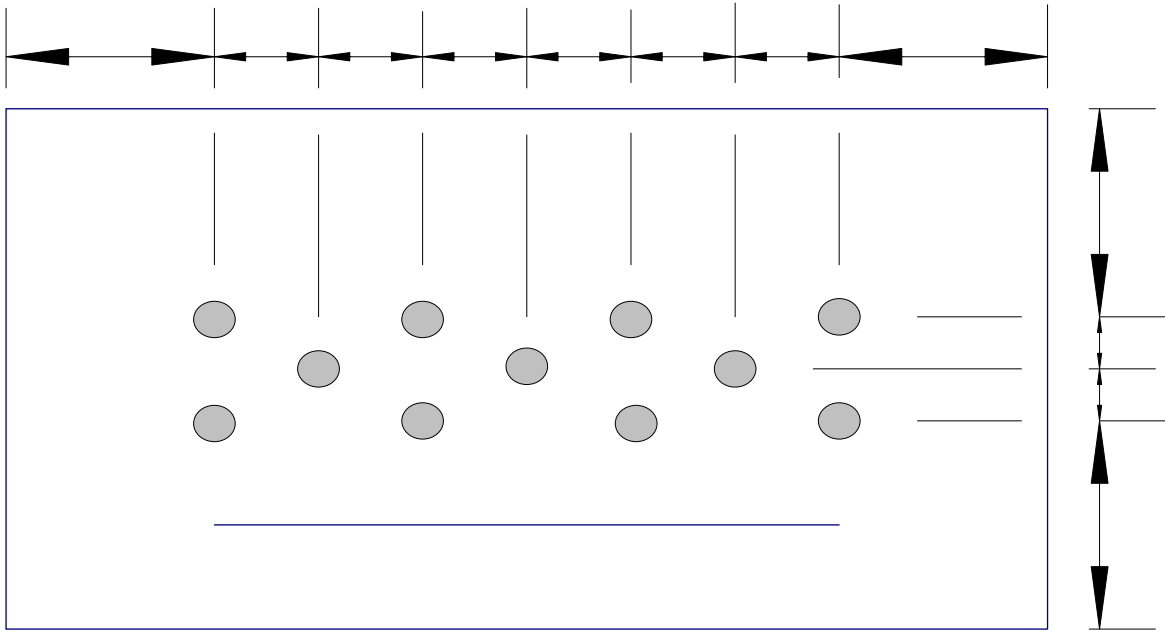
Figure 15 The geometry of the steel reinforcement with the stainless steel mesh in the concrete for the impressed current sample.

9.3. SAMPLES FOR MECHANICAL TESTING

A cylindrical mould was designed to create samples with the same concrete mix for mechanical tests (compression tests).The dimensions of the cylinder are:

Height: 20cm

Diameter: 10cm
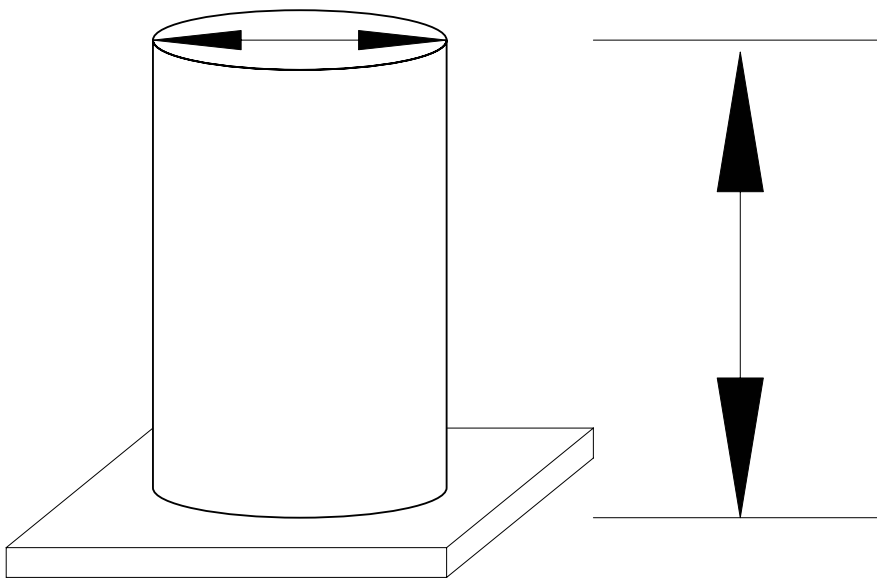
Figure 16 Diagram of the cylindrical mould for the test samples

Four samples were cast for each concrete block from the same concrete mix used to cast the blocks. These were done so as to have a direct comparison of compressive strength with those of the concrete blocks.

Table 5 Concrete cylinder composition

Ingredient	Weight(Kg)
Cement	0.628
Sand	1.257
Aggregate	1.885
Water	0.314

10c

The samples were left to set for 2 to 3 days, after which they are removed from the mould and put in a bath of fresh water for about 60 days for curing. They are brought out and let to dry 3 days before the compression test was done.

Figure 17 Cylindrical Concrete curing in fresh water bath.

Table 6 Composition for each concrete mix

Ingredient	Concrete Block(Kg)	Concrete Cylinder(Kg)	Concrete Mix per sample(Kg)
Cement	1.2	0.628	1.828
Sand	2.4	1.257	3.657
Aggregate	3.6	1.885	5.485
Water	0.6	0.314	0.914

9.4. ACCURACY OF MEASUREMENT

Accuracy is an important subject to consider in measurements. Due to the different measurement devices, the accuracy of a measurement depends on the least scale of the instrument used. This is called the reading accuracy of the instrument.

Eight different standard calomel reference electrodes (SCE) were used in the course of the experiments. Each electrode was slightly different in potential from the others. To have an accurate reading for good comparism, one reference electrode was chosen and the difference in potential between the chosen electrode and the other reference electrodes is termed the measurement error. This is subsequently effected in the potential measurements before comparison.

A high resistance voltmeter was used to measure the mixed potentials of the reinforcing steels in the concrete. This allowed a small amount of current to flow through the concrete. The mix potential will decrease as the distance between the steel and the reference electrode increases. The amount by which the potential decreases is called the voltage drop. The more the distance apart, the more the voltage drop and the lesser the mixed potential of the reinforcing steel in the concrete.

$E = iR_m - iR$ (voltage drop).

Where: E = mixed potential (volt)

i = the current that flows through the circuit (ampere)

R_m = Resistance of the voltmeter

R = Resistance of the concrete

A large is R_m is required so as to have a very small voltage drop (error).
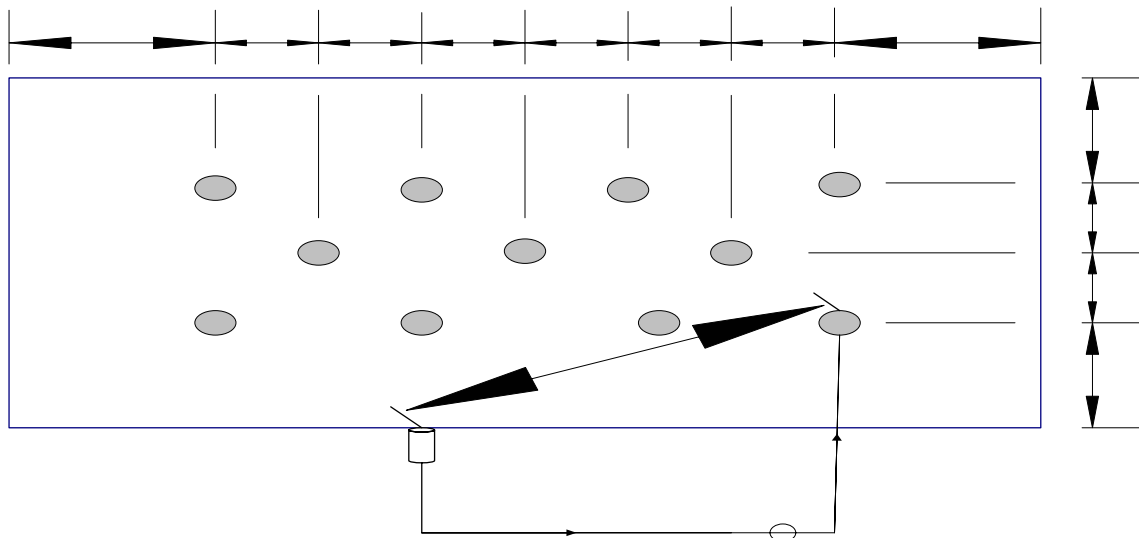
Figure 18 Schematic diagram showing the effect of distance on potential (voltage drop)

In the course of the linear polarization resistance experiments, the instrument used read the self-corrosion rates of Zinga in millimeter per second (mmPs) and recorded them in millimeter per year (mmPY).Accuracy demands that I multiply these readings by the corresponding factors to get millimeter per year (mmPY).

The voltmeter was also regulated for accurate measurement by choosing the right scale for each measurement.

10. EXPERIMENTAL TESTS AND RECORDS

10.1. INTRODUCTION TO THE EXPERIMENTATION

The aims are:

- To measure the current requirement for cathodic protection of steel rebar in concrete.
- To assess the effectiveness of Zinga in cathodic protection of steel reinforced concrete.
- Understand the behavior of reinforced concrete under corrosion.
- To compare conventional Zinga against Aqua-Zinga.

To achieve these objectives, voltages and currents are measured on the concrete blocks. The conditions of these experiments do not apply to real situations. The blocks are dipped in still fresh water and artificial seawater (3.5% by weight of NaCl in of water). And the water depth was about eleven centimeters (11cm). On site, the problems of corrosion are severe in the splash zone and in the mud due to sulphate reducing bacteria. Other effects such as waves and vortex shedding increases corrosion rate as they increase the reduction of oxygen and impacts directly on the structures.

10.2. PURPOSE OF THE EXPERIMENT

The experiment should enable us to assess the following:

- The corrosion rate of conventional Zinga in fresh water and artificial sea water.
- The behavior of impressed current cathodic protection.
- The behavior of conventional Zinga as a sacrificial anode for cathodic protection in sea water and fresh water.
- The behavior of Aqua- Zinga as a sacrificial anode for cathodic protection in sea water and fresh water.
- The behavior and properties of the concrete under cathodic protection.
- The behavior of the reinforcing steels under cathodic protection.

The reference electrode used for the experiments was a standard calomel electrode (SCE) commonly used in the laboratory, the common ion with the electrolyte is the chloride ion.

The experiments were set up to measure the following:

- Potential
- Current
- Potential versus time
- Current versus time
- Corrosion rate
- Compression force

10.3 POTENTIAL MEASUREMENT

This is the measurement of the mixed potential of each reinforcing steel from the side of the concrete with one centimeter interval across the concrete face.

