

The corrosion characteristics of galvanized reinforcing bars

Author: Herzog, Henry

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THE UNIVERSITY OF NEW SOUTH WALES SCHOOL OF METALLURGY

THESIS

FOR THE DEGREE OF MASTER OF ENGINEERING

"THE CORROSION CHARACTERISTICS OF GALVANIZED REINFORCING BARS"

HENRY HERZOG, B.E December, 1976

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ABSTRACT

In recent years much work has been done on the corrosion characteristics of galvanized steel reinforcing bars. Hot dip galvanizing is now widely used in construction to provide added protection to steel reinforced concrete structures. The addition of chromates to concrete, reinforced with galvanized steel reinforcing bars has also come into practice in recent years, but literature on this is not well documented. The primary objectives of this work were to assess the comparative corrosion resistance of galvanized bars of different diameters to that of the untreated steel, and to obtain an understanding of the action of chromates on the passivity of zinc in the absence, and presence, of aggressive chloride ions.

The results of the accelerated corrosion tests on the concrete beams revealed that, as the amount of protection of the steel reinforcement was increased, the uniformity of corrosion and thus time for corrosion to occur also increased. The accelerated corrosion tests on the concrete beams showed that the time required for rust stains to appear on the concrete surface increased with an increase in bar diameter.

The experiments where potential was measured with respect to time and the galvanostatic polarization experiments where potential was measured with respect to current showed that the passivity of zinc was increased with increased concentrations of inhibitor anions. When 70 p.p.m. or 300 p.p.m. of sodium chromate were used the passive film consisted of zinc chromate, chromic oxide and some calcium hydroxo-zincate. When 70 p.p.m. or 300 p.p.m. of chromic oxide were used, the passive film consisted mainly of calcium hydroxo-zincate which covered a thin under-layer of zincchromate and chromic oxide. At chloride ion concentrations of 10^{-3} M and 10^{-2} M, the passive film formed when 70 p.p.m. and 300 p.p.m. of chromic oxide were present took longer to form. While at chloride ion concentrations of 10^{-1} M and $10^{-.5}$ M passivity was not established and the zinc became more active. When 70 p.p.m. and 300 p.p.m. of sodium chromate were present passivity was established in all chloride ion concentrations but to a lesser degree with increased chloride ion concentrations.

When 70 p.p.m. and 300 p.p.m. of sodium chromate were present, the concentration of inhibitor anions were greater than the critical concentration for all aggressive anion concentrations. When 70 p.p.m. and 300 p.p.m. of chromic oxide were present, the concentration of inhibitor anions was always less than the critical concentration for all concentrations of aggressive anions.

It was also found from the experiments where potential was measured with respect to time that at a certain pH value, passivity of zinc was destroyed when the concentration of chloride ions present was above a certain concentration.

PART A

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LITERATURE REVIEW

1. INTRODUCTION

A composite material is one which incorporates two or more materials of different properties with an interface between them. The properties of the individual components compliment each other, and the properties of the resultant composite being governed largely by the law of mixtures. Steel reinforced concrete is a composite material, where the high tensile properties of steel have been combined with the high compressive strength properties of concrete.

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The use of composite materials stems back to the days of ancient Egypt. Pyramids and other great temples were constructed from bricks comprised of chopped straw mixed into clay to make them stronger. The Egyptian's aim was to make their structures last for eternity. To this day they stand as remnants of their ancient culture.

More recently, man has used other composite materials such as steel reinforced concrete for building structures, not necessarily to gods, but nevertheless with the intention of having strength and passing the test of time.

The clays have been replaced by concrete and the straw by steel bars. Although the straw and steel play different roles as composite fibres, the principle of bringing together materials with different properties is the same.

Concrete is a material which has good compressive strength. On the other hand, steel has much better properties. In addition, concrete has the ability to produce an environment around the steel to reduce corrosion, so that together they make an excellent composite material. Under certain conditions, such as a marine environment, the concrete is not able to provide adequate protection for the reinforcing steel unless the depth of cover is considerably increased. Other methods and materials have been introduced to the concrete and steel to help resist corrosion and increase the life of the reinforced concrete.

Corrosion of the reinforcing bar causes the build up of corrosion products which produce cracks in the concrete beams (Figure 1.1). For example reinforced concrete beams used in the construction of a building on the lower campus of the University of New South Wales showed the formation of cracks on the surface of the beams. To combat this corrosion of the reinforcement, the concrete was removed from around the reinforcement bar and zinc chromate paint was applied to the bar (Figure 1.2). The concrete was then restored and a tar based paint was applied.

The steel is protected by a passive film which forms on the surface of the metal owing to the high pH value of the concrete (19). Migration of chloride ions and carbonation of the concrete will, however, lower the corrosion resistance and corrosion of the reinforcing bar will take place (37). One method of overcoming the effects of chloride ions and lowering the pH is galvanising of the steel Hot dip galvanized steel can withstand high chloride bar. concentrations and tolerate lower pH values than steel. However, another problem now arises. Hydrogen evolves at the zinc surface, diffuses through the zinc and penetrates the steel causing a reduction in bond strength and hydrogen embrittlement of high tensile steels. The presence of

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FIGURE 1.1

Concrete columns reinforced with untreated steel - situated on the lower campus of the University of N.S.W.



FIGURE 1.2 Concrete columns on the lower campus of the University of N.S.W. where the concrete was removed from the corroding reinforcing bars, and the bars were coated with zincchromate paint. of chromates in the concrete had been observed to eliminate these effects, thus providing added protection.

The main objectives of this work were to provide a comparative indication of the effects of similar amounts of corrosion in different diameter reinforcing bars on the concrete beams, and to observe the effects and roles played by chromate additions to the concrete in relation to the passivity of the zinc. The effect of different chloride ion concentrations on the passivity of zinc was also studied.

2. CORROSION

2.1 THEORY OF CORROSION

Corrosion by definition, is the deterioration occurring when a metal reacts with its environment (1). Uhlig (2) defines corrosion as the destructive attack of a metal by chemical or electrochemical reaction with its environment.

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While corrosion occurs in several widely different modes, classification is usually based on one of three forms:

- 1. nature of the corrodent corrosion can be classified as either 'wet' or 'dry' - a liquid or moisture being necessary for the former while dry corrosion usually involves reaction with high temperature gases,
- 2. mechanism of corrosion involving either electrochemical or direct chemical reactions,
- 3. appearance of the corroded metal corrosion is either when metal corrodes at the same rate over its entire surface, or it is localised in which case only small areas are affected.

The corrosion of reinforcing black steel or galvanized steel in concrete is an electrochemical process and consequently is the main concern of this section.

2.1.1. Electrochemical Corrosion

Most metals exist in nature in such combined forms as oxides, hydroxides, sulphates, carbonates and silicates. The extraction of metal from their ores requires a considerable amount of energy. The isolated metals can therefore be regarded as being in a much higher energy state than in their corresponding ores and they will show a natural tendency to return to their lower energy or combined state. Thus, the corrosion of metals can be regarded as the reverse process of that of reducing metals from their ores.

In all cases of electrochemical corrosion, the anodic reaction consists of oxidation of the solid metal to its ions in solution:

 $M \rightarrow M^{Z^+} + Ze \qquad (2.1).$

There are different cathodic reactions which can occur. For example:

Hydrogen evolution in acid solution

 $2H^{+} + 2e \rightarrow H_{2}$ (2.2).

Oxygen reduction in acid solution

 $0_2 + 4H^+ + 4e \rightarrow 2H_20$ (2.3).

Oxygen reduction in neutral or alkaline solution

 $0_2 + 2H_20 + 4e \rightarrow 40H^-$ (2.4).

Hydrogen evolution and oxygen reduction are the most common cathodic reactions. Different cathodic reactions can occur simultaneously on a corroding metal surface (2).

2.1.2 Free Energy Consideration of Corrosion

When a metal oxidizes there is a change in the free energy, G of the system which is equal to the work done or absorbed during the process (2).

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There must be a decrease in free energy of the system for the reaction to take place; thus, ΔG must be negative for a reaction to work. For an electrochemical reaction:

 $\Delta G = -nFE \tag{2.5}$

where n is the number of electrons in the reaction, F is the Faraday constant and E is the standard cell potential(1):

The change in free energy ΔG can also be expressed as:

 $\Delta G = G (\text{products}) - G (\text{reactants})$ (2.6)

The standard free energy charge for the formation of nearly all metal oxides is negative, i.e., oxides are thermodynamically stable in oxygen atmospheres whereas metals are not. Oxidation of metals will therefore always tend to occur (2).

If a solid piece of metal is placed in a solution containing its ions, a potential difference $E[Fe^{2+}/Fe]$ exists between the metal atoms in the solid and the metal ions in solution. This potential can be measured against an inert standard hydrogen electrode. This potential is called a "half-cell potential" because it is the potential for an electrode that forms half (the anode) of a corrosion cell. Similarly the same half-cell potential exists for the cathode reaction.

The electrode potentials of many metals have been measured directly or calculated from thermodynamic data and compiled to give standard potentials. In addition, they have been combined with solubility data of oxides and hydro-

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xides and with equilibrium constants for reactions of these to produce Pourbaix diagrams (5), which indicate thermodynamically stable phases as a function of electrode potentials and pH.

2.2 METAL DISSOLUTION

Consider the surface of a metal M contained in a vacuum. Each of the atoms in the metal surface, is in fact, an ion occupying its own energy well and stabilized in its position by the electrons in the metal. These electrons help bond the positive ions together and give the metal its special properties. If sufficient energy is available, (~6eV) it will be possible to pull an ion out of its energy well in the surface, so forming a highly unstable gaseous metal ion M²⁺ which will exert a restoring force on the ion.

However, if the metal is immersed in a polar such as water instead of a vacuum, there exists an solvent alternative deep energy well having the same sort of chemical free energy as that corresponding to a metal ion bound to the metal surface. This second energy well corresponds to the state wherein the metal ion is surrounded by four to six water molecules called "the primary solvation sheath". The primary solvation sheath may consist of other entities besides water molecules. It may for example, contain complexing ions or molecules such as hydroxyl or ammonia. The general term for such entities is ligands. The ligand water molecules for example, are held fairly rigidly in a particular orientation around the central metal ion (Figure 2.1). In this way they tend to shield the neighbouring water

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molecules or ions from the intense electric field of the metal ion, and provide the metal ion itself with an electronic environment as similar as possible to that existing in the metal surface. Now, because water molecules are relatively small and mobile and can approach very close to the metal surface, the two energy wells are very close together in space so that there is no need for an ion to acquire an energy of ~6eV before it can go into aqueous solution. It needs only a thermal energy of about 0.5eV after which it decreases its energy state until a lower stable state is achieved by the presence of water molecules. The activation energy for dissolution is shown here as $\overline{\Delta G}^*$. In order to return to the metallic state it needs in the instance given, a greater activation energy ΔG^* and the solvated state is favoured relative to the metallic state by a chemical free energy charge ΔGm (which here, is negative) (Figure 2.2)(6),

2.3 POLARIZATION AND CORROSION RATES

When electrochemical corrosion occurs, the current that flows between anode and cathode causes a change in the electrode potentials. This change is termed polarization. An electrode is no longer at equilibrium. The anode always becomes cathodic in potential. The cathode becomes more anodic and the difference in potential becomes small. Polarization affects the rate of corrosion and when equilibrium is reached, the corrosion potential and the corrosion current density can be measured (12).