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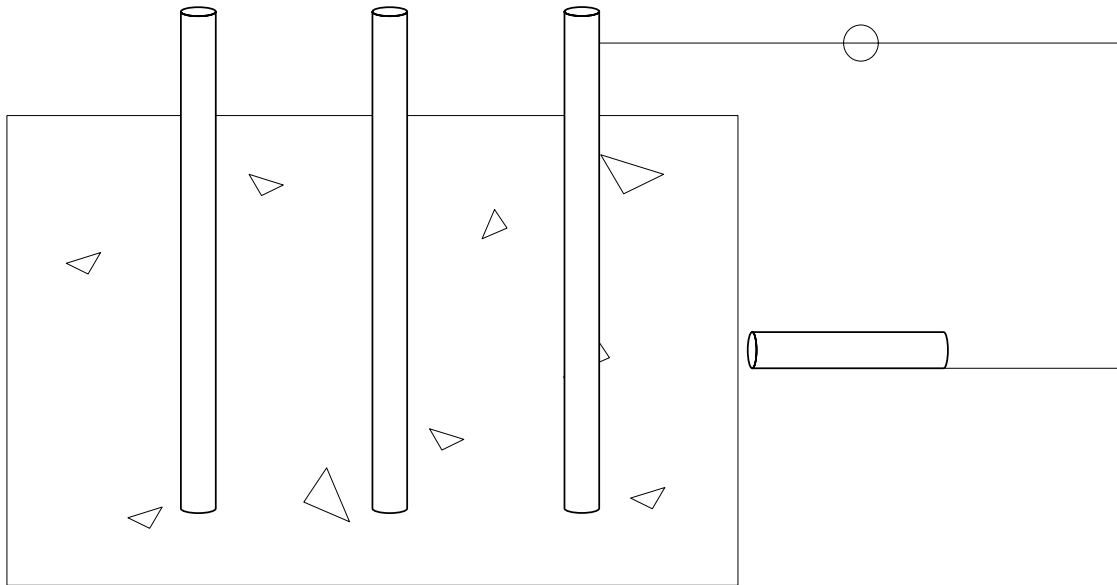
Figure 19 Mixed potential measurement set up.

The mixed potential of each reinforcing steel was measured with the aid of a standard calomel reference electrode and a high résistance voltmeter so as to reduce the error in the measurement. The high resistance voltmeter permits only a small amount of current to flow through the set up into the concrete and out. When the small circuit current flows through the concrete, a potential difference is set up. This is as a result of the resistance of the concrete. This potential difference is called the voltage drop and its value is dependent on the amount of the circuit current. Hence dependent on the characteristics of the meter used.

The mixed potentials of the steel rods contaminated with sodium chloride were also measured. The potentials generated by the self-corroding Zinga and Aqua-Zinga were also recorded and plotted against time.
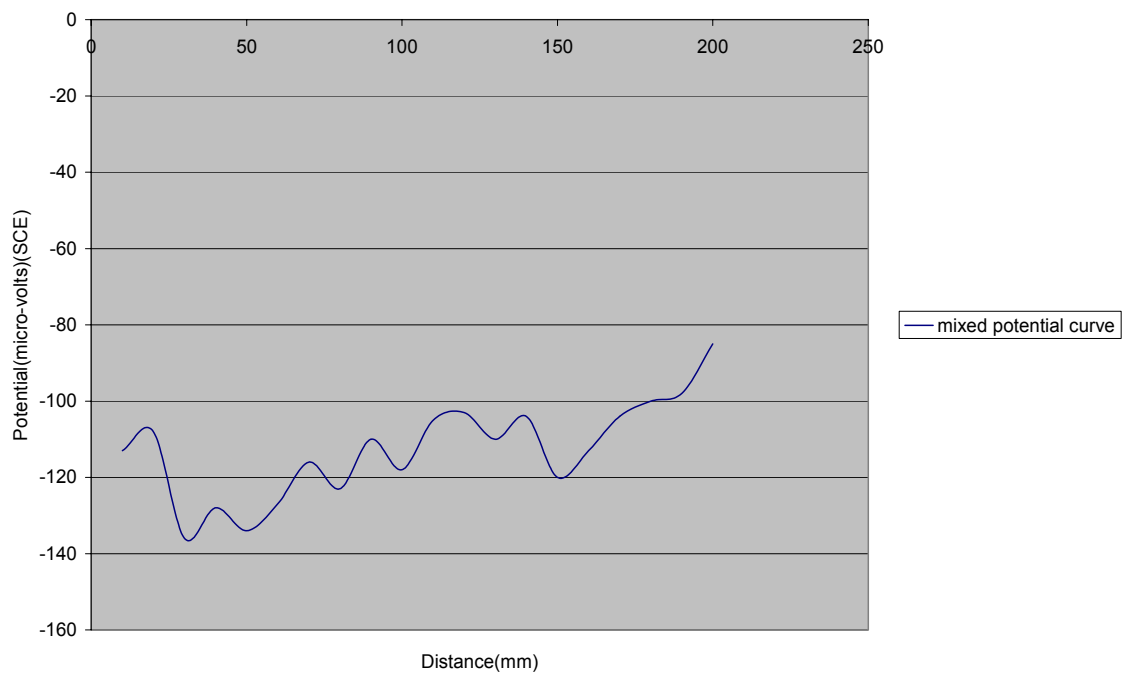
Graph 2 Mixed potential variation with distance.
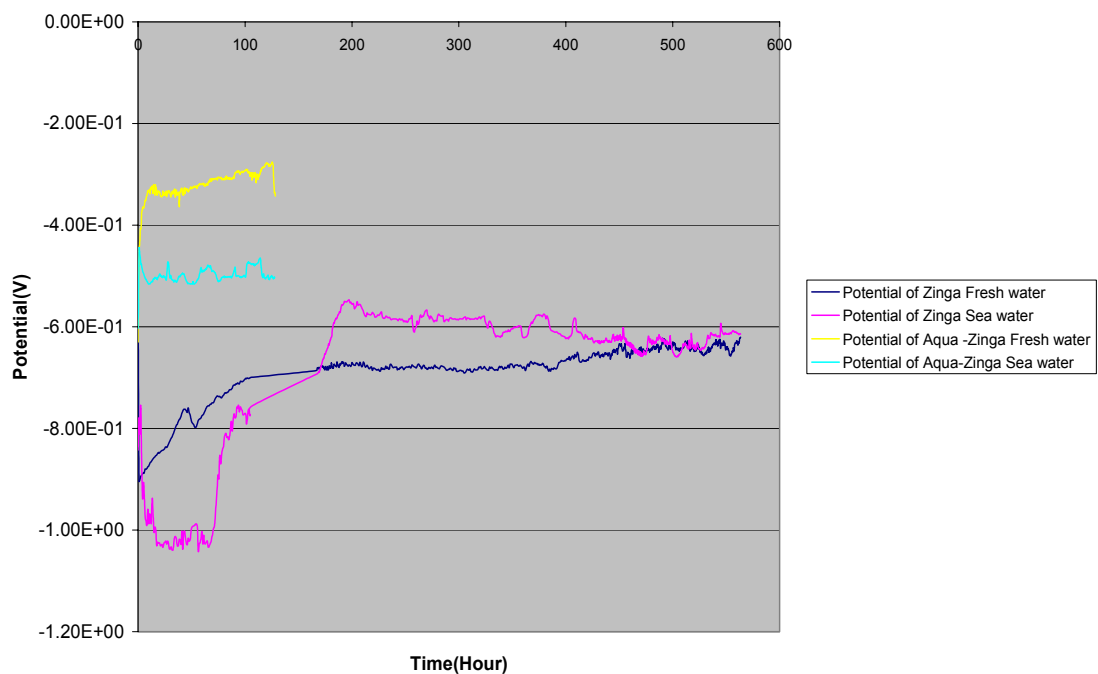
Graph 3 Potentials generated by the self-corroding Zinga and Aqua-Zinga.

10.4. CURRENT MEASUREMENT

The two current measurements here were the self-corrosion current of Zinga in seawater and fresh water and the impressed current in the impressed current cathodic protection.

The current from the self-corrosion of Zinga was measured using the linear polarization resistance set up.

Faraday's law states that 96500 coulombs is the charge needed to corrode an equivalent weight in grams of a metal. The equivalent weight of a metal is the atomic weight divided by the valency of that metal.

For Zinga: $Zn \rightarrow Zn^{2+} + 2e^-$

The equivalent weight = 65.39/2 = 32.695 grammes. Hence 96500 coulombs will corrode 32.695 grams of zinc.

The charge produced by a corroding metal is the product of the current generated and the time taken to generate that current. For a current-time graph, the area under the curve is the charge produced.

Charge, Q =, I * t.   Where I = current and t = time
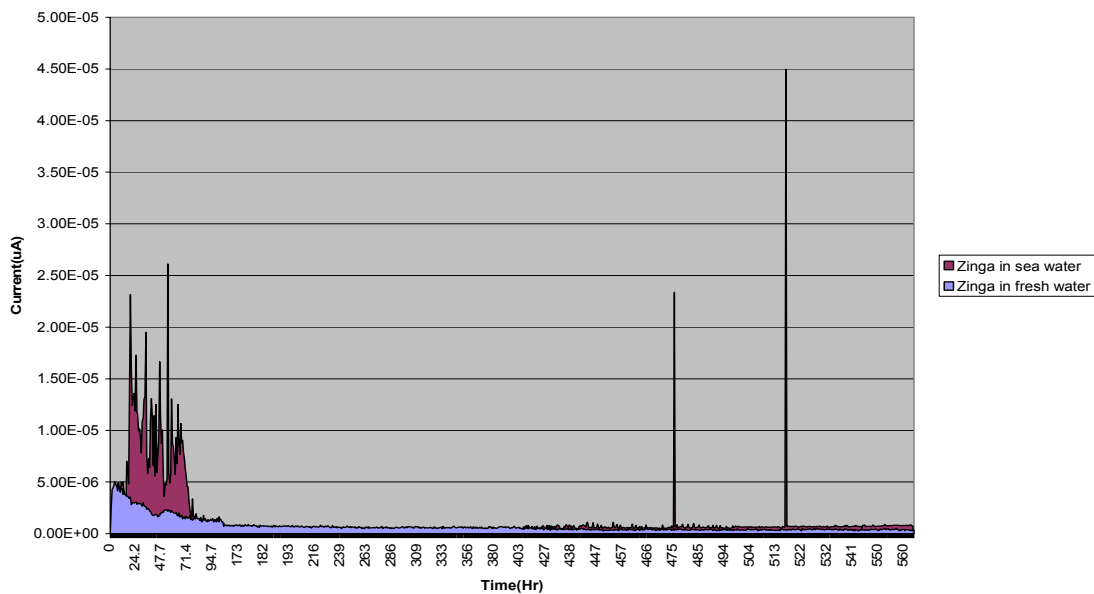
Graph 4 Current -Time graphs for the self-corrosion of Zinga.