Measuring the corrosion current directly is not usually feasible because it is the current that flows between many small anode and cathode areas of the metal surface.

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FIGURE 2.1 The chemical free energy of a family of metal ions pulled out of the metal surface and subsequently saturated. After West (6).



FIGURE 2.2 The chemical free energy profile of a family of metal ions passing directly into aqueous solution. After West (6).

The current is thus measured indirectly. It is done by accentuating the anodic or cathodic process on a metal specimen with the aid of an inert electrode and an external circuit. The specimen can be made to be the anode, while the inert electrode plays the part of the cathode. This would be anodic polarization. Its counterpart would be cathodic polarization.

The causes of electrode polarization fall into three different catagories: concentration polarization, activation polarization and IR drop (1).

- Concentration polarization is the slowing down of the reaction due to an insufficiency of desired ions or an excess of unwanted ions at the electrode surface. It is dependent on diffusion (3).
- Activation polarization is the polarization 2. caused by a slow electrode reaction stated in another way: the reaction at the electrode requires an activation energy in order to go. Consider the formation of hydrogen gas due to the cathodic reaction at a platinum electrode. $H^{\dagger} \rightarrow H(ads) - e^{-1}$ (2.7) where H (ads) represents hydrogen atoms adsorbed on the metal surface. This relatively rapid reaction is followed by a combination of adsorbed hydrogen atoms which form hydrogen molecules and bubbles of gaseous hydrogen. (2.8) 2H (ads) \rightarrow H₂ This is relatively slow, and the rate of which determines the value of hydrogen overpotential (2).

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(The oven potential of hydrogen is the difference between the potential at the electrode at which evolution of hydrogen gas is actually observed and the theoretical value of the potential at which hydrogen gas is in equilibrium with the hydrogen ions (4)). Activation polarization is also characteristic of metal ion deposition or dissolution (2).

3. IR drop is also included in polarization measurements. This ohmic potential drop is through either a portion of the electrolyte surrounding the electrode or through a metalreaction product film on the surface, or both. This contribution to polarization is equal to IR, where I is the current density and R, equal to $1/\kappa$, represents the value in ohms at the resistance path of length 1 cm. anode area of 1 cm.³ and specific conductivity κ .

3. PASSIVITY

3.1 INTRODUCTION TO PASSIVITY

A metal is said to be passive in a certain environment if it shows a very low corrosion rate when thermodynamically it would be expected to corrode rapidly (1), or as Uhlig (2) states - "passive metal is one that is active in the E.M.F. series but which corrodes nevertheless at a very low rate". Passivity is the property underlying the useful, natural corrosion resistance of many structural metals including aluminium chromium and the stainless steels. Some metals and alloys can be made passive by exposure to passivating environments - e.g. iron in chromate or nitric solutions, or by anodic polarization at sufficiently high current densities.

Schonbein (7) in 1836, defined iron in the corrosion resistant state as passive. Faraday (8) at the same time, was also experimenting on passivity and after research defined a passive metal as one that is appreciably polarized by a small anodic current.

3.2 DEFINITION OF PASSIVITY

There exists two definitions of passivity (9): 1. A metal active in the E.M.F. series or an alloy composed of such metals is considered passive when its electrochemical behaviour becomes that of an appreciably less active or noble metal.

2. A metal or alloy is passive if it substantially resists corrosion in an environment where thermodynamically there is a large free energy

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decrease associated with its passage from the metallic state to appropriate corrosion products.

Wagner (10) offered an improvement of 'definition 1'. A metal is passive if on increasing the electrode potential towards more noble values, the rate of anodic disdolution in a given environment under steady-state conditions, becomes less than the rate at some less noble potential.

Some metals which are considered passive by 'definition 2' are not passive by 'definition 1', e.g. iron in inhibited pickling acid is called passive by 'definition 2' based on low corrosion rates despite pronounced corrosion tendencies, but is not passive by 'definition 1' (2).

In the literature, there is not much discussion of the two definitions of passivity. One definition is a kinetic consideration of passivity, while the other one is a thermodynamic consideration. Thus in different cases, such as the one above, one definition will apply while the other will not.

3.3 THEORIES ON PASSIVITY

There are two common points of view on the nature of the passive film. The first one maintains that the passive film is a diffusion barrier made from a layer of reaction products. This could be the metal oxide or some other compound which separates the metal surface from the environment thus slowing down the rate of reaction. This film, which is considered to be insoluble non-porous, is of such a self-healing nature that when broken, it will repair itself on re-exposure to oxidizing conditions (2, 11).

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The second theory states that metals are passivated by a chemisorbed film of say, oxygen molecules or passivating ions. Such a layer displaces adsorbed water molecules and slows down the rate of anodic dissolution. Even less than a monolayer of oxygen molecules on the surface may have some passivating effect hence it is suggested that the film cannot act primarily as a diffusion barrier layer (2).

These two theories do not contradict but complement each other. Although Uhlig (2) strongly believes in the chemisorbed theory, he still states that an oxide film cannot be ignored as a diffusion barrier for anodic dissolution.

During a dissolution process where oxidation takes place, a metal goes from M to M^{Z^+} + Z electrons. Pourbaix diagrams show that oxidation of a metal can take other forms as well. If a metal can be oxidized to an oxide that is stable in the elctrolyte, then the metal is rendered passive. Strong oxidation conditions are required for this, while reducing condition would make the metal chemically active (36).

Considering West's (6) view point that a metal becomes passive if some sort of barrier exists between the metal surface and the polar solvent, it would be much more difficult for metal ions to leave the metal surface. A chemisorbed film of oxygen would satisfy this requirement. A diffusion barrier such as an oxide film would isolate the solvent from the metal surface, but the essence of a diffusion barrier is that the rate of anodic dissolution is slowed down, thus slowing down the corrosion rate.

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Uhlig (12) in 1967 proposed a sequence of events which occur when oxygen reacts with a clean metal surface. Firstly adsorption of an oxygen layer occurs, secondly oxide nuclei form and then a continuous oxide film grows. In the first stage physical adsorption of molecular oxygen is followed by chemisorption of atomic oxygen. The adsorbed film functions not as a diffusion barrier, but instead increases the activation energy for hydration and dissolution of the metal lattice by displacing adsorbed H_20 and anions.

Physical adsorption of molecular oxygen is rapid and the binding forces of 0_2 to the metal surface are very strong. Because of the high affinity of oxygen for most metals, physical adsorbed molecular oxygen interacts further to form a stronger chemical bond corresponding to chemisorption.

Oxide forming on a metal surface tends to nucleate at sites which favour maximum or multi-layers of 0_2 . These sites are located at edges of slopes or facets of the metal surface and at lattice imperfections. The number of favourable sites increases as oxygen gas pressure increases.

The initial oxidation behaviour of metals corresponding to growth of continuous films up to $10^2 - 10^{40}$, is usually observed to follow the logarithmic equation $y = k_0 \ln (t/\tau+1)$ where y is the thickness of the film in time t and τ and ko are constants. Other equations may sometimes hold for example, the cubic $x^3 = k_1 t$ or inverse logarithmic $1/y = k_1 - k_2 \ln t$. This suggests some modification of mechanism, or perhaps that the available data extends to only short intervals of time and actually fits more than one

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possible equation (13). The logarithmic equation however, is obeyed by most thin film data (12).

Gouda (14) stated that the amount of electricity required to passivate steel, used for reinforcing concrete, is constant at all current densities used, and depends on the degree of coverage by the air-formed film. The mechanism of passivation is thus always coulombic in nature. This suggests that passivity will be reached when a certain thickness of oxide film is attained. This is contradictory to Uhlig's (12) conclusion that oxygen is required to form the oxide film, and some oxygen would be chemisorbed onto the surface thus according to Uhlig (2), passivate the steel.

More recent work by Uhlig (15) on passivity of aluminium shows that the pitting potential is the same for samples with and without an oxide film. Potentiostatic polarization curves showed that specimens with a clean surface had the same pitting potential as specimens with an oxide film on the surface. This indicates that the presence of an oxide film does not influence passivity breakdown nor the onset of anodic dissolution or hydration once the passivity has been established. Thus for aluminium, the activation energy required for ions to leave the metal surface is the same if the metal surface and the polar solvent are separated by a chemisorbed oxygen layer or an oxide layer.

Much has been written on passivity and the means by which a metal becomes passive. On the subject of passivity of steel in concrete, Artamonou (17) in 1960 concluded that passivity is attained by an adsorbed film formed at the metal concrete interface built up by Portland cement.

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However, concrete would provide the chemicals and the chemical reactions for passivating the steel with an oxide layer and not an adsorbed film. This is not to say that a chemisorbed film does not form, as it could quite possibly do. Scott (18) and Hausman (19, 20) attributed the corrosion control to anodic and cathodic polarization as well as to calcium hydroxide in the cement, which maintains a protective iron oxide film on cement coated steels. Other such work is discussed in a later chapter.

To conclude, it would be reasonable to say that passivity can be created by either an oxide film, a chemisorbed film or both. Each type of film reduces the rate of corrosion in an oxidization environment, whether it be by creating a diffusion barrier, as an oxide film would do, or by displacing water molecules or anions and increasing the activation energy for dissolution or hydration, as a chemisorbed film would do.

3.4 MEASUREMENT OF PASSIVITY

To make polarization measurements for a metal that exhibits passivity, it is necessary to control the potential rather than the current (3). To ensure that the potential across the cell is kept constant, a resistance much lower than that of the cell is connected across the electrodes in parallel. Under such conditions, changes in the cell resistance will not affect the potential across the compound resistance. This arrangement is the basis of the classical potentiostat (21). Hickling (22) introduced the technique of automatic control of the potential of a working electrode and described an electronic device (the

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'potentiostat') for this purpose. Potential static polarization is used to investigate the electrical conductivity of a passive layer.

This method for investigating passivity has been used for a considerable time. Between 1908 and 1949 the source of D.C potential was a battery. Simple ammeters and voltmeters were used as the measuring devices. Artamonou (17) used similar equipment with a standard calomel electrode (S.C.E.), as did Hausman (20). Koizumi and Uhlig (21) used the potentiostat in 1974 in evaluating the passivity of the Ni-Cu alloy series in NaCl solutions. Alvarez et al (16) stated that any method used for measuring pitting potentials should assure that the oxide film is disrupted, otherwise high and irrelevant results will be measured.