Impressed current was measured at -750millivolts, which is a reasonable potential for cathodic protection in fresh water, then in sea water.
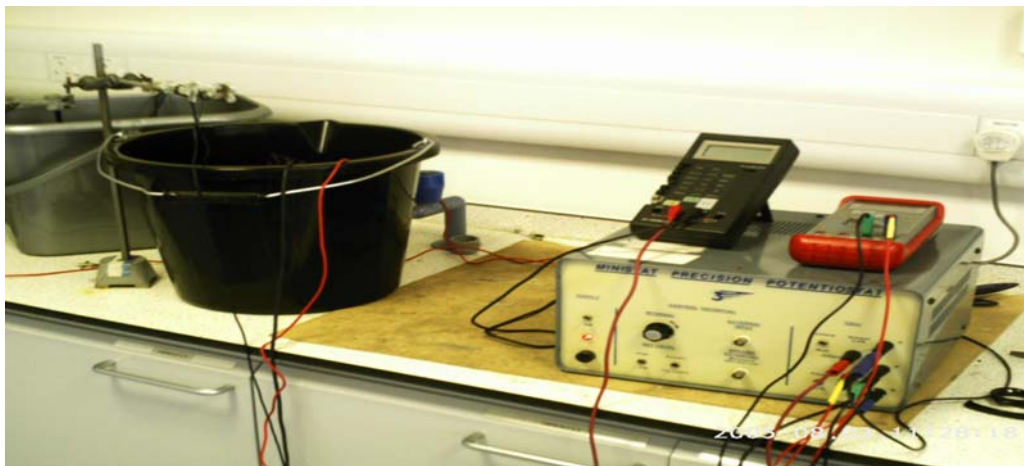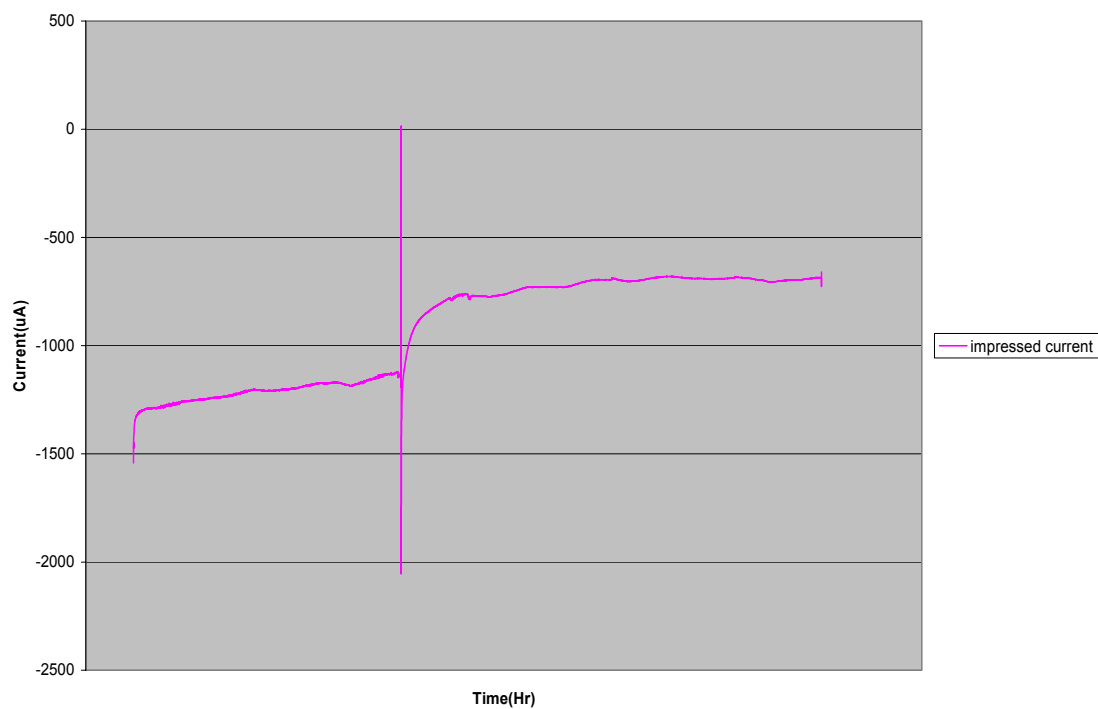

Figure 20 Potentiostat set up for impressed current cathodic protection.


Graph 5 Graph of impressed current at -750mV (SCE) in fresh water, then in sea water.

The current measurements from the impressed current concrete sample were recorded when the reading was stabilized. The measurements were done for a range of potentials between -400millivolts to -750millivolts in seawater and tabulated bellow.

Table 7   Impressed Current measurement after stabilization for a range of potentials

Potential(mV)	Current(mA)
-400	-0.0517
-450	-0.0725
-500	-0.1138
-550	-0.1353
-600	-0.1918
-750	-0.6574
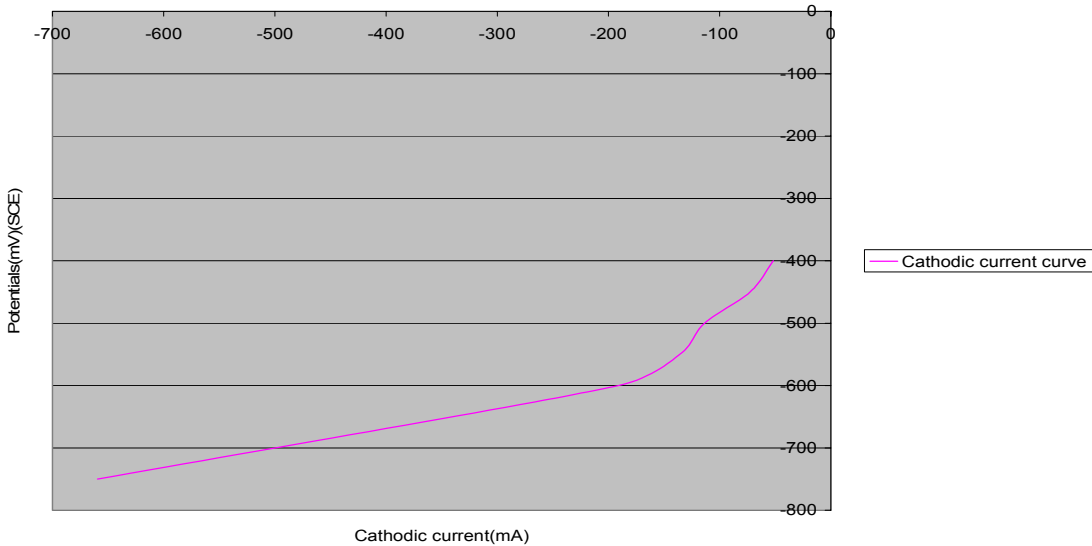
Graph 6 Stabilized Impressed current for a range of potentials between -400millivolts (SCE) to -750millivolts (SCE).

10.5. CURRENT VERSUS TIME AND POTENTIAL VERSUS TIME MEASUREMENTS.

The experiments here involved only three of the four concrete blocks. The concrete blocks were labeled blocks one to four (1-4).But the experiments here involved only concrete blocks one, two, and four. The third concrete block was used for the impressed current cathodic protection experiment. After connecting the reinforcing steel rods together to form a steel mesh, the surface of each of the blocks was gritted so as to have a surface prepared closed to the specified standard of surface roughness-SA 2.5 (ISO8501-1) or WJ-1 (NACE-5/SSPC-SP12).

Concrete block one was coated with Zinga without pre-coating with lithium chloride. The sample was left to dry and the necessary connections made, including the standard calomel reference electrode before immersing it in an eleven centimeter deep fresh water bath. The potentials and currents were monitored and recorded for fifteen days. It was then removed from the fresh water bath and placed in an artificial sea water bath (3.5% by weight NaCl in water) of the same depth as the fresh water, where the potentials and currents were monitored and recorded for thirty days.

Figure 21 Concrete block one experimental set up

Concrete block two had similar surface preparation. But it was pre-coated with lithium chloride before applying Aqua-Zinga coating on it. Aqua-Zinga is Zinga in

silicate binder, and it is water soluble, while the conventional Zinga is an organic binder. This was also immersed in eleven centimeter deep fresh water for ten days. It was removed from the fresh water bath and immersed in artificial sea water bath (3.5% by weight NaCl in water) of the same depth for thirty days. The potentials and currents were all monitored and recorded throughout the experiment.


Figure 22 Concrete block two set up.

Concrete block four had similar preparations with the other concrete blocks. It was coated with Zinga after pre-coating with lithium chloride. It was also immersed in a fresh water bath of the same depth for twenty days after which it was removed and immersed in an artificial sea water bath (3.5% by weight NaCl in water) for thirty days. All potentials and current were monitored and recorded during the experiment.
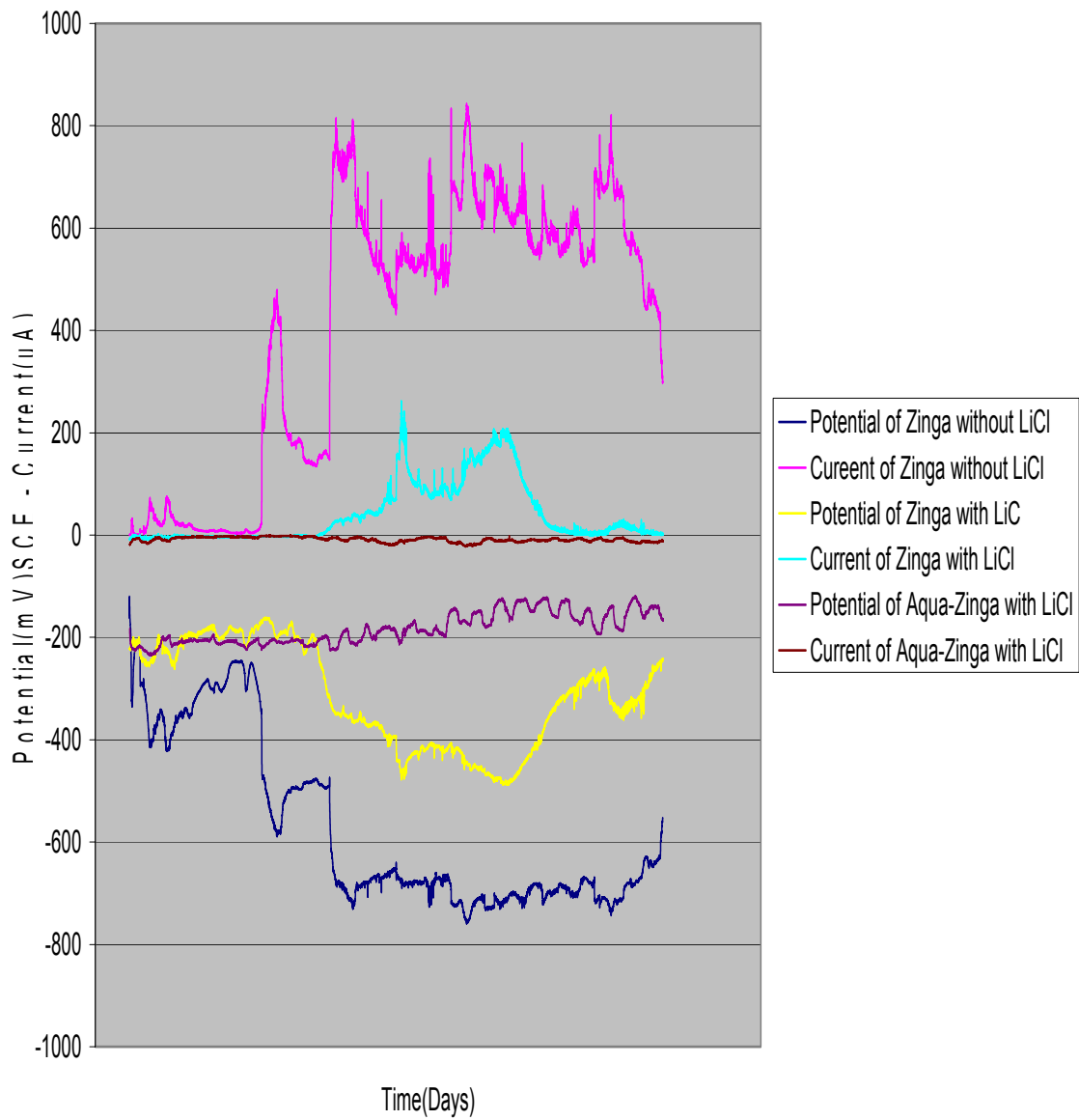
Figure 23 Concrete block four experimental set up.