3.5 BREAKDOWN OF PASSIVITY

The breakdown of passivity occurs at the pitting potential (pitting will only occur in environments favouring stable passivity (24)). The commonly encounted halide ions promote pitting. Passivity cannot be easily established nor maintained in the presence of agressive chloride ions. As the concentration of these ions is increased a number of changes take place: the critical current density is increased, the primary passive potential is raised, the current density under the condition of passivity is enlarged and the passive potential range is lowered.

Consider pitting of a steel surface which has been passivated by an oxide film. The passive film becomes discontinuous at separate points. Small corrosion marks are

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formed which remain active and extend inward. A quasistable condition arises which is reflected by the fact that the regions around the pit 'holes' remain protected against corrosion and only at the base of the hole does extremely rapid dissolution of iron take place (25).

Many explanations are offered on how chloride ions break down the passivity of a metal passivated by an oxide film: chloride ions can penetrate the oxide film through pores, or grain boundaries, or defects easier than do other ions, or chloride ions may colloidally disperse the oxide film and increase in permeability (2). Cornet, Ishikowa and Bresler (26) proposed that the chloride ions in an oxide film produce lattice vacancies which facilitate transport of metal ions. The chloride ions present are not consumed but act in a manner of a catalyst (25). Scully (3) writes that chloride ions can migrate easily because of the high charge density; then become incorporated in the oxide film and reduce the resistivity of the oxide. This would be true if the oxide film was a semi-conductor and the chloride ions functioned as impurities or produced imperfections. Uhlig (12) states that the excess charge can be accommodated at imperfections or impurity sites of a semi-conducting oxide lattice, thus increasing the conductivity of the oxide film. This is in agreement with Rauen (25), in that the chloride ions act as a catalyst.

Another explanation could be that chloride ions can form complex molecules with oxygen or metal ions; these will crack the oxide film either by adsorption on the surface of the oxide, or by being incorporated inside the oxide (peptization). Yet another explanation could be that the

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chloride ions will cause local dissolution of the passive film (27).

Now consider the breakdown of a chemisorbed passive film. Chloride ions may be adsorbed onto the metal surface in competition with dissolved oxygen molecules or hydroxide ions. Once in contact with the metal surfaces, chloride ions favour the hydration of the metal ions and increase the ease with which metal ions enter into solution. This is opposite to the effect of adsorbed oxygen which decreases the rate of metal dissolution. In other words, adsorbed chloride ions increase the exchange current (decrease overpotential) for anodic dissolution of metals, such as iron over the value prevailing when oxygen covers the surface.

Gouda and Sayed (28) researched the relationship between concentrations of inhibitor ions and aggressive ions and concluded that there is a competition for the adsorption onto the metal surface between the inhibitor and aggressive ions. When the concentration of aggressive ions reaches a critical value they are then adsorbed onto the surface of the metal and cause pitting corrosion. This could indicate that oxygen is adsorbed on the metal surface and at the critical concentration of aggressive ions the competition would be so great that the aggressive ions would displace the oxygen layer. Matsuda and Uhlig (29) postulated that the competition is between the aggressive ions that destroy the air-formed film, and inhibitor ions that repair it by being themselves, reduced on the cathodic areas. All these views are in agreement with each other and Gouda et al(28) also indicates that the passive film could be oxygen chemisorbed onto the surface of the metal.

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A linear log/log relationship exists between the concentrations of aggressive and inhibitor ions (28, 29, 30, 31, 32, 33). Gouda et al (28) researched this and concluded the above relationship. However, Brasher, Reichenberg and Mercer (34) suggested that this linear log/log relationship is related to ion exchange equilibrium in the oxide film surface and the slope is determined by the ratio of the valencies of the two opposing ions. This shows that the linear log/log relationship can also be used to explain the breakdown of passivity by chloride ions of an oxide film.

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4. THE CORROSION OF REINFORCEMENT

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4.1 INTRODUCTION

Reinforced concrete based on Portland cement, will resist corrosion of the steel reinforcement under normal service conditions provided that the concrete is of low permeability and the steel to concrete interface is free of voids and discontinuities so that corrosive agents such as salt, air and water cannot permeate the concrete causing severe deterioration (35, 36). Where the structure is exposed to an aggressive environment or where design and workmanship are poor, the concrete may no longer provide adequate protection and corrosion of the steel reinforcement may ultimately lead to failure (35). As the external environment becomes more aggressive the possibility of reinforcement corroding increases (37). Some particularly aggesssive environment vicinities are where the atmosphere and water are polluted, especially where the pollutants are sulphur dioxide or hydrogen sulphide, and marine environments where tidal zones provide conditions of alternate wetting and drying (38, 39). The factors which determine the rate of corrosion are either internal or external. The internal factors are connected with the metal itself, while the external factors include the concrete cover and the environment surrounding it (40).

Normally, wet Portland cement has a pH of about 12.4. This high alkaline nature of the pore electrolyte is due to the calcium hydroxide present, and when in contact with iron or steel provides corrosion resistance by passivating the steel (41, 42). Thermodynamic considerations and electrochemical measurements show that steels are passivated in solutions having high basicity and this is confirmed in practice. Examinations of old buildings show that in highly alkaline concrete the steel does not corrode over a practically unlimited period. This protection is achieved by a sub-microsopicity thin continuous oxide film (25).

As previously stated, Artamonou (17) stated that passivity is attained by an adsorbed film formed at the metal-concrete interface built up by the Portland cement. Scott (18) and Hausman (19, 20) attributed the corrosion control to anodic and cathodic polarization, and to the calcium hydroxide in the cement which provides hydroxyl ions which maintain a protective iron oxide film on cement coated steels. The general opinion is that passivity is attained by an oxide film on the steel surface. Although a chemisorbed oxygen layer is not mentioned in the literature, it is possible that a chemisorbed layer does initiate passivity by itself being a passive layer, and also by assisting in the nucleation of a passive oxide film as stated by Uhlig (12).

4.2 CAUSES OF CORROSION OF REINFORCEMENT

Under the action of sufficient chloride ions (43, 44, 26) and also, according to recent investigations, by the action of sulphides (44, 45) in highly alkaline concrete; concrete can lose its corrosion protection properties. That is, passivity may breakdown or may not even be established (46). This is because the critical pitting potential becomes more active with increasing chloride ion concentrations (24)

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It is for this reason that admixtures containing chloride ions such as calcium chloride (46) or marine environments, are able to induce corrosion of the reinforcement (47). Rosa, McCallum and Peters (48) stated that the chloride ions have a two fold destructive effect on concrete. The chloride ions significantly increase the initial concrete conductivity (initial because in the early stages of concrete hydration, the resistivity of concrete is low) and secondly, they reduce the passivating influence of the concretes on the steel.

Carbonation of the concrete can have similar effects on the steel. Carbonation involves the reaction where calcium hydroxide reacts to form calcium carbonate, thus reducing the pH and setting up passive-active cells (49).

Other causes of steel corrosion in concrete are possible.

A difference in oxygen concentrations along a reinforced concrete structure may result in formation of a corrosion cell with up to ½ volt difference in potential (50). This is enough to cause damaging corrosion if the total resistance of the system is not sufficiently high.

A difference in potential of steel in concrete can be created by a galvanic couple such as copper connected to active steel. The difference in potential which arises at a junction of this type can cause corrosion and if the resistivity of the concrete is low, the rate will be quite high.

Another cause of steel corrosion in concrete is due to the presence of stray currents created by electrical

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grounding, or by cathodic protection in the vicinity under conditions where the steel is not properly bonded to other structures being protected (26).

It has been shown by Tremper (51), Lewis et al (52) and Stratfull (53, 54) that the corrosion of reinforcing steel in concrete structures is essentially galvanic where micro and macro galvanic corrosion cells exist. Micro cells are caused by the heterogoneity of metal surfaces such as crystal lattice imperfections (55, 56) mechanical stresses (57, 58) and distribution of contaminations (59).

Heterogenity of the environment over the surface of the metal whether due to the liquid phase or the physical conditions, causes the formation of macro corrosion cells. Examples of these are: differential salt concentrations of solution (60), differential hydrogen ion concentrations (61), differences in concentration of oxidizing agents (62), and differences in pH values (52, 63) in absence or presence of aggressive ions.

It has also been proposed that heterogeneity on the metal surface can be caused by breaks in the mill scale or variations in the degree of cold work along the bar. While as far as the concrete is concerned voids on the steel surface, cracks in the concrete or variable concrete density are responsible for heterogeneity (64) (Figure 4.1).

4.3 THE MECHANISM OF CORROSION OF REINFORCEMENT

Either micro or macro heterogeneities on the metal surface or in the concrete give rise to potential differences between different areas. This will set up small anodic and cathodic regions connected by a conductor (the reinforcement

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(a) Inclusion on surface (b) Scratch on surface

(c) Break in mill scale

(d) Grain boundaries.



FIGURE 4.1

Potential differences that may be formed by variations in cement or steel quality. After Bresler (65). bar) and an electrolyte (the concrete). All these will satisfy the requirements necessary for an electrochemical reaction; thus corrosion of steel will occur. (Figure 4.2) (37).

The following reactions take place at anodic areas:-

 $20H^{-} \rightarrow {}^{1}_{2}0_{2} + H_{2}0 + 2e^{-}$ (4.1)

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 (4.2)

The dissolution of iron (equation 4.2) would occur when the alkalinity at the anode was exhausted and the potential would be that of the Fe²⁺ half cell (18, 19, 20). The decrease in pH due to reaction 4.1, lowers the corrosion resistance of the steel. On the other hand, 4.1 might be necessary for the formation of the iron oxide film. This also indicates that a chemisorbed oxygen layer alone, does not create passivity since iron dissolution occurs quite rapidly as soon as reaction 4.1 reaches equilibrium. The iron dissolution reaction is normally quite rapid, and it is the rate of the cathodic reaction which normally is the slower and controls the overall reaction (2).

In deaerated solutions, the cathodic reaction is:

 $H^+ + e^- \rightarrow \frac{1}{2} H_2$ (2.2) which proceeds rapidly in acids but only slowly in neutral or alkaline aqueous media. The cathodic reaction is accelerated by the presence of dissolved oxygen in accord with the following reaction (2):

 $2H^{+} + \frac{1}{2}0_{2} + 2e^{-} \rightarrow H_{2}0$ _____ 2.3).

The dissolved oxygen reacts with hydrogen atoms



FIGURE 4.2

Electrochemical corrosion cell in reinforced concrete. After Bresler (65). adsorbed at random on the iron surface, independent of the presence or absence of impurities in the metal. The oxidation reaction proceeds as rapidly as oxygen reaches the metal surface. The overall equation for the oxidation reaction is:

Fe +
$$H_2^0$$
 + $I_2^0_2$ + Fe(OH)₂ (4.3).

Hydrous ferrous oxide (FeOn H_2^{0}) or ferrous hydroxide (Fe(OH)₂) form the diffusion barrier layer next to the iron surface through which oxygen must diffuse. The pH of saturated ferrous hydroxide is approximately 9.5 so that the surface of the iron corroding in an aqueous solution of pH, between 4 and 9.5, is always alkaline. The colour of ferrous hydroxide, although white when pure, is normally green to greenish black because of incipient oxidation by As diffusion of oxygen through the hydrous ferrous oxide air. determines the corrosion rate of values above pH4, metallurgical factors such as the degree of cold work do not affect the corrosion rate above that pH reading. At the outer surface of the oxide film, excess of dissolved oxygen converts ferrous oxide to hydrous ferric oxide or ferric hydroxide in accordance with:

 $Fe(OH)_2 + \frac{1}{2}H_2^0 + \frac{1}{4}O_2 \rightarrow Fe(OH)_3$ (4.4).

Hydrous ferric oxide is orange to red brown in colour and is mostly comprised of ordinary rust. The pH of saturated $Fe(OH)_3$ is nearly neutral. A magnetic hydrous ferrous ferrite Fe_30_4 nH₂0, often forms a black intermetallic layer between hydrous Fe_20_3 and Fe0. Hence, rust films normally consist of three layers of iron oxide in different states of oxidation (2).

If the surface of the steel should have scratch lines, surface cavities, inclusions or sheared edges (12), breakages in the oxide film may occur and the film will thus try to repair itself. Film repair is usually preceded by a preliminary removal of oxide from the various weak spots in the film structure, leading to the formation of open pores which offer sufficiently high corrosion susceptibility. The iron at the base of the pores passivates with what later grows into a plug of oxide Fe_20_3 (6).

Gouda (14) gives the following different oxide formations. In aerated solution, ferro ferric oxide (Fe_30_4) is the intermediate oxidation product on the steel surface, while ferrous hydroxide is the intermediate product in deaerated solution. This can only be reconciled with Uhlig (12) if an aerated solution is considered.

The occurrence of passivation or corrosion of iron immersed in aqueous media, depends on which of the following anodic reactions predominates (103):

 $Fe \rightarrow Fe^{2+} + 2e^{-}$ (4.2) A

or $2Fe + 60H^{-} \rightarrow Fe_2 0_3 + 3H_2 0 + 6e^{-}$ (4.2) B

Reaction (4.2) A occurs at a lower potential than reaction (4.2) B and is the prevailing reaction on iron that is free from oxide film. When steel covered with the air-formed film is immersed in aqueous solution, the film tends to breakdown at certain points (weak spots) and corrosion commences from these points. It is probable that in sufficiently alkaline

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solutions i.e. at pH > 11.5, reaction(4.2)B may predominate. Repair of the weak points in the film will take place and passivity will be established. On the other hand, in solutions of pH < 11.5, reaction(4.2)A may be enhanced, probably owing to a local drop in pH. This leads to the formation of ferrous hydroxide (14).

This discussion is quite valid for reinforcing steel in concrete. As stated by Gouda (14) the anodic processes which take place on reinforcing steel embedded in concrete, are very similar to those that occur in saturated calcium hydroxide solutions. The drop in pH could be associated with reaction (4.1). This is in agreement with Scott (18) and Hausman (19, 20) who state that anodic dissolution of iron would occur when the pH drops.

As already mentioned, under normal conditions concrete has a pH of around 12.5 due to the presence of calcium hydroxide (65). The alkalinity of the environment raises the pH on the steel surface, and the corrosion rate correspondingly decreases as the steel becomes increasingly passive. When the passivity breaks down, severe pitting occurs (2).

The brown iron oxide formed by the corrosion of the steel reinforcement is soft, laminated and unable to resist any significant tension stress. Deep pitting of the reinforcement which accompanies the loss of passivation, contributes to the loss of cross-sectional area of the reinforcing bar (37, 66). The bond between the concrete and steel is also reduced, resulting in a reduction of the composite action of the steel and concrete (48, 67).

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The thick crusts of rust which appear as a result of corrosion, have a much greater volume than the iron from which they were formed. This rust forces the concrete cover apart (25). The force, or mechanical pressure resulting from the build-up may be up to 32.4 MPa. Since the Bedworth-Pilling (68) ratio for steel is 2.06, the iron oxide occupies that much more volume than does the original iron volume (36,68) and is greater than the tensile strength of the concrete (69) (Figure 4.3).

The longitudinal cracks formed by the pressure build-up of corrosive products will widen as corrosion proceeds, and may eventually cause spalling of the concrete. This will naturally increase the rate at which the corrosive environment can reach the reinforcement, and in addition different oxygen concentrations will set up anodic and cathodic areas on the reinforcing bar considerably increasing the rate of corrosion.

4.4 CONCRETE AND ITS PROPERTIES

The chemical and physical properties of concrete are important with regard to the corrosion protection of reinforcing steel. As stated already, calcium hydroxide which gives the concrete a high pH value, has a significant effect on the corrosion resistance of steel embedded in the concrete; not only in formation of a passive oxide layer, but also in increasing the hydration of concrete.

The permeability of concrete is directly related to the structure of the hydrated cement paste. During setting, the constituent particles in the concrete form colloidal products. These have a considerably greater surface area than

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(a) Before corrosion (b) Build-up of (c) Further corrosion, (d) Eventual spalling corrosion surface cracks, —corroded ber products stains exposed.

FIGURE 4.3

Progressive deterioration of reinforced concrete due to corrosion. After Bresler (65). the original mix particles. Diagramatically the hydration process may be represented as shown in Figure 4.4. In general the gross space available for hydration products is equal to the sum of the cement and water volumes.

In Figure 4.4, 100 per cent cement hydration is shown. The diagram, however is indicative only of changes that occur in the cement paste, and the proportions of the constituents depend on the water cement ratio.

Hydration products may occupy more than twice the volume of the original solid phase and hence the porosity of the cement paste will depend on the water-cement ratio and the degree of hydration (36).

The permeability of concrete is directly related to the macro and micro-pore systems in the cement paste.

Passive protection of the reinforcement in the concrete can be achieved by (36):

- proper compaction of the concrete to its most dense form,
- selection of the most suitable cement type,
- selection of the most suitable aggregate and aggregate grading and,
- 4. use of the lowest possible cement ratio.

The corrosion of reinforcement depends greatly on the electrochemical behaviour of concrete. Rosa et al (48) concluded that the salt in the concrete increases the initial conductivity of the concrete. Mole (70, 71) reported that if the concrete remains wet, the increase in the resistance

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FIGURE 4.4

Hydration process in concrete. After Ninnis et al (36).

is due to the formation of corrosion products at the anode, and the deposition of calcium carbonate. This may also increase the bond strength.

The formation of calcium carbonate on one hand, can increase the corrosion resistance of steel in concrete by reducing the conductivity of the concrete. On the other hand, carbonation reduces the alkalinity of the concrete and thus reduces the ability of the concrete to form a passive oxide layer on the steel.

Monfore (72) in 1968 concluded:

- the resistivity of cement paste with a watercement ratio of 0.4 was about twice that of the paste with a water-cement ratio of 0.6,
- the resistivity could vary by seven orders of magnitude depending on the age and amount of evaporable water,
- concrete with the same water-cement ratio as cement paste, had about five times the resistivity,
- 4. cement paste with a lower alkali content, had a higher early resistivity but a lower resistivity after five days than cement with a higher alkali content,
- aggregate type had little effect on the resistivity.

Size distribution of aggregates is one of the factors which determines the size and distribution of pores, which in turn determines the water content. Monfore (72)

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further stated that only about 10 per cent of the evaporable water took part in electrical conduction. Nevertheless, the aggregate size and distribution affects, to a certain extent, the resistivity of the concrete especially in the initial stages of curing.

As previously mentioned, during the carbonation of concrete, calcium carbonate is formed and the pH of the concrete is lowered. This could be caused by the action of gases such as CO_2 , SO_2 and NO_2 which diffuse through the porous concrete (25).

A corrosion phenomenon which might not firstly be thought related to carbonation, is found on closer examination to be greatly dependent on this process. This is the rust formed on the reinforcement in the region of the cracks. Steel reinforced concrete always has cracks and the concrete carbonates relatively quickly along the edges of them. Corrosion only starts if the electrolyte reaches a pH value less than 7 (25).

4.5 METHODS OF OVERCOMING CORROSION OF REINFORCEMENT

Several methods of protecting reinforcement in concrete are available. These include increasing the concrete cover, coating the concrete or reinforcement with resins, passivation of the steel bar with chemical inhibitors or metal cladding including hot dip galvanized coatings (37).

4.5.1 Increased Concrete Cover

The most common method of protection of reinforcement in concrete is to increase the amount of concrete cover over the reinforcing bar. This makes it more difficult for diff-

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usion and penetration of the corrosive reagents (74). However, in some cases this is impracticable. In horizontal beam members, for example, the reinforcing bar is positioned in the tensile region of the beam where it can take up the tensile forces. These forces would normally fracture the concrete (73). Other problems also exist. Magee (75) found that increasing the cover of steel reduced the rate of corrosion but did not eliminate corrosion or reduce cracking. Also, investigations on existing concrete structures in marine environments, indicate that chloride can penetrate even high quality concrete to what is normally prescribed as the thickness of concrete cover (76). In submerged seawater the concrete may also be subjected to high hydro-static pressure which reduces the time taken for sea salts to reach the reinforcing steel (77).

4.5.2 Protection of the Reinforcement with a Non-Metallic Coating

The purpose of coating reinforcement with a nonmetallic coating is to form an inert, impervious barrier between the steel and the corrosive environment. To offer such protection the coating must be continuous. If the epoxy is not continuous due to improper application or to accidental damage during handling, concentrated corrosion attack will occur at the breakage (anode) resulting in corrosion damage. The concrete reinforcement bond is improved by spraying the still wet coating with sand.

Another method for using non-metallic coatings is to cover the surface of the concrete with the epoxy. This precludes problems involved with the accidental removal of the coating from the reinforcement. This coating is, how-

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ever, subject to the external environment and weathering (78). Monfore (72) however, suggests that the coating of the concrete has little effect on electrical resistance but will still form an inert impervious barrier between the concrete and the corrosive environment. He also suggested that electrode coating has a significant effect, i.e. the coating of the reinforcement bar is more effective in controlling corrosion.

4.5.3 Chemical Inhibitors

The addition of inhibitors to the concrete, or applied to the reinforcement, is to develop and help maintain a passive film formed on the steel by the alkalinity of the concrete. In the case of zinc coated reinforcing bar, inhibitors are used to form a passive film on the zinc. A wide range of inorganic and organic compounds can be used including phosphates, chromates, ethyl aniline and mercaptobenzolthiazole. The most commonly used inhibitors are sodium and potassium chromates, sodium nitrate, benzoate and stannous chloride (79).

The chromates do not provide sufficient protection against corrosion of the reinforcement when chlorides are present, and as such, are not recommended for passivation of black steel for use in marine environments. The effectiveness of sodium benzoate (80) and sodium nitrate is also decreased by chlorides, and if the concentration of inhibitors is too low, corrosion of the reinforcement may be enhanced by their presence. The sodium benzoate and sodium nitrate can also bring about appreciable reductions in the compressive strength of the concrete. Stannous chloride

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readily oxidizes to stannic chloride, which does not passivate the steel, and consequently is only effective if the steel is dense.