The potentials and currents of the test samples in their environment were plotted against time and compared for the three samples.
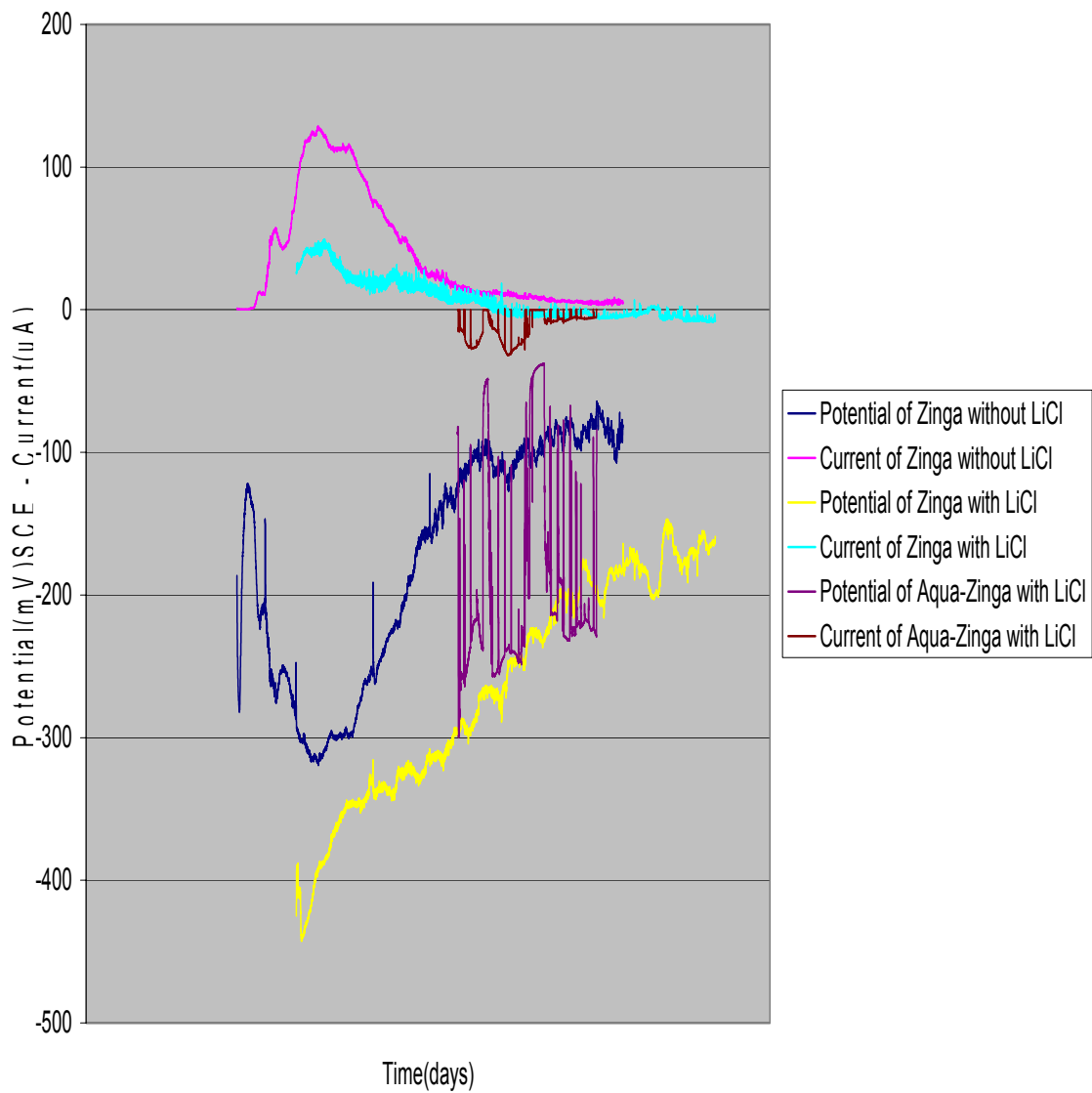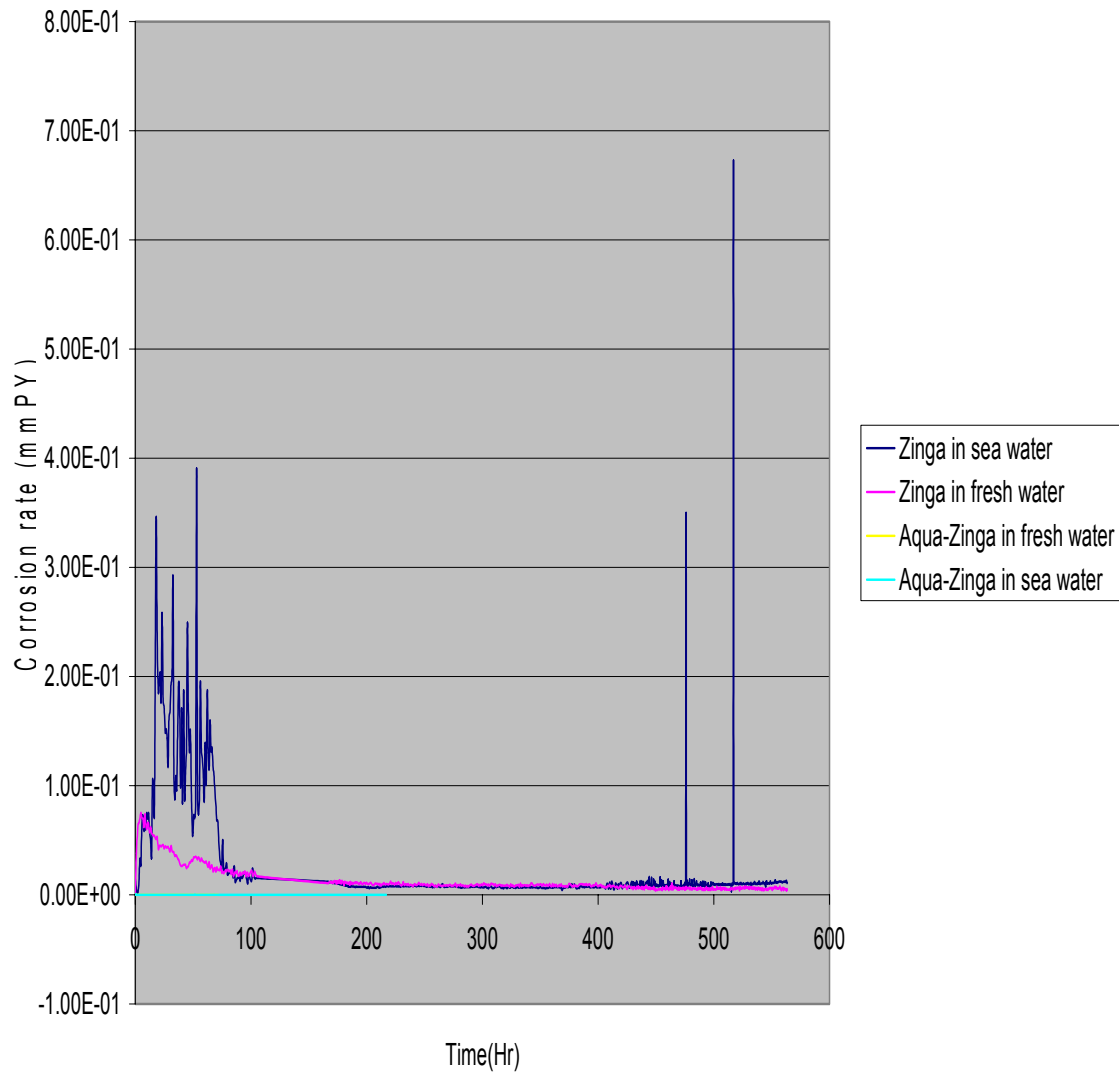
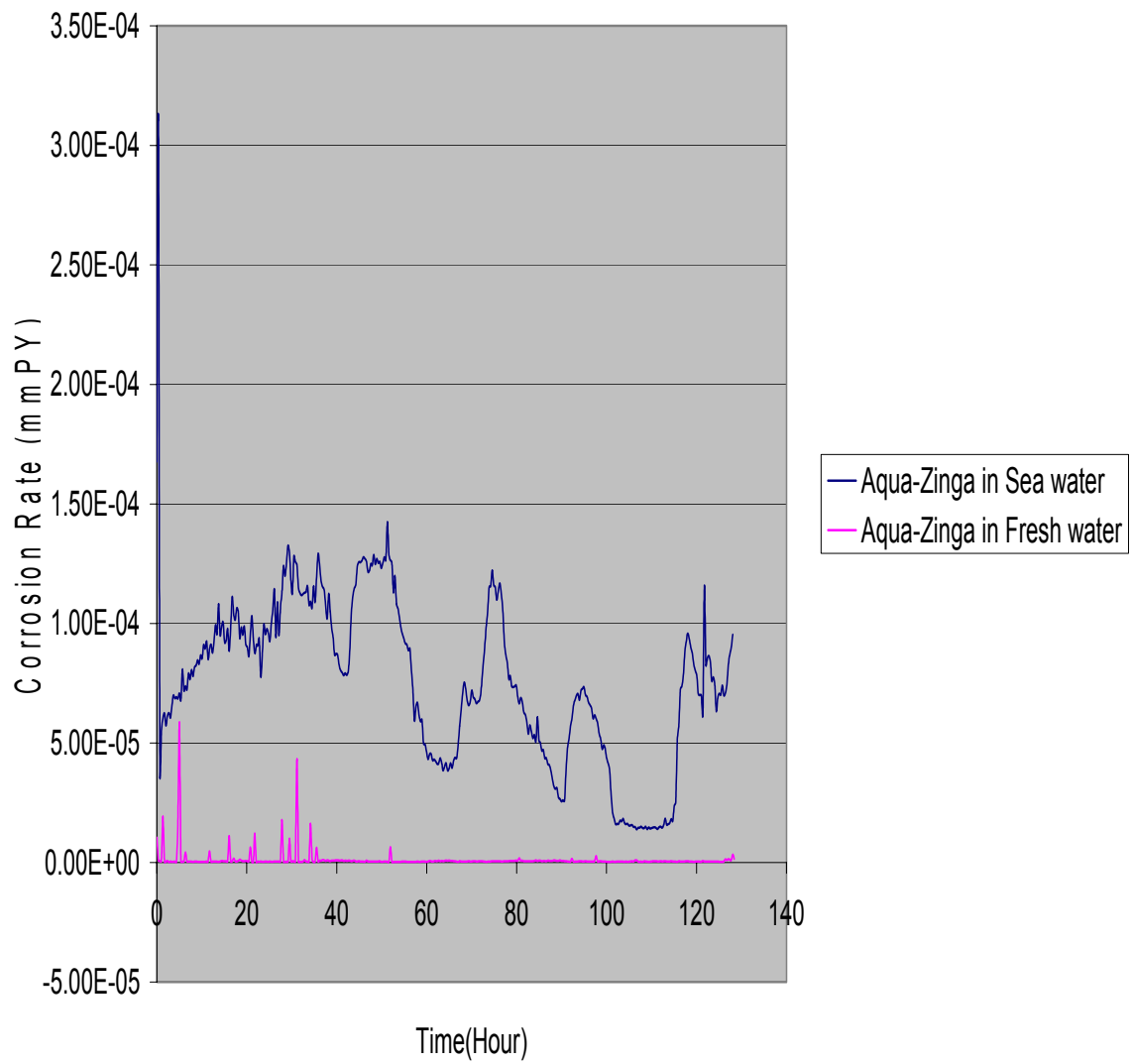**Graph 7 Graphs of concrete blocks in fresh water bath**

Graph 8 Graphs of concrete blocks in artificial sea water (3.5%by weight NaCl in water) bath.