Gouda et al (28) working on the relationship between aggressor and inhibitor anions, found by both visual observation as well as potential measurements, that the critical concentration of the inhibitor for protection in distilled water could tolerate a range of concentrations of aggressive anions. The linear double logarithmic relationship (28-33) between the concentration of an inhibitive anion and the maximum tolerated concentration of an aggressive anion, applies only beyond a certain critical concentration of an aggressive anion (Figure 4.5). In this condition, the inhibitor anions rather than the aggressive anions may be preferentially adsorbed on the metal surface.

This linear log/log relationship resembles the linear relationship between the pH of an alkaline solution and the highest concentration of sodium chloride, that can be tolerated

$$pH = n\log C_{C1} + K$$
 (4.5)

where n and k are constants.

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FIGURE 4.5

"Tolerance" of sodium chromate towards aggressive ions, sulphide, sulphate, chloride or nitrate. After Gouda et al. (30).

4.6 HOT DIP GALVANIZED REINFORCEMENT

4.6.1 Introduction

The most common metal used to protect steel reinforcement is zinc, although others have been suggested for use in concrete, including aluminium, nickel, copper and lead (81, 82). Of these only aluminium and zinc are anodic with respect to steel. The others are cathodic with respect to steel, and if used would give the same type of corrosion protection as an epoxy coating. Aluminium reacts vigorously with wet concrete and hydrogen is evolved. This attack is exaggerated in the presence of steel (2).

Zinc is not as severely attacked by wet concrete as aluminium. Protection, if not provided naturally by the chromate content of the concrete, can be offered by chromate passivation (83, 84). Studies on galvanized steel in concrete reveal that structures over 54 years old still have the zinc coating intact (81).

4.6.2 Hot Dip Galvanizing Process

Hot dip galvanizing is carried out by immersion of prepared steel items in a molten zinc bath, so that the steel surface reacts with the molten zinc to form an iron-zinc alloy together with a heavy uniform zinc coating, preferably containing a minimum of 600 grams of zinc per square metre (85).

Before galvanizing, scale, rust, oil and other surface contaminents must be removed from the steel surface by a suitable preliminary treatment, and subsequent pickling in dilute sulphuric or hydrochloric acids. Any iron salts remaining on the steel after pickling, are removed by a sub-

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sequent water rinse. The clean pickled steel is then immersed in a flux solution, usually 30 per cent zinc ammonium chloride with added wetting agents and then is dried. The flux reacts with any impurities, especially thin oxide films to form a coating of chlorides on the surface. An alternative method of fluxing is to have a floating layer of molten flux on the surface of the zinc bath where the steel passes through the flux before being galvanized (86).

The zinc bath is held at a temperature between 445°C and 465°C and the reinforcement is immersed between 2 and 5 minutes, after which it is removed and allowed to cool. In Australia, the quality of the finished coating should conform to As 1650 - 1974 (Galvanized Coatings on Ferrous Articles). The zinc bath must contain at least 98.5 per cent by mass of zinc, the other major alloy element being lead (37).

4.6.3. Corrosion Performance of Zinc

Zinc, being anodic to steel cathodically, protects steel and prevents the formation of small anodic and cathodic regions on the steel surface. The anode half reaction is:

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$
 (4.6)

with the zinc ions reacting with hydroxyl ions to form zinc hydroxide:

$$Zn^{2+} 2OH^{-} \rightarrow Zn (OH)_{2}$$
 (4.7).

The electrons made available by the dissolution of the zinc, travel to the cathode (the steel reinforcement) when it is exposed to the electrolyte where the cathodic reaction and the formation of hydrogen gas occurs in accord with:

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$$2H^+ + 2e^- \rightarrow H_2$$
 (gas) (2.2)

thus the steel is cathodically protected by the zinc coating. The hydrogen gas liberated envelopes the bar, such that the reinforcing bar-concrete bond is greatly reduced.

When the zinc corrodes, zinc hydroxide (which is an insulator) is formed, and so the current from the anode decreases as corrosion products build up. The zinc corrosion products would also tend to form insulating layers across any defect in the coating (2). There are conflicting views as to the nature of the passive layer on zinc. Rehm and Lambe (104) as well as Duval and Arliguic (95) state that the passive film is calcium hydroxo-zincate, and the formation of this is only possible in calcium hydroxide.

The Pilling Bedworth ratio for the zinc corrosion product is 1.59 which is considerably lower than the value of 2.06 for steel. Consequently the zinc corrosion products occupy less volume than that of iron for a similar amount of corrosion (69), so that there is less pressure to crack the concrete. It has also been suggested that the zinc corrosion products can diffuse through alkaline concrete more readily than those of steel. Hence the build up of pressure caused by the corrosion products may be relieved by this mechanism (87).

The lowest overall corrosion rate for the galvanized coating is in the pH range of 7 to 12 (88) (Figure 4.6). As such, the coating is able to withstand a lowering of the pH due to carbonation of the concrete to a greater degree than the steel reinforcement (81) (Figure 4.7).

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FIGURE 4.6

Effect of pH on corrosion of zinc in aerated solutions at 30°C. After Roetheli et al. (88).



FIGURE 4.7 Effect of pH on corrosion of iron in aerated soft water at room temperature. After Whitman et al. (90).

When the passive zinc hydroxide coating is subjected to a chloride environment, it has been shown that zinc remains passive in chloride solutions of much higher concentration than those eliminating the passivity of steel (89, 90). Cornet et al (91) in their investigation, observed that the passivity of black steel broke down at sodium chloride concentrations of approximately 0.2 wt. per cent, while galvanized steel was able to withstand sodium chloride concentrations of approximately 2 wt. per cent. Once passivity was lost, zinc corroded in preference to steel (Figure 4.8).

Electrochemical characteristics of mild steel and pure zinc have been measured potentiostatically in saturated calcium hydroxide solution in order to further investigate the corrosion behaviour of galvanized steel in concrete (20, 83, 92). From Figure 4.9 it can be seen that when the chloride ion concentration exceeds approximately 0.08N, normal steel becomes susceptible to pitting attack at potentials of about -0.40 to -0.50 volts Vs.S.C.E. Zinc becomes susceptible to pitting attack at concentrations of chloride ions approximately 0.45N or higher at potentials of -0.80 to -0.85 Volts Vs. S.C.E. At higher chloride ion concentrations and more anodic potentials, anodic dissolution may occur (93).

4.6.4. Passivity and Breakdown of Passivity of Zinc

The electrode behaviour of zinc and galvanized steels in calcium hydroxide solutions and in Portland cement was investigated by Kaesche (89). Zinc can be passivated in calcium hydroxide solutions free of oxygen. Kaesche (89, 94) interpreted the behaviour of zinc as passivation by a

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FIGURE 4.8

Graph showing the ability of galvanized steel to withstand high chloride concentration. These potential-time curves are for galvanized steel in saturated calcium hydroxide solutions in the presence of sodium chloride. Passivity of black steel breaks down at concentrations over 0.2 wt % NaCl. Passivity of galvanized steel, established in about four days of exposure, withstands salt concentrations of almost 2 wt %. Note the change in potential scale. After Ishihawa et al. (91).



FIGURE 4.9

Corrosion characteristics of steel and of zinc in presence of chloride ion. After Bresler et al. (93) covering layer of zinc oxide. The oxide layer first allows further dissolution of zinc, which leads to the growth of the layer up to the occurrence of visible corrosion products, and at this stage corrosion is negligable.

Rehm et al (104) observed that the formation of calcium hydroxo-zincate takes place at high velocities on metallic zinc. First zinc corrodes with the formation of calcium hydroxo-zincate if calcium hydroxide is present. In the case of completely carbonated concrete, this reaction does not occur. Other studies carried out by Duval et al (95) show that zinc is passivated in a calcium hydroxide solution by the formation of calcium hydroxo-zincate on the surface. However, the passivity of the zinc diminishes considerably in the presence of chloride and as a result intense pitting occurs.

The formation of calcium hydroxo-zincate is associated with the formation of hydrogen, and this formation is strongly hindered by small amounts of chromate contained in the concrete (95).

High strength steel is susceptible to hydrogen embrittlement, and hydrogen formed on the surface of a galvanized coating can diffuse through the zinc and penetrate the steel (96).

Bird (97) in 1962, observed that when galvanized steel was embedded in concrete, hydrogen was liberated and the concrete surrounding the reinforcement became spongy with loss of bond between the concrete and the reinforcement. Kaesche (89) has observed that when pure zinc is immersed in Portland cement of pH 12.8, no hydrogen is liberated but when clean steel was brought in contact with the pure zinc under

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these conditions, hydrogen is liberated cathodically on the steel. Bird (83) in 1964, established that the evolution of hydrogen by some cements could not be attributed to their higher In view of this, the effect of soluble chromalkalinities. ates in the cement was considered. The following conclusions were drawn: zinc, whether pure or containing impurities will liberate hydrogen when embedded in concrete. The reaction is, however, inhibited by small amounts of chromate in some The formation of hydrogen on zinc could be prevented cement. by rinsing the galvanized rods with a 20% chromic acid or with 6, p.p.m chromic oxide in sodium hydroxide of a pH value of 12.7. The evolution of hydrogen is eliminated basically by preventing the reduction of water and instead, reducing chromate. At pH values of approximately 12.5 chromium trioxide (CrO₃) will be reduced to chromic oxide (Cr₂O₃). A film consisting of zinc-chromate, chromic oxide and passive possibly zinc hydroxide or calcium hydroxo-zincate will form.

Research carried out on the passivating properties of chromates on zinc, reveal the following: that insoluble compounds were formed in all chromic acid solutions and that these compounds were identified as being mixed oxides of chromic oxide $(Cr_2 0_3)$ and chromium trioxide $(Cr 0_3)$ sometimes given the generic name chromium chromates. The presence of a zinc surface is not necessary (105). It must be noted that these tests were not carried out on zinc in concrete where the pH is about 12.5. They were performed in highly acidic solutions of pH at about 1.4. It would be reasonable to say that zinc can be passivated in the acidic solutions with chromic acid, and then placed into the concrete for reinforcement. However, the nature of the passivation of

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zinc by chromates has not been established in an alkaline environment.

Other reports by Gebbart, Neuhaus and Bluthgen (98) and Christensen and Williamson (99) have studied inhibition properties of chromium compounds. They have shown that the inhibition is due to the formation of very thin layers, often monomolecular, of chromium oxides on the zinc.

The addition of chromates to cement can also cause an increase in the concrete strength (37).

Different authors and researchers recommend different amounts of chromium or chromate compounds for the elimination of hydrogen evolution and total passivation of the zinc. In an I.L.Z.R.O. report in June, 1976 (100) 10^{-3} M of potassium chromate is recommended to inhibit the formation of hydrogen gas while in another I.L.Z.R.O. report dated 1974, (101) 300 p.p.m. by weight of chromium trioxide in the mix water is the recommended amount required to passivate the zinc. On the other hand, Mahaffey (84), Bracket et al (96) and Bird (83) report that 70 p.p.m. of chromium trioxide is required.