10.6. CORROSION RATE OF ZINGA

The corrosion rates of Zinga in sea water and fresh water from the linear polarization resistance experiment were plotted against time.

Graph 9 Self-corrosion rate against Time

Graph 10 Aqua-Zinga Self-Corrosion rate against Time

10.7. MECHANICAL TESTING

The four concrete cylinders were tested in compression until breaking. This was done so as to know the compression force that will result in failures for each of the concrete blocks.

Figure 24 The four concrete cylinders before compression test.

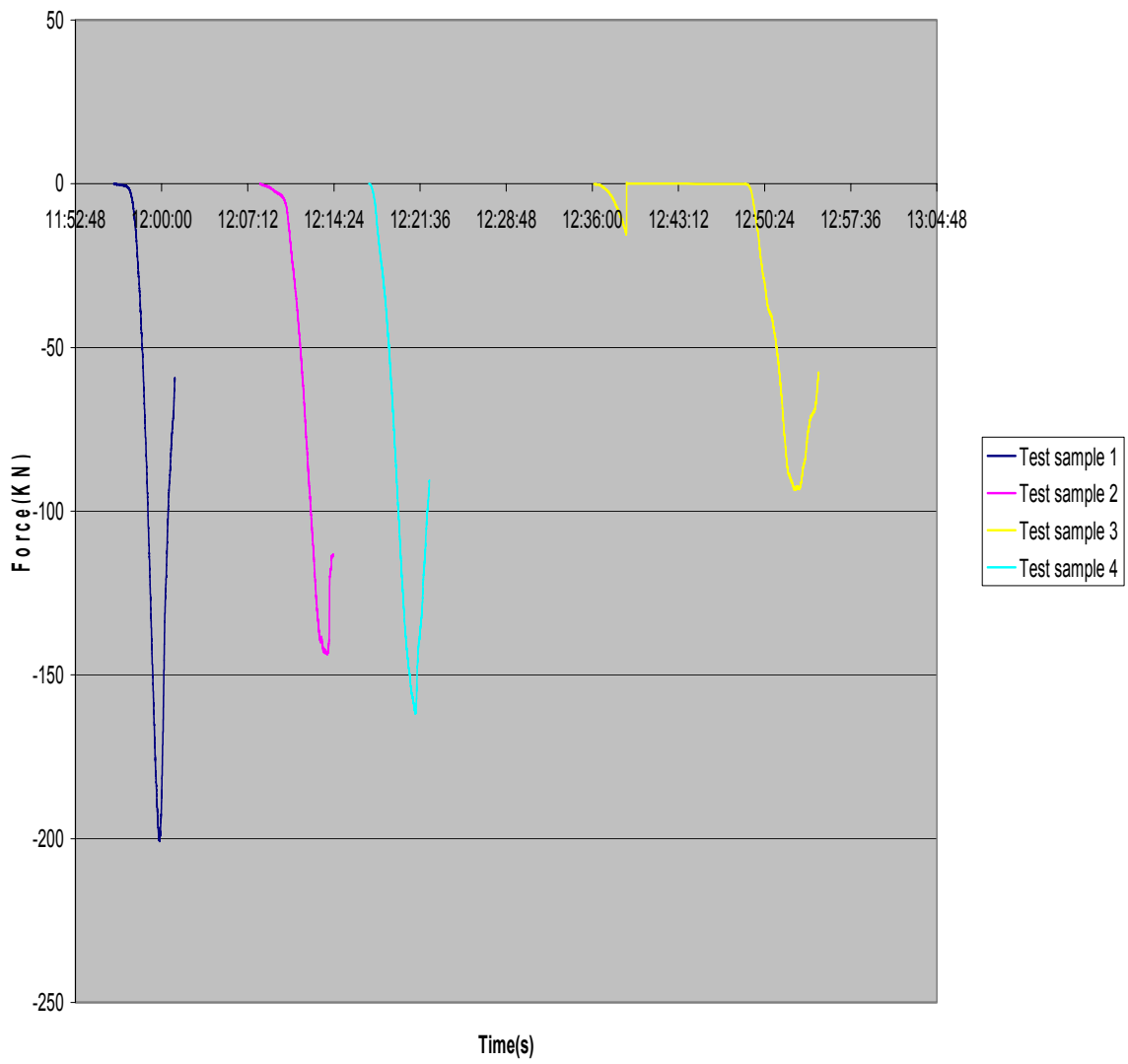**Figure 25 Concrete cylinder one after compression test**

Figure 26.Concrete cylinder two after compression test.

Figure 27 Concrete cylinder three after compression test

Figure 28 Concrete cylinder four after compression test.

Graph 11 Graphs showing the compression load against time for the four concrete cylinders.

11. ANALYSIS

11.1. MIXED POTENTIALS.

Graph 2 shows the mixed potential behaviour of concrete block one with distance. The first steel rod was connected to the voltmeter so also the reference electrode. There is more voltage drop (IR drop) as the distance between the steel rod and the reference electrode contact on the face of the concrete increases (graph.2). This is as a result of the resistance of the concrete.

The resistance of the concrete is a function of the resistivity of the concrete with respect to the length and cross sectional area of the concrete. Thus the increased distance between the steel rod and the reference electrode contact on the concrete face increases the resistance of the concrete since the area is constant.

Potential, $E = iR_m + iR$

Hence $iR_m = E – iR$

But $R = \rho L/A$

Therefore $iR_m = E - \rho L/A$

Where i   =   Circuit current (A)
      R_m =   Resistance of the meter (Ω).
      R   =   Resistance of the concrete (Ω).
      L   =   Distance or Length apart (m).
      A   =   Cross sectional Area of the concrete (m^2).
      ρ =   Resistivity of the concrete (Ω/m).

Factors such as the quality of the concrete affect the nature of the graph (graph 2). Concrete is a composite material and each of the constituents that make up the concrete has its unique properties. The size of the aggregates also affects the resistance of concrete in the sense that larger aggregates tend to create more voids than smaller aggregates. These produce more pore spaces than smaller aggregates that will tend to occupy every available space.

The result of the mixed potential measurement also showed that the steel rods contaminated with sodium chloride have more negative potentials than those without sodium chloride.

The potential of the concrete blocks pre-coated with lithium chloride were more negative than those without lithium chloride,

11.2. LINEAR POLARISATION RESISTANCE EXPERIMENT

The linear polarization resistance experiment results for Zinga and Aqua-Zinga in sea water and fresh water showed significant differences. The graph (graph.9) shows that the corrosion rate of Zinga in sea water and in fresh water were equal for the first twenty hours. By the second day the corrosion rate of Zinga in sea water had doubled while that in fresh water was reducing. The corrosion rate of Zinga in sea water started showing significant reduction after three days.

By the tenth day the corrosion rates of Zinga in sea water and fresh water were almost equal again, showing an almost constant rate of corrosion. These went on reducing gradually for more than ten days. On the twenty first day, the corrosion rates were both close to zero.

The corrosion rate of Zinga in fresh water was below 0.1mm per year while that for Zinga in sea water got above 0.2mm per year. The graph (graph.9) showed that the corrosion rate of Zinga in sea water doubled that of Zinga in fresh water. This graph suggests that Zinga corrodes faster in sea water than in fresh water. Therefore it might be more effective in cathodic protection in sea water. The result also tells that the corrosion rate reduced and maintained a rate close to constant for great period of time.

The difference in the corrosion rates of Zinga in sea water and fresh water was as a result of the more electrolytic nature of sea water because of the mobile ions than fresh water. The artificial sea water used for this experiment contained 3.5% of sodium chloride which is an electrovalent compound and a good electrolyte in molten and in solution. This made the Zinga environment more corrosive than the fresh water.

1.7 grams of Zinga was used for each of the linear polarization resistance experiment. Does it mean that the whole of the Zinga corroded as indicated in the graph? Graph 3 shows the current- time relationship for the samples in both sea water and fresh water. The area under the graphs indicate the charge (coulomb) generated by each sample in the course of corrosion. By analytical methods, the areas under the graph 3 are 539 coulomb and 892 coulomb for Zinga in fresh water and sea water respectively. But 95600 coulomb is required to corrode 32.5 grams of zinc. Hence 0.183 grams and 0.303 grams of Zinga corroded in fresh water and sea water respectively.

The corrosion rates of Zinga in sea water and fresh water reduced not because all the Zinga had corroded but because of the formation corrosion products that masked the corroding Zinga.This kept reducing the effective Zinga area. Hence reducing the corrosion rates. Like in every chemical reaction, accumulation of

products decrease a forward reaction and removal of products increases a forward reaction.

Graph 9 also showed that the corrosion rates of Aqua-Zinga in fresh and artificial sea water were almost equal. Due to the scale of the graph, the difference cannot be noticed. But graph 10 showed that Aqua-Zinga in sea water corroded at rates up to 0.0001mmPY, while that in fresh water never got close to 0.00005mmPY. This also suggest that sea water is more conducting than fresh water.

11.3. POTENTIOSTAT EXPERIMENTS

The potentiostat experiment was set up to for the concrete block four. The potential was kept fixed at -750millivolts, which is a reasonable potential for cathodic protection. The current generated was monitored and recorded in fresh water, then in sea water. This current is called the impressed current.

Graph 5 shows that the amount of impressed current needed to maintain a potential of -750millivolts was more in fresh water than in sea water. More than 1milliampere is needed to maintain a potential of -750millivolts. While less than 1milliampere is needed to maintain the same potential in sea water.

This can be attributed to the more conducting nature of the sea water due to the mobile sodium chloride ions present in it. These reduce the effective resistance of the concrete block. On the other hand, more current is needed in fresh water as a result of the work needed to be done in driving the current through the concrete block.

Graph 6 shows the impressed current needed for a potential range between -400millivolts (SCE) to -750millivolts (SCE).This will subsequently be compared with the sacrificial Zinga coating. To see if the Zinga sacrificial anode coating can generate the amount of current needed to drive the potential to a more negative potential as obtained from the impressed current system. This negative potential can be referred to as the protective potential. This graph was plotted with the stabilized impressed current readings after polarization.