As previously stated, the chromates do not provide sufficient protection against corrosion of galvanized steel when chlorides are present, and a double log/log relationship exists for concentrations of aggressive and inhibitor anions (Figure 4.5).

The first visible signs of corrosion of chromated zinc usually appear as small dark spots on the surface. The initial step seems to be the breakdown of the chromate or chromium oxide film, followed by corrosion of the zinc. The film remains over the corrosion products until it is bro-

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ken free and white corrosion products are released (98, 99 102) and corrosion of the zinc continues.

Since corrosion of the reinforced concrete may take many years to occur, accelerated corrosion tests such as salt sprays, and sustained impressed direct currents have been used to determine the performance of black and galvanized reinforcing bars in concrete. Cornet et al (91) observed that black reinforcement showed vertical cracking in one month when using impressed anodic current in a 4 per cent salt solution. Cracks appeared in specimens with galvanized reinforcement after two months exposure (Figure 4.10). All specimens, regardless of the type of reinforcement, appeared to be in bad condition after exposure to the impressed current for six months.

Ford (37) observed, after performing impressed current experiments on concrete beams reinforced with both black and galvanized reinforcing bars, that it took twice as long for rust stains to appear on the surface of concrete beams reinforced with galvanized bar, as for rust stains to appear on concrete beams reinforced with black reinforcing bar (Figure 4.11).

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FIGURE 4.10

Corrosion performance of black and galvanized reinforcement under sustained direct current. After Bresler (91).



FIGURE 4.11

Time taken for corroding reinforcing bars to stain the concrete surface after exposure to impressed anodic currents. After Ford (37).

PART B

EXPERIMENTAL WORK

5. INTRODUCTION

5.1 CORROSION OF GALVANIZED REINFORCEMENT IN CONCRETE

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A number of methods exist for improving the corrosion resistance of reinforcement, all of which offer varying degrees of protection. A method which is now widely used is hot dip galvanizing of the reinforcement. Research has shown a number of advantages in using this method. For one, zinc provides sacrificial protection of the steel and is itself rendered passive, Secondly, zinc can withstand higher chloride ion concentrations than steel, and can also tolerate lower pH levels. The corrosion products of zinc occupy less volume than those of steel, thus increasing the life of concrete beams reinforced with galvanized steel. These properties of zinc together with the better bond properties of the iron zinc alloy layer, make hot dip galvanizing an excellent method of adding extra protection to reinforcement steel.

The work carried out in this project is a continuation of work done by P. Ford (37). Ford's work on the corrosion characteristics of galvanized reinforcement consisted of a series of experiments using accelerated corrosion tests and natural corrosion sites on concrete beams reinforced with bars in both the black and galvanized conditions and using different depths of concrete cover.

The work carried out for this project consisted of accelerated corrosion tests similar to those of Ford. Different diameter reinforcing bars were used together with two different depths of concrete cover, so that the effect of reinforcing bar geometry on depth of concrete could be studied. Chromates in the form of sodium chromate were added to the concrete of all concrete beams to study its effects on the elimination of the evolution of hydrogen.

It must be understood that the results obtained from these tests are only comparative. The experimental situation does not correlate with a natural corrosion situation since the impressed current dictates the corrosion rate. However, the effects on the concrete beams of corrosion products produced in certain intervals of time can be analysed and hopefully related to the natural corrosion situation, and in addition the experimental arrangement is directly related to the stray current situation.

Other accelerated tests were performed on concrete beams using a much higher current density to obtain comparative results, and to observe more closely the corrosion of black and galvanized reinforcement.

5.2 PASSIVATION AND CORROSION CHARACTERISTICS OF ZINC

Zinc in high pH concrete corrodes with the evolution of hydrogen at the zinc surface. This hydrogen diffuses into the steel underlayer and causes hydrogen embrittlement of high tensile steel and loss of bond. This phenomenon can be eliminated by the introduction of chromate into the concrete. The evolution of hydrogen is caused by the reduction reaction of water. However, if chromate ions are present, the chromates are reduced instead of water, and a passive film is believed to form on the zinc surface due to the reaction of zinc with chromate ions.

It is common practice to-day to either passivate the zinc before or during embedding galvanized reinforcing steel into concrete. This is done in a number of ways; to

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passivate zinc before embedding the galvanized reinforcing steel into concrete, the galvanized reinforcement is dipped into a bath containing 6 p.p.m.of chromic oxide in a sodium hydroxide solution. To passivate the zinc when the reinforcement bar is embedded into the concrete, 70 p.p.m. of chromium trioxide or 70 p.p.m. of sodium chromate is added to the concrete mix.

A number of experiments involving the measurement of potential, with respect to time, and galvanostatic polarization experiments were performed on zinc. A saturated calcium hydroxide solution with a pH value of 12.5 was used and different quantities of sodium chromate and chromic oxide were added to study the passivity of zinc. Chromic oxide was used in these experiments to produce a comparison between the passivating action of chromates and chromic oxide, since chromate ions are reduced to chromic oxide. It is this reduction reaction which stops the reduction of water and thus the evolution of hydrogen gas. Different chloride ion concentrations were also added in order to study the effect of chloride ions on the passivity of zinc, both before and after a passive film was formed.

6. MATERIALS AND PROCEDURES

6.1 MATERIALS AND PROCEDURES USED TO ASCERTAIN THE <u>CORROSION CHARACTERISTICS OF GALVANIZED</u> REINFORCEMENT IN CONCRETE

6.1.1. Materials

In the accelerated corrosion tests two different grades of deformed steel reinforcing bars were used, namely, 230S having a yield stress of 230MPa and cold twisted 410C bars having a 0.2 per cent proof stress of 410MPa. Bars in both the black and galvanized conditions having diameters of 16 mm, 20 mm and 28 mm were used. (Table 6.1).

The concrete used in the reinforced beams was prepared from commercial concrete using Portland cement and local aggregates (Table 6.2). The concrete was air entrained with fly ash and retarding admixtures to form 20MPa concrete of the type used for construction work in New South Wales.

Specimens of concrete were prepared in standard cylindrical compression test moulds as described in AS1012 part B-1973, so that the compressive strength of the concrete could be obtained. The compressive strength was found to be 22 MPa. 70 p.p.m. of sodium chromate was added to the concrete. Mechanical vibrations were performed on the concrete in the moulds to produce a well packed, dense, concrete beam. The concrete beams were removed from the moulds 36 hours after the concrete was poured. They were subsequently subjected to curing in water for a period of 28 days in accordance with AS0112, Part B-1973 before the commencement of the corrosion tests.

The cement used for the cylindrical concrete beams in the inhibition studies were prepared from 'Goliath' cement (Table 6.3). Three batches of concrete were prepared; the
first batch contained 70 p.p.m. of sodium chromate, the second batch contained 70p.p.m.of chromic oxide and the third batch contained neither sodium chromate nor chromic oxide. These concrete beams were also subjected to vibration and were cured for a period of 14 days before tests were commenced on them.

6.1.2 Procedure

The reinforced concrete beams used for the corrosion studies measured 550 mm x 190 mm x 180 mm, while the depths of concrete cover used were 10 mm and 20 mm in accordance with the Australian concrete code AS 1480-1974. The effect of different bar diameters and different depth of concrete cover on the rate of corrosion at the reinforcing bars was compared and analysed by the performance of accelerated corrosion tests in a 3 per cent sodium chloride solution with an impressed constant current of 3.0 milli-amps on each concrete beam.

The concrete beams were prepared in moulds made from wooden cases. The cases were divided into two equal separate moulds. Each mould was lined with a polyethylene sheet to obtain a good surface finish on the concrete beam and also to help with the removal of the beam after setting of the concrete. The depth of concrete cover was determined by placing, at each end of the mould, a wooden board which had a hole bored at the required distance from one end. The reinforcing bars were then inserted into the holes in the end blocks. The concrete was poured at the Artarmon plant of Ready Mix Concrete Pty. Limited.

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TABLE 6.1

<u>Chemical Composition</u> (weight percent)

Bar No.		С	Р	Mn	Si	S	Zn wt/m ²
16 mm	'A'	.25	.024	.88	.056	.020	
16 mm	'B'	.25	.022	.90	.070	.019	
16 mm	'C'	.25	.013	.77	.055	.015	980
16 mm	'D'	.25	.013	.75	.055	.015	1020
20 mm	'A'	.24	.017	.74	.055	.023	
20 mm	'B'	.21	.036	.88	.055	.027	
20 mm	'C'	.24	.014	.80	.050	.014	1080
20 mm	'D'	.24	.022	.72	.070	.020	875
28 mm	'A'	.25	.015	.76	.030	.026	
28 mm	'B'	.25	.012	.75	.029	.027	
28 mm	'C'	.24	.018	.75	.036	.023	1076
28 mm	'D'	.24	.014	.74	.028	.025	1124
		· ·					

- A = Black 230 S
- B = Black 410 C
- C = Galvanized 230 S
- D = Galvanized 410 C

TABLE 6.2

The Concrete Used for Corrosion Tests

Quantity per Cubic Mete	r Additions					
220 Kg	Goliath cement					
75 Kg	Fly Ash (classified)					
220 Kg	10 mm Dolerite					
950 Kg	20 mm Dolerite					
300 Kg	Nepean Sand					
460 Kg	Lane Cove Sand					
<u>A</u>	dmixtures					
110 m1/100 Kg	Retarder 200					
220 $m1/m^{3}$	Air Entrainer M B U R					
168 1/m ³	Water in additions					
128 $1/m^3$	Additional water					
70 p.p.m.	Sodium Chromate					

TABLE 6.3 The Concrete Used for the Corrosion Tests

Quantity per Cubic Me	eter Additions
220 Kg 460 Kg	Goliath Cement Nepean Sand
Admiz	ctures
290 1/m ³ 70 p.p.m.	Water in additions Sodium Chromate or Chromic oxide

To ensure that only the face with the particular depth of concrete cover, was exposed to the impressed current, hydro-epoxy resin was used to coat all the other faces of the concrete beam. After this was done, the concrete beams were placed into plastic bins containing a 3 per cent salt water solution. A cathode, which was made from a reinforcing bar, was set in the salt water facing the exposed face of the concrete beam. A circuit was connected to produce the constant current (Figure 6.1). The circuit which was used is shown in Figure 6.2

The effects of corrosion in the reinforced beams were determined by the time taken for rust from the corroding bars to appear on the concrete surface.

The smaller concrete beams were made in cardboard moulds. These beams were made using only the 16 mm diameter bar with a 10 mm depth of concrete cover.Cold twisted deformed 410C and deformed structural grade 230S bars, in both black and galvanized condition, were used. They were all subjected to accelerated corrosion tests in 3 per cent sodium chloride solution with an impressed constant current of 3.0 milli amps (Figure 6.3). The circuit used to produce the constant current is shown in Figure 6.2

Three concrete blocks made from the same concrete as used for the cylindrical beams were prepared. All were reinforced with 16 mm dia. deformed structural 230S bars in the galvanized condition. One block contained 70 p.p.m. of sodium chromate, another had a chromic oxide content of 70 p.p.m. (Figure 6.4) and the third had neither sodium chromate nor chromic oxide.