11.4. CURRENT AND POTENTIAL MEASUREMENTS.

The experiments carried out involved the measurement of the galvanic potentials and currents of the concrete blocks in fresh water and sea water under sacrificial (Zinga coating) anode cathodic protection. The results here will be compared to that of concrete block three, the impressed current cathodic protection system to see how effective the Zinga is in sacrificial anode cathodic protection in the two environments.

11.4.1. CONCRETE BLOCK ONE

This concrete block had a mean mixed potential of -192millivolts. This is the concrete block that was coated with Zinga without pre-coating with lithium chloride. The effectiveness of Zinga was tested in sea fresh water, then in artificial sea water.

Under sacrificial anode cathodic protection in fresh water, the maximum current generated by the coating was about 128microAmperes corresponding to a potential of about -320millivolts (graph 7). After which corrosion products formed started masking the coating. Hence reducing the surface area of the corroding Zinga. The potentials and currents generated were not adequate for a good protection of the reinforcing steels in the concrete when compared with the impressed current system which provides a good reference to check the effectiveness of Zinga, since active stainless steel has a potential of about -600millivolts and carbon steel has a potential of about -700millivolts.

In sea water, this sample generated currents up to about 843microamperes corresponding to potentials of about -760millivolts (graph 8). This is quite protective when compared with the impressed current system. Although it started gradually, there was a sharp increase in the rate of Zinga corrosion. The results in the sea water condition were far more impressive than those in the fresh water condition.

Again the reaction rate started reducing due to the formation of corrosion products that mask the reacting or corroding Zinga. These reduced effective corrosion area of the Zinga.

11.4.2. CONCRETE BLOCK TWO

This concrete block had a mean mixed potential of about -156millivolts. It was pre-coated with lithium chloride, after which it was sprayed with water base Zinga (Aqua-Zinga). It was tested in fresh water, then in sea water.

Graphs 7and 8 showed that in both environments, aqua-Zinga was not impressive. Rather than protecting the reinforcing steel, it was behaving cathodic and generating cathodic current. It never generated an anodic current. It could suggest that it was not corroding sufficiently to protect the steel.

11.4.3 CONCRETE BLOCK FOUR

This block had a mean mixed potential of about -380millivolts. This concrete block was pre-coated with lithium chloride before coating with the Zinga sacrificial anode coating. The effectiveness of the Zinga sacrificial anode coating was tested in fresh water, then in sea water.

Under sacrificial anodic cathodic protection in fresh water, the maximum current generated was about 43microamperes corresponding to a potential of about -440millivolts (graph 7). These potentials and currents were not adequate for cathodic protection as such the reinforcing steels was under protected when compared with the impressed current system of cathodic protection. These results were mainly due to the low rate of reaction of Zinga in fresh water. The corrosion products formed then mask the surface of the Zinga, reducing its effective surface area. Hence reducing the corrosion rate. This was why the potentials and currents increased at the beginning of the experiment, got to a peak and started declining. This finally led to the block generating cathodic current, which is a negative current.

In sea water, the block produced an initial cathodic current before producing anodic current. The currents generated got to a peak of about 262microamperes corresponding with a potential of about -482millivolts (graph 8). Even if the potentials here were higher than those generated in the fresh water environment, they were still not adequate for good cathodic protection of bare steel in seawater. However, they are probably sufficient to protect steel in the less corrosive conditions found within concrete.

11.5. COMPRESSION TEST

Test sample one (figure 25) was made from the same concrete mix as concrete block one. This had a breaking load of about 201KN (graph 10). With an area of $0.62832*10^{-2}$ m^2, the compressive strength became about 32MNm^{-2}.This concrete cylinder has the same compressive strength with the concrete block that was coated with Zinga sacrificial anode casting without pre-coating with lithium chloride.

Test sample two (figure 26) was made from the same concrete mix as concrete block two. This was the concrete block that was pre-coated with lithium chloride before spraying with Aqua-Zinga. The breaking load recorded was at about 144KN (graph 10). The compressive strength will be about 23MNm^{-2}.

Test sample three (figure 27) had a breaking load of about 95KN (graph 10). This test was not a good test as shown in graph 8. The top surface was not level enough for a good test. Hence the load was concentrated on the contact areas. Subjecting the test sample to side loading and breaking until full contact was made. This test sample was made from the same concrete mix as the concrete block used for the impressed current cathodic protection experiment (Potentiostat experiment). The compressive strength with this result was about 15MNm^{-2}.

Test sample four (figure 28) was made from the same concrete mix as concrete block four, the one that was pre-coated with lithium chloride before coating with Zinga. The breaking load was at about 162KN (graph 10), corresponding to a compressive strength of about 26MNm^{-2}.

Concrete cylinder one as shown in graph 10 proved to have the highest compressive strength. This was followed by concrete cylinder three, and then comes concrete cylinder two. Finally we have concrete cylinder four.

CONCLUSION

The experiments carried out in this project have confirmed the influence of chloride ions on the potentials of reinforcing steels. These make the rebar more vulnerable to corrosion. Hence influencing the durability of the reinforced concrete.

The reaction of pure zinc metal with pure water raises concerns over the use of zinc alloys as a sacrificial anode for cathodic protection. Pure zinc metal does not react well with pure water. Hence further research on how to improve the conductivity of Zinga in fresh water should be carried out.

Aqua- Zinga appears not to be effective if used as a sacrificial anode for cathodic protection. This may be because it is made of zinc particles in a water base and from the experiments carried out in this project it never produced the potential and current needed for adequate protection when used as a sacrificial anode for cathodic protection. Further research should be carried out to improve the effectiveness of Aqua-Zinga.

The pre-coating of the concrete surface with lithium chloride appeared to be beneficial in fresh water by driving the potentials more negative. Further research is recommended to study the interaction between zinc in varying concentrations and lithium chloride salts. Zinc then reacts with the chloride ions to form a white zinc (II) chloride. The product formed masked the surface of the remaining zinc particles, hence reducing the effective corrosion surface area.

Applying Zinga without pre-coating with lithium chloride appeared to be effective in providing cathodic protection to steel rebar in artificial sea water but not in fresh water. This may be because pure zinc does not react well with pure water and the difference in the rate of self-corrosion of Zinga in artificial sea water and fresh water.

Cathodic protection has proved to be a rehabilitation method as the steel rods contaminated with sodium chlorides were actually protected and the chloride ions repelled out of the concrete structure to complete the electrical circuit when electrons flow into the concrete through the reinforcing steels.

Zinga appeared to behave like pure zinc, generating potentials of about -1.03volts. It is also very important to clean the coating surface at intervals so as to get rid of the corrosion products that might have masked the surface. This might be too tedious. Therefore further research might be necessary to develop means of monitoring and cleaning the coating surface.

REFERENCES

Australasian Corrosion Association Inc. *Galvanic series*
http://www.corrprev.org.au/Galvanic.htm. (Accessed 30th July, 2005)

Broomfield, John (1996). The building conservation directory: *The repair of reinforced concrete.*
http://www.buildingconservation.com/articles/concrete/concrete.htm.
(Accessed 2nd August, 2005)

Building Success (1998). Concrete basics: *The role of water in the mix*.
Bayer Construction. http://www.beyer.com/news_fall98_concretebasics.htm
(Accessed 25th July, 2005).

Chen, W.F. and Richard Liew, J.Y. (2003). The civil engineering hand book: *Constituents and properties of concrete*, edited by Tam C.T. CRC Press, Boca Raton, FL. http://www.engnetbase.com/books/844/0958%20ch40.pdf
(Accessed 16th July, 2005)

Chen, W.F. and Richard Liew, J.Y. (2003). The civil engineering hand book: *Durability of concrete*, edited by D.W.S.Ho. CRC Press, Boca Raton, FL. http://www.engnetbase.com/books/844/0958%20ch41.pdf
(Accessed 17th July, 2005)

Construction, Civil Engineering: *Corrosion monitoring in reinforced concrete*
http://www.corrosion-club.com/concrete.htm (Accessed 8th August, 2005).

Davison, D. et al. *Innovative approaches to electrochemical remediation of concrete.*
Fosroc International Limited, Coleshill Road, Tamworth.

Federal Highway Administration: *Infrastructures, Materials group, Admixtures*, U.S Department of Transport:
http://www.fhwa.dot.gov/infrastructure/materialsgrp/admixture.html
(Accessed 25th July, 2005).

Federal Highway Administration: *Infrastructures, Materials group, Fly A*sh, U.S Department of Transport
http://www.fhwa.dot.gov/infrastructure/materialsgrp/flyash.htm
(Accessed 27th July, 2005).

Federal Highway Administration. *Infrastructures, Materials group, Portland cement*, U.S Department of Transport.
http://www.fhwa.dot.gov/infrastructure/materialsgrp/cement.html
(Accessed 20th July, 2005).

Francois, S.B. (2000). *Corrosion control of reinforcing steel in concrete.*
MSC Thesis. Cranfield University, Cranfield.

Guides to practice in corrosion protection 9. (1981). *Cathodic protection*. Department of Industry (DTI) UK.

Headed reinforcement corps*: Hibernia - Grand banks, Canada*.
http://www.hrc-usa.com/offshore_oil_platforms.htm (Accessed 17th July, 2005).

How Zinga works. http://www.zinga-uk.com/how.html (Accessed 10th August, 2005).

Hukseflux thermal sensors: *Thermal conductivity science*.
http://www.hukseflux.com/thermal%20conductivity/thermal.htm
 (Accessed 20th July, 2005)

Infrastructure technology: *Minimizing infrastructure deterioration*, CorrTech, Inc.
http://www.corrtech-inc.com/technicalpapers.html (Accessed 6th August, 2005).

Katrina, Jones. (1999). The physics fact book: *Density of concrete*, edited by Glenn Elert. http://hypertextbook.com/facts/1999/KatrinaJones.shtml.
(Accessed 16th June, 2005).

Kelly Baldwin. (1998). Electrically conductive concrete: *Properties and potential*. Construction Canada, 98(2), p.28-29

Marine structures: *Heidrun*.
http://www.aas-jakobsen.no/Marine/marine_e.htm#Referanser
(Accessed 17th July, 2005).

Neville, A.M. (1998). *Properties of concrete*. 4th ed. Addison Wesley Longman, Essex.

Portland cement association: *Cement and concrete basics*.
http://www.cement.org/basics/concretebasics_aggregate.asp
(Accessed 18th July, 2005).

Ramachandran, V.S. and Beaudoin, J.J. (2001). *Handbook of analytical techniques in concrete science and technology*. Noyes Publications; Norwich, N.Y.: Park Ridge, N.J.: William Andrew Publishing, p. 37-55.

Ramchandran, V.S. (1995). Concrete admixtures handbook: *Properties, science, and technology*, 2nd ed. Noyes Publications, Park Ridge, New Jersey, U.S.A.

Rowlands, J.C. et al. (1976). Marine engineering practice: *Corrosion for marine and offshore engineers*, 2(2), p.3.

Steven F. Daily. *Understanding corrosion and cathodic protection of reinforced concrete structures*, Corrpro Companies, Inc.http://www.cathodicprotection.com/concrete/daily.htm
(Accessed 4th August, 2005)

Steven F. Daily. *Using cathodic protection to control corrosion of reinforced concrete structures in marine environments*, Corrpro Companies, Inc. http://www.corrpro.com/Concrete/cp-49.pdf (Accessed 7th August, 2005)

The Electrochemical series.
http://www.chemguide.co.uk/physical/redoxeqia/ecs.html.
(Accessed 29th July, 2005).