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FIGURE 6.1 The accelerated corrosion tests used to determine the corrosion characteristics of different diameter black and galvanized reinforcing bars.



FIGURE 6.2(a) The circuit which provided a constant current for the accelerated corrosion tests.



FIGURE 6.2(b)



FIGURE 6.3

The accelerated corrosion tests performed to determine and compare the corrosion characteristics of black and galvanized reinforcing bars in the cylindrical concrete beams.



FIGURE 6.4 Concrete blocks with additions of 70 p.p.m. sodium chromate and 70 p.p.m. chromic oxide respectively to determine the effects of these additions on the concrete reinforcing bar interface.

6.2 MATERIALS AND PROCEDURES USED TO ASCERTAIN THE PASS-IVATION AND CORROSION CHARACTERISTICS OF ZINC.

6.2.1. Materials

The equipment used for performing the experiments where the potential of zinc was measured with respect to time and current is shown in Figure 6.5

A number of working zinc electrodes 1 cm^2 in area were cut from a sheet of zinc plate. The electrodes were set in cold setting resin so that only one face would be exposed to the electrolyte. The electrolyte was a saturated calcium hydroxide solution of pH of 12.5 containing 10^{-3} M of potassium sulphate. For the various experiments sodium chromate, chromic oxide and sodium chloride were added to the calcium hydroxide solution.

6.2.2. Procedures

The circuit, as shown in Figure 6.6, was established using the equipment shown in Figure 6.5. The first experiments carried out measured the potential, with respect to time of the zinc in the calcium hydroxide solution. The reference electrode used to measure potential was a saturated calomel electrode. The potential, with respect to time, was then measured after 70 p.p.m. of sodium chromate and chromic oxide were added.

These experiments were continued adding different amounts of sodium chloride. The chloride ion concentrations used were 10^{-3} M, 10^{-2} M, 10^{-1} M and $10^{-.5}$ M. These sodium chloride additions were made into the calcium solutions containing 70 p.p.m. and 300 p.p.m. sodium chromate respectively.



FIGURE 6.5

Equipment used for experiments performed to study the passivity of zinc.



FIGURE 6.6

The circuit used for measuring potential with respect to time, and for performing galvanostatic polarization experiments. The same experiments were performed using 70 p.p.m. and 300 p.p.m. of chromic oxide respectively. Experiments where additions of 70 p.p.m. sodium chromate and 70 p.p.m. chromic oxide were made to the calcium hydroxide solution, were performed on both clean and already passivated zinc electrodes. The electrodes were polished so that a clean equipotential surface was obtained, while the passivated electrodes were the same, except they were allowed to passivate in their respective solutions of calcium hydroxide with either 70 p.p.m. sodium chromate or 70 p.p.m. chromic oxide for five (5) hours. For all these experiments the current through the ammeter was maintained at zero.

Galvanostatic polarization experiments were carried out using the same circuit. A platinum counter electrode was used for these experiments, and a variable resistor was used to control the current. The potential was measured at intervals of .025 Milliamps. The calcium hydroxide solution was used with additions of 70 p.p.m. sodium chromate and 70 p.p.m. chromic oxide respectively. Additions of different amounts of sodium chloride were made, and already passivated electrodes were used for these polarization experiments.

Pieces of zinc plate were immersed in calcium hydroxide solution which contained sodium chromate and chromic oxide, after which the zinc was allowed to dry. The film which formed on the zinc surface, was then carefully removed and examined by infra red spectroscopy.

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7. RESULTS

7.1 CORROSION OF GALVANIZED REINFORCEMENT IN CONCRETE

7.1.1 <u>Corrosion Characteristics of the Cylindrical</u> <u>Concrete Beams</u>.

Accelerated corrosion tests were performed on a set of reinforced cylindrical concrete beams in a 3 per cent sodium chloride solution using an impressed current density of .36 Amps/m². The reinforcing bars used for these tests were 16 mm diameter deformed structural 230S and cold twisted deformed 410 C reinforcing bars in both the black and galvanized conditions. The depth of concrete cover used in these tests was 10 mm. The effects of corrosion on the reinforcing bars was determined by the time taken for rust stains from the corroding bars to appear on the concrete surface, and also by splitting the concrete beams open and noting the appearance of the reinforcing bars and the concrete reinforcing bar interface.

The first concrete cylinder to have rust stains appearing on the concrete surface was the one with the cold twisted deformed 410C bar in the black condition. The concrete contained neither sodium chromate nor chromic oxide. The rust stains which were composed of red iron oxide appeared on the surface after 4 days or $34.5 \text{ Amp hour/m}^2$ exposure. These stains appeared only in separate areas on the concrete On inspecting the reinforcing bar it was observed surface. that corrosion occurred on separate areas of the reinforcing The rust was usually found on ridges of the deformabar. tions (Figure 7.1) and opposite air voids in the concrete. The second concrete cylinder to show red iron oxide stains on its surface, was that with the cold twisted deformed 410C black bar, and the concrete contained 70 p.p.m.

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FIGURE 7.1 Corrosion of the 410C 16 mm black reinforcing bar after 4 days exposure to an impressed anodic current where the concrete contained neither sodium chromate nor chromic oxide. of sodium chromate. The same type of stains appeared on this beam as on the first beam. The bar itself corroded more uniformly than the first one, with the most severely attacked areas being on the ridges of the deformation and opposite air voids on the concrete (Figure 7.2). There was a grey film deposited on the reinforcing bars surface and also on the concrete opposite the bar (Figure 7.3), while the concrete opposite the bar of the first cylinder showed rust stains. The time taken for rust stains to appear on the surface of the second concrete cylinder was six (6) days at 52 Amp hours/ m^2 . The third concrete cylinder to show rust stains on its surface was with the deformed structural 230 S black bar. The that concrete contained neither sodium chromate nor chromic oxide and the stains appeared after eleven (11) days or 97.5 Amp hours/ m^2 . Once again the rust stains on the concrete surface were non-uniform, although they were more uniform than those on the previous two cylinders. The stains on the reinforcing bar were relatively uniform and were initiated on ridges at the deformations. A few isolated areas on the reinforcing bar, opposite air voids in the concrete were severely attacked. (Figure 7.4). The stains reinforcing bar and on the concrete opposite the on the reinforcing were red. The fourth cylinder to show rust stains on the concrete surface was that with the deformed structural 230 S black bar and the concrete contained 70 p.p.m. sodium chromate. This occurred after 14 days or 120 Amp hours/m². The rust stains here were more uniform still, while the rust on the reinforcing bar was also relatively uniform (Figure 7.5). A grey film was broken



FIGURE 7.2 Corrosion of the 410C 16 mm black reinforcing bar after 6 days exposure to an impressed anodic current, where the concrete contained 70 p.p.m. of sodium chromate.



FIGURE 7.3 Corrosion on the concrete, 410C black 16 mm reinforcing bar interface where the cement contained 70 p.p.m. of sodium chromate.



FIGURE

7.4 Corrosion of the 230 S 16 mm black reinforcing bar after 11 days exposure to an impressed anodic current where the concrete contained neither sodium chromate nor chromic oxide.



FIGURE 7.5 Corrosion of the 230S 16 mm reinforcing bar after 14 days exposure to an impressed anodic current where the concrete contained neither sodium chromate nor chromic oxide. where corrosion occurred and this was mainly on the ridges of the deformations.

The concrete cylinders with the deformed structural 230 S bars in the galvanized condition showed no signs of rust staining after 21 days. On splitting the concrete cylinders open, the galvanized bar in the concrete cylinder containing no sodium chromate or chromic oxide showed a thick layer of white corrosion products on its surface (Figure 7.6) and in some isolated spots some red iron oxide was coming through the white corrosion product layer (Figure 7.7). A concrete cylinder with a deformed structural 230 S reinforcing bar in the galvanized condition and the concrete containing 70 p.p.m. sodium chromate was split open. Once again a layer of white corrosion products was present but these were quite non-uniform and formed where a grey film was broken (Figure 7.8). The concrete interface had a similar appearance to the interface in Figure 7.3.

Three other concrete test blocks were made. A11 had 16 mm diameter deformed structural 230 S reinforcing bars in the galvanized condition embedded in them. The first concrete block contained 70 p.p.m. sodium chromate. The second contained 70 p.p.m. chromic oxide, while the third contained neither sodium chromate nor chromic oxide. The purpose of this exercise was to study the difference between sodium chromate and chromic oxide additions, and to observe their effects on hydrogen evolution at the reinforcing bar concrete Three weeks after the concrete was poured, the interface. blocks were split open. It was observed that the concrete opposite the reinforcing bar, where chromic oxide was used, was quite porous (Figure 7.9) compared to the concrete where sodium chromate was used (Figure 7.10). However, the concrete opposite the reinforcing bar where neither sodium chromate

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FIGURE 7.6 Corrosion of the 230 S galvanized 16 mm reinforcing bar after 21 days exposure to an impressed anodic current where the cement contained neither sodium chromate nor chromic oxide.



FIGURE 7.7 Corrosion of the 230 S galvanized 16 mm reinforcing bar under the same conditions as those in Figure 7.6, here there are no signs of rust formation.



FIGURE 7.8 Corrosion of the 230 S 16 mm galvanized reinforcing bar after 21 days exposure to an impressed anodic current where the concrete contained 70 p.p.m. of sodium chromate.



FIGURE 7.9 Concrete surface of concrete galvanized reinforcing bar interface where 70 p.p.m. of chromic oxide was added.



FIGURE 7.10 Concrete surface of concrete galvanized reinforcing bar interface where 70 p.p.m. of sodium chromate was added. nor chromic oxide was added was the most porous (Figure 7.11).

A 16mm diameter deformed structural 230 S reinforcing bar in the galvanized condition was exposed to a natural corrosion environment for sixteen (16) weeks. The reinforcing bar was placed against a support such that it was resting in a sloping position. Both ends of the bar were cut off so that the steel was exposed with a thin zinc layer around the The natural corrosion environment was on the perimeter. University of New South Wales lower campus. The purpose of this exercise was to observe the sacrificial protection properties at hot dip galvanizing of reinforcing bars. After six (6) weeks exposure there was a considerable amount of red iron oxide in the centre of the end steel section, while the area around it and the perimeter of the bar was clean (Figure 7.12). After sixteen (16) weeks the appearance of the end at the bar changed quite considerably. The iron oxide in the centre of the steel section thickened and spread out to the perimeter of the bar. There was little iron oxide present at the outermost part of the perimeter but instead a deposit of white corrosion product was present (Figure 7.13).