Tend 2000 Ltd (2002). Degradation of materials in aggressive environments programme: *Guide to the maintenance, repair and monitoring of reinforced concrete structures*, DTI. UK.
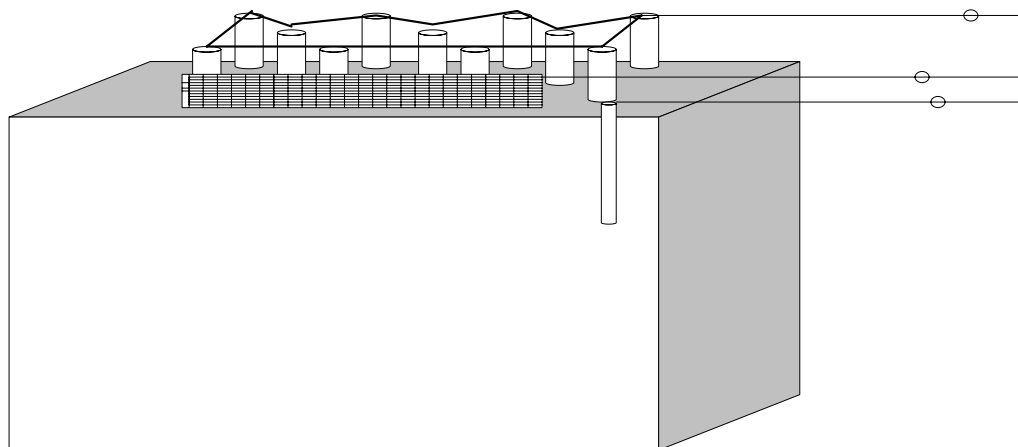
APPENDICES

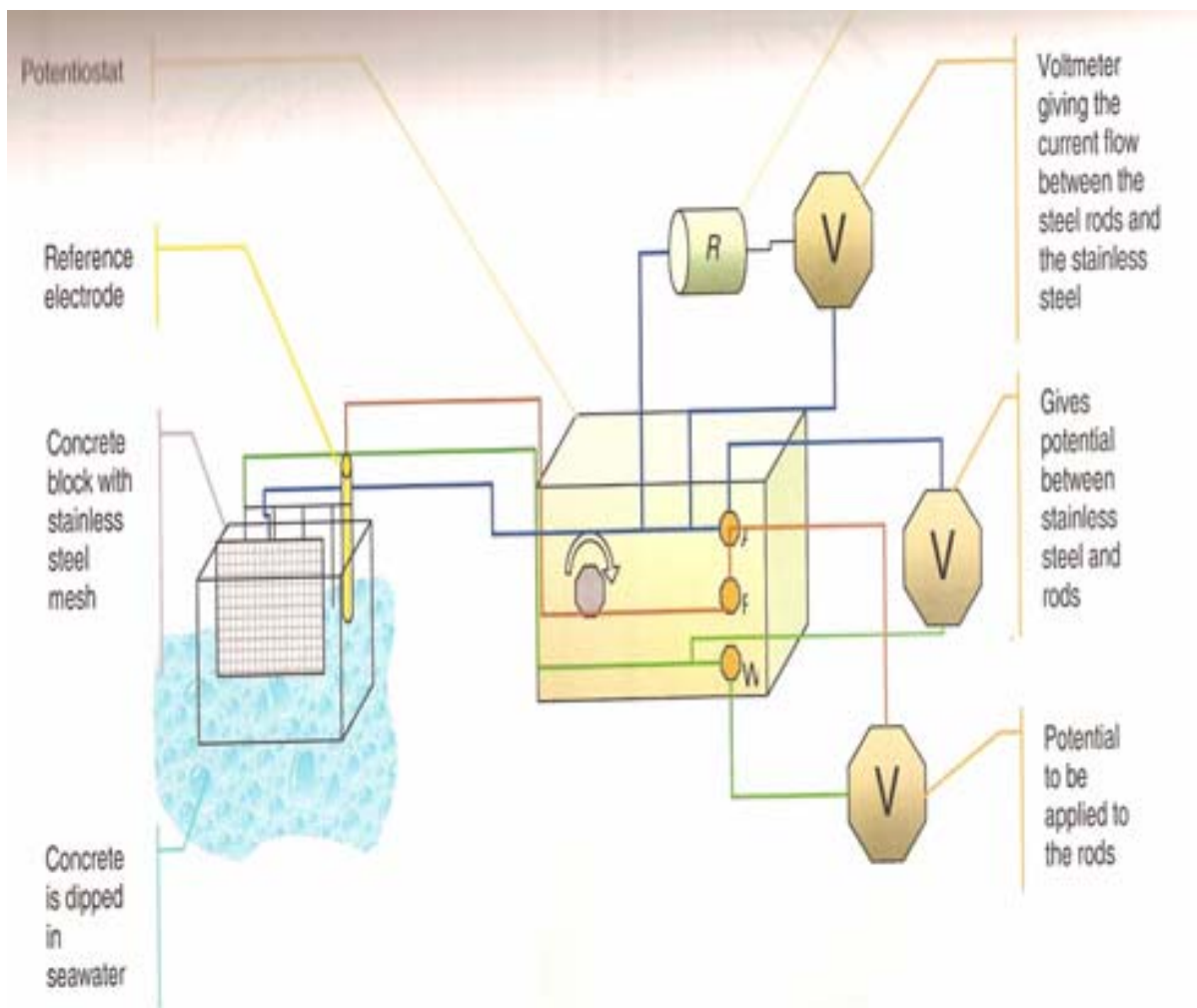**Appendix A**
Impressed current cathodic protection
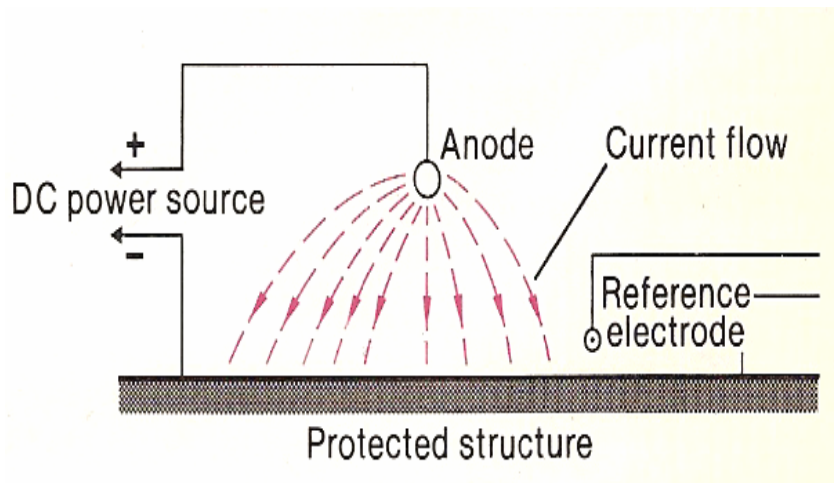
Schematic diagram of the impressed current system of cathodic protection.
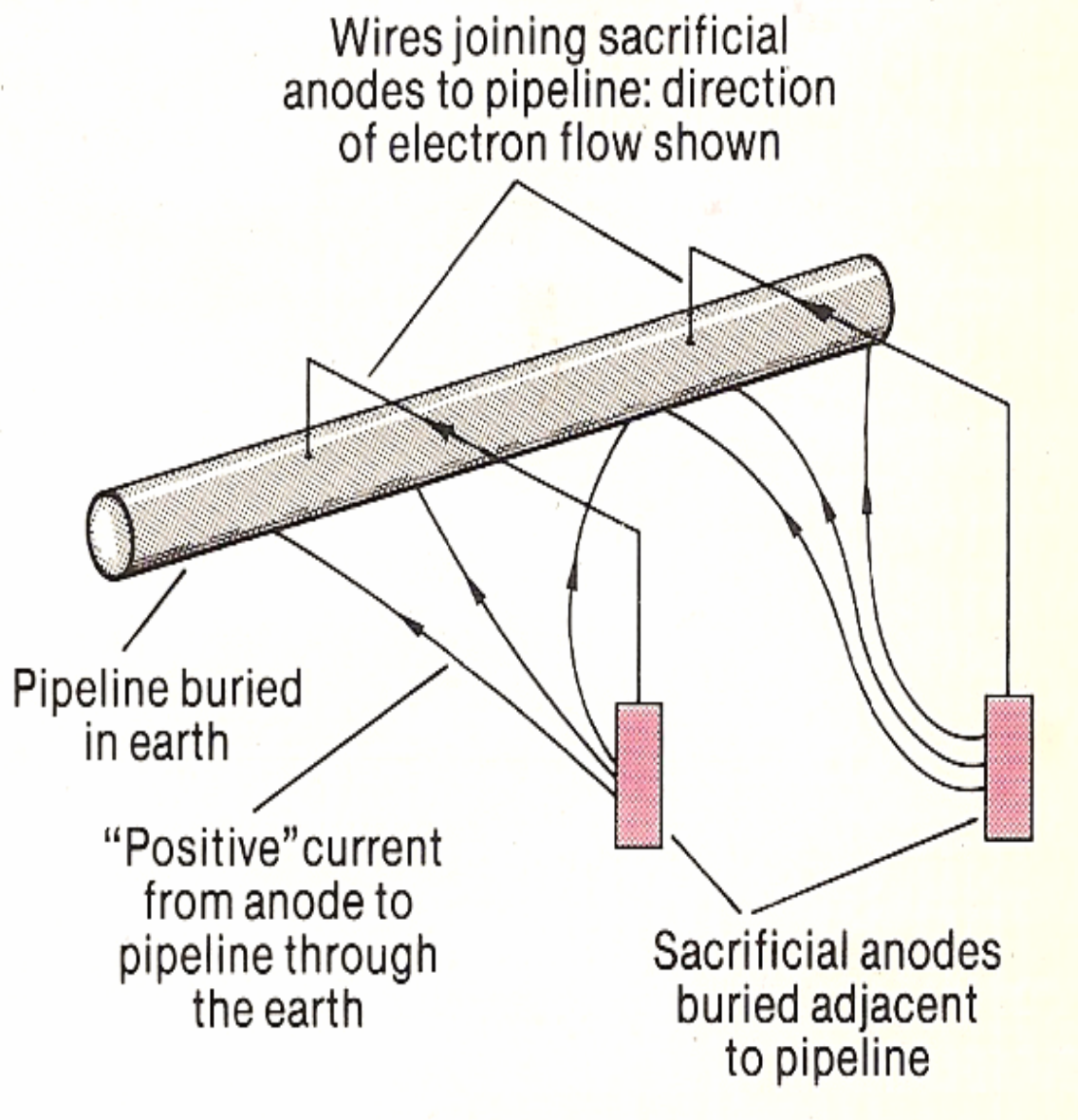

Concrete block diagram for impressed current cathodic protection.

Appendix A
Impressed current cathodic protection

Schematic diagram of potentiostat set up for impressed current measurement

Appendix B
Sacrificial coating cathodic protection

Wires joining sacrificial
anodes to pipeline: direction
of electron flow shown

Pipeline buried
in earth

"Positive" current
from anode to
pipeline through
the earth

Sacrificial anodes
buried adjacent
to pipeline

Schematic diagram of sacrificial anode cathodic protection.

Appendix B
Sacrificial coating cathodic protection

Concrete block for sacrificial coating cathodic protection.

Appendix B
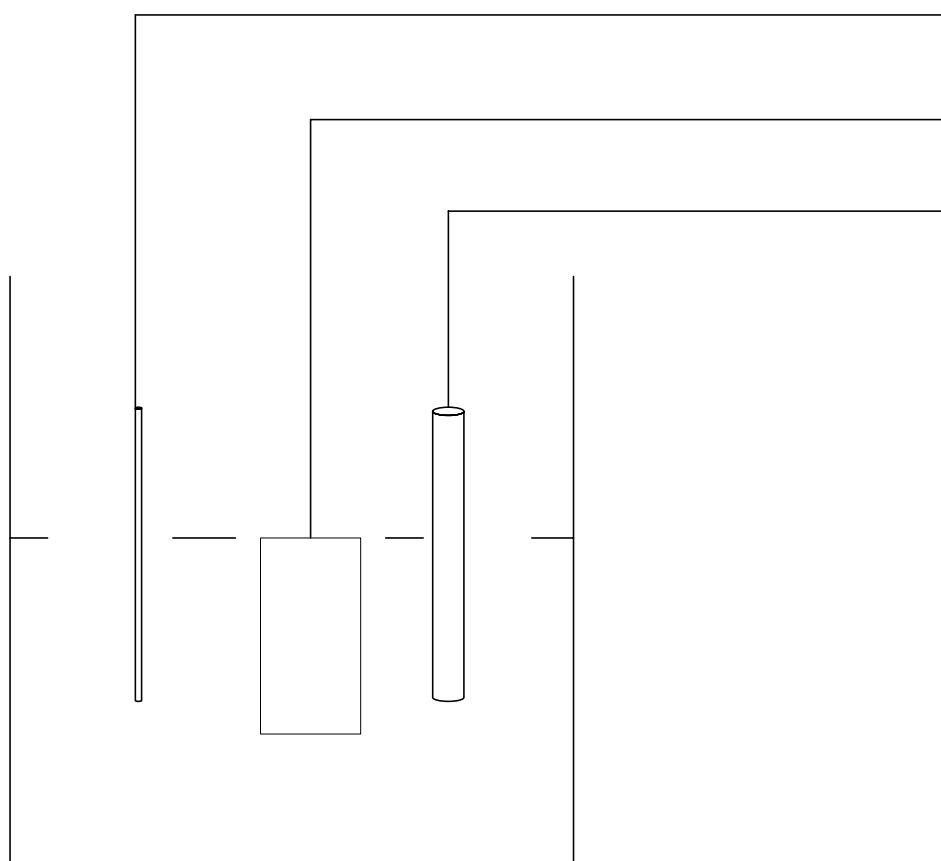Sacrificial coating cathodic protection

Sacrificial Zinga coating as applied to a harbour in Belfast.

Appendix B
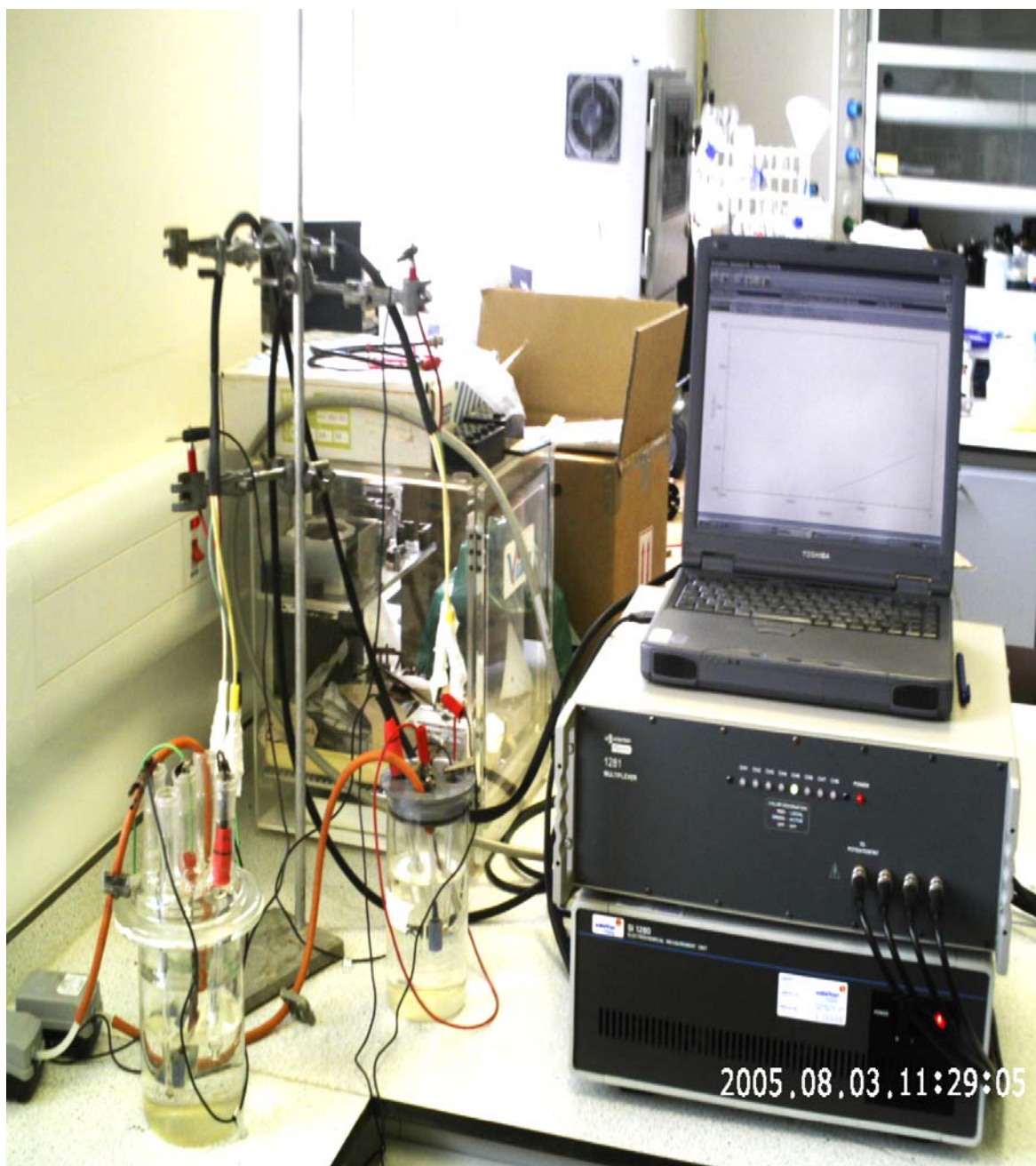Sacrificial coating cathodic protection

Sacrificial Zinga coating applied to a harbour in Belfast.

Appendix C
Self-Corrosion

Schematic diagram of linear polarisation resistance experiment set up.

Appendix C
Self-Corrosion

Linear polarization experiment set up.

Appendix D
Concrete Blocks

Concrete block one (Zinga without LiCl) with corrosion products masking the surface.
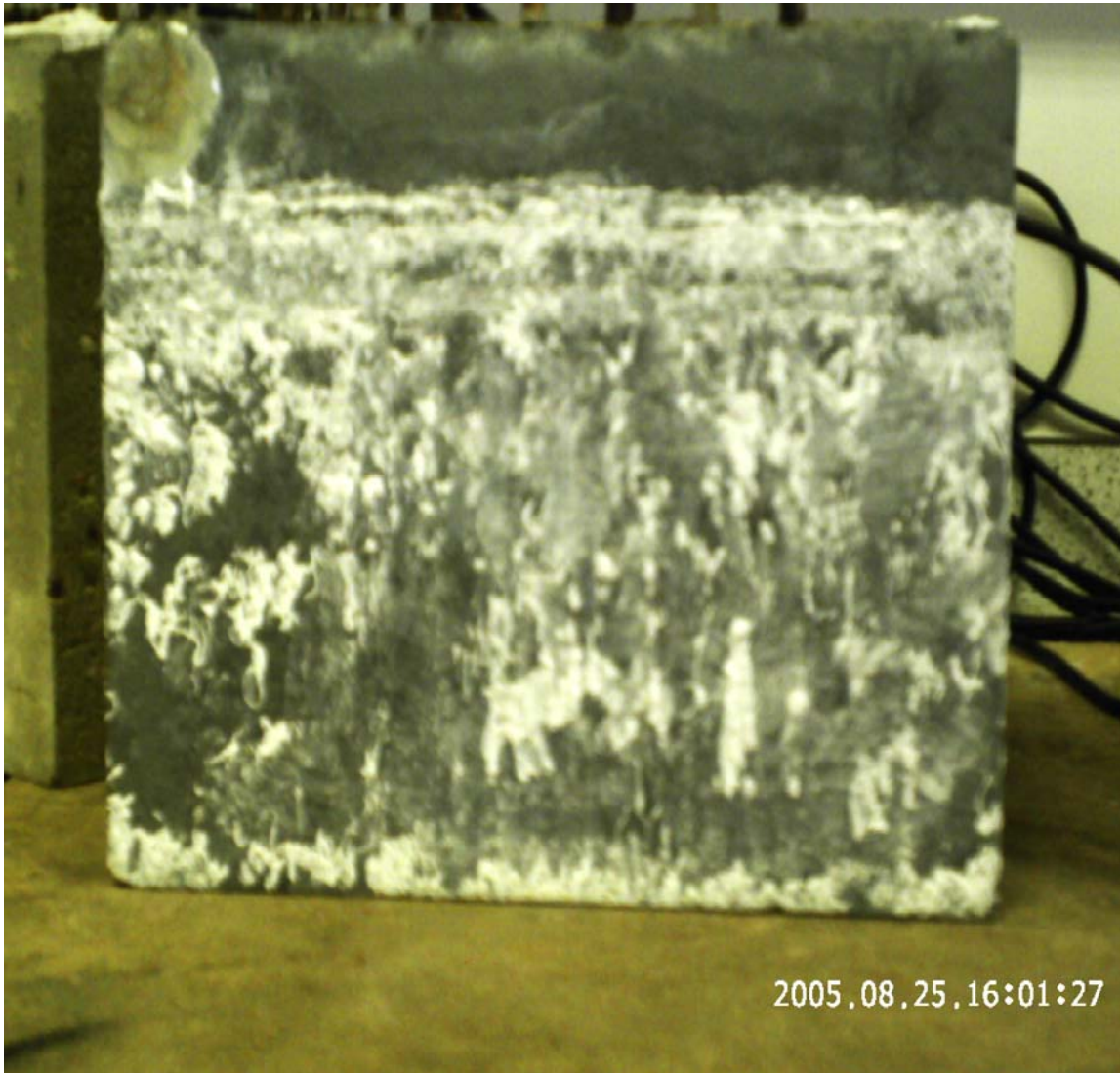
Appendix D
Concrete Blocks

Concrete block two (Aqua-Zinga) after the experiments.

Appendix D
Concrete Blocks

Concrete block three (impressed current) after the experiments.

Appendix D
Concrete Blocks

Concrete block four (Zinga with LiCl) with corrosion products on the surface.