7.1.2. Corrosion Characteristics of Concrete Beams

Accelerated corrosion tests were performed on reinforced concrete beams in a 3 per cent sodium chloride solution using an impressed current density of .114 Amps/m^2 . The effects of the corrosion at the reinforcing bars were determined by the appearance of rust stains on the exposed surface of the concrete beam (Figure 7.14).

As already stated, corrosion at the black bars

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occurred much carlier than corrosion of the galvanized bars, and staining of beams reinforced with small diameter bars occurred earlier than beams reinforced with large diameter bars. The first signs of corrosion of the black bars was the formation of red iron oxide on the bars. White corrosion products were formed on the galvanized bars, after which red rust stains appeared.

The first concrete beam to show rust staining through the concrete during the accelerated corrosion tests was the beam with a 10 mm concrete cover over a 16 mm diam æter cold twisted deformed 410 C black bar. The staining was evident after 3.5 weeks or 67 Amp hours/m². The stains which appeared were in non-uniform patches (Figure 7.15). With time these patches grew in area and a thick deposit of rust on the surface of the concrete also grew. Some longitudinal rust stains also appeared after some time (Figure 7.16).

The next concrete beam to show rust staining through the concrete was the beam with a 10 mm concréte cover over a 16 mm deformed structural 230 S black bar. The stains here were also non-uniform. These rust stains appeared after 5.5 weeks or 100 Amp hours/ m^2 . The third concrete beam to show rust staining was the beam with 20 mm concrete cover over a 16 mm cold twisted deformed 410 C black bar; the stains here were also non-uniform and relatively dull. They appeared after six (6) weeks or 115 Amp hours/ m^2 . The fourth concrete beam to show rust staining was the one with 10 mm concrete cover over a 16 mm cold twisted deformed 410 C galvanized bar. The stains here were relatively uniform and were longitudinal along the face of the beam (Figure 7.17). It took seven (7) weeks or 134 Amp hours/m 2 for the rust stains

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FIGURE 7.11 Concrete surface of concrete galvanized reinforcing bar interface where neither sodium chromate nor chromic oxide were added to the concrete.



FIGURE 7.12 Section of a 16 mm diameter galvanized reinforcing bar showing rust formation after 6 weeks exposure to a natural corrosive environment.



FIGURE 7.13 Section of a 16 mm diameter galvanized reinforcing bar showing corrosion products after 16 weeks exposure to a natural corrosive environment.

x	16 mm	410C	black	a	20 mm	410C	black
0	16 mm	2305	black	a	20 mm	2305	black
Δ	16 mm	410C	galvanized	A	20 mm	410C	galvanized
٥	16 mm	230S	galvanized	∇	28 mm	410C	black .
				•			



RE 7.14 Time taken for corroding reinforcing bars to stain the concrete surface after exposure to impressed anodic current.



FIGURE 7.15 Rust stains on the surface of a concrete beam reinforced with a 410C 16 mm black reinforcing beam.



FIGURE 7.16 Rust stains on the surface of a concrete beam reinforced with a 230S 16 mm black reinforcing bar.



FIGURE 7.17 Longitudinal rust stains on the surface of a concrete beam reinforced with a 410C 16 mm galvanized reinforcing bar.

to appear. The fifth concrete beam to show rust stains on the surface was the concrete beam with 10 mm depth of concrete cover over a 20 mm diameter cold twisted deformed 410C reinforcing bar in the black condition. Once again the rust stains were non-uniform. The stains covered a considerably greater area on this beam than they did on the concrete block reinforced with the 16 mm 410C reinforcing black bar. It took 8.5 weeks or 162 Amp hours/m² for these stains to appear on the concrete surface. The next two beams to show rust stains were as follows:-

> The concrete beam with 10 mm of concrete cover over a 16 mm deformed structural 230 S galvanized bar, and

The concrete beam with 20 mm concrete cover over a 16 mm deformed structural 230 S black bar.

These two beams had the stains appear after nine (9) weeks or 172 Amp hours/ m^2 . The beams reinforced with the 230 S galvanized bar had uniform rust stains on the surface (Figure 7.17), while the beam reinforced with the 230 S black bar had non-uniform rust stains on its surface, resembling the rust stains on the first concrete beam. The stains did not grow in area with time, and stayed relatively dull. (Figure 7.15). The next concrete beam to show rust stains was the concrete beam with 10 mm concrete cover over a 28 mm diameter cold twisted deformed 410C black bar. These stains appeared after 11.5 weeks or 220 Amp hours/m². The stains were non-uniform and grew in area with time. The ninth beam to show rust stains was the one with 10 mm of concrete cover over a 20 mm deformed structural 230 S black bar. These stains appeared after 12 weeks on 230 Amp hours/ m^2 , and

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were also non-uniform. The beam reinforced with the 16 mm 410C black bar which had 20 mm of concrete cover was the tenth beam to show rust stains on the concrete surface. The stains here were non-uniform, dull and did not grow much with time. These appeared 13.5 weeks or 258 Amp hours/m² after the commencement of the tests. The next beam after that to show rust stains was the one with 20 mm of concrete cover over the 20 mm 410C black bar; the stains were non-uniform and it took 16 weeks or 307 Amp hours/m². The twelfth beam to show rust stains was the one with 10 mm of concrete cover over the 20 mm 410C galvanized bar. The stains were uniform and appeared after 17.5 weeks or 336 Amp hours/m².

9.2 PASSIVATION AND CORROSION CHARACTERISTICS OF ZINC

9.2.1. <u>Passivation of Zinc in the Presence of Inhib-</u> itor Anions

A series of experiments involving the measurement of potential with respect to time and potential with respect to current of zinc in a saturated calcium hydroxide solution of a pH value of 12.5 were performed, with different concentrations of sodium chromate and chromic oxide being added, with the intention of providing information on the passivity of zinc in simulated concrete conditions in the presence of inhibitor anions.

The potential of zinc was measured with respect to a saturated calomel electrode, and all potential measured were converted relative to a standard hydrogen electrode (Table 7.1).

The first experiments involved the measurement of potential with respect to time. The results of these are

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TABLE 7.1

(a) "Potential Versus Time Measurements for Zinc at Different Concentrations of Sodium Hydroxide".

1.	70 j	p.p.m.	of	Sodium	Chromate	2,	300	p.p.m.	of	Sodium	Chromate
----	------	--------	----	--------	----------	----	-----	--------	----	--------	----------

Tim	ie I	Potential (Volts)) <u>Time</u>	e P	<u>otential (Volts)</u>
0		726	0		725
5	min	608	5	min	581
10	min	478	10	min	442
15	min	409	15	min	407
30	min	365	30	min	301
60	min	332	60	min	297
90	min	310	90	min	291
120	min	284	120	min	262
5	hrs .	283	5	hrs	240

3. 70 p.p.m. of Chromic Oxide 4. 300 p.p.m. of Chromic Oxide

Tin	ie l	Potential	(Volts)	Time	e P	otential	(Volts)
0		732		´ 0		73	0
5	min	639		5	min	63	6
10	min	570		10	min	51	5
15	min	474		15	min	47	0
30	min	448		30	min	44	6
60	min	432		60	min	42	8
90	min	425		90	min	42	4
120	min	415		120	min	41	6
5	hrs	402		5	hrs	39	2
(b) "Potential Versus Current Measurements for Zinc at Sodium Chromate and Chromic Oxide"

Current (milliamps)	Potential (Volts)	Current (milliamps)	Potential (Volts)
0	365	0	402
.025	1.030	.025	- 1.112
.050	- 1.061	.050	- 1.170
.075	- 1.088	.075	- 1.173
.100	- 1.117	.100	- 1.178
.125	- 1.122	.125	- 1.184
.150	- 1.180	.150	- 1.194
.175	- 1.197	.175	- 1.203
.200	- 1.201	.200	- 1.208
. 225	- 1.209	.225	- 1.218
.250	- 1.214	.250	- 1.221
.300	- 1.256	.300	- 1.278
.350	- 1.287	.350	- 1.308
.400	- 1.304	.400	- 1.329
.450	- 1.317	.450	- 1.348
.500	- 1.334	. 500	- 1.368
.550	- 1.356	. 550	- 1.383
.600	- 1.369	.600	- 1.398
.650	- 1.391	.650	- 1.415
.700	- 1.412	.700	- 1.430
.750	- 1.424	.750	- 1.442
.800	- 1.447	.800	- 1.464
.850	- 1.452	.850	- 1.468
.900	- 1.463	.900	- 1.471
.950	- 1.473	.950	- 1.475
1.000	- 1.488	1.000	- 1.488

1. 70 p.p.m. Sodium Chromate 2. 70 p.p.m. Chromic Oxide

"Potential Versus Time Measurements for Unpassivated (c) Zinc at Different Chloride ion Concentrations and 70 p.p.m. Sodium Chromate"

 10^{-3} M C1⁻ 1.

2. $10^{-2} M C1^{-1}$

Time	Potential (Volts)	Time P	otential	(Volts)
0	749	0	756	,
5 min	658	5 min	701	
10 min	614	10 min	697	
15 min	575	15 min	662	
30 min	536	30 min	619	
60 min	514	60 min	601	
90 min	501	90 min	572	
120 min	479	120 min	570	
5 hrs	478	5 hrs	569	

3. 10^{-1} M Cl⁻

4. 10^{-.5} M C1⁻

Time	Potential (Volts)	Time	<u>Potential (Volts)</u>
0	772	0	776
5 min	739	5 min	728
10 min	732	10 min	737
15 min	727	15 min	740
30 min	719	30 min	740
60 min	721	60 min	741
90 min	714	90 min	741
120 min	710	120 min	742
5 hrs	708	5 hrs	742

"Potential Versus Time Measurements for Unpassivated (d) Zinc at Different Chloride Ion Concentrations and 70 p.p.m. Chromic Oxide"

1. 10^{-3} M C1⁻

2. 10^{-2} M Cl

Time	Potential (Volts)	Time	Potential	(Volts)
0	932	0	934	
5 min	921	5 min	930	
10 min	915	10 min	928	
15 min	903	15 min	910	
30 min	886	30 min	901	
60 min	867	60 min	878	
90 min	841	90 min	852	. ·
120 min	802	120 min	841	
5 hrs	672	5 hrs	764	
			•	

3. 10^{-1} M C1⁻

4. 10^{-.5}M C1

Time	}	Potential	(Volts) Ti	me	Potential	(Volts)
0		941	0		940	
5	min	942	5	min	945	
10	min	951	10	min	947	
15	min	951	15	min	948	
30	min	954	30	min	959	
60	min	954	. 60	min	963	
90	min	955	90	min	966	
120	min	957	120	min	967	
5	hrs	960	5	hrs	969	
		-			-	

"Potential Versus Time Measurements for Unpassivated (e) Zinc at Different Chloride Ion Concentrations and 300 p.p.m. Sodium Chromate"

 $10^{-3}M$ C1⁻ 1.

2. 10^{-2} M C1⁻

Time		Potential	(Volts) <u>Ti</u>	me	Potential	(Volts)
0		750	0		747	•
5 mi	n	644	. 5	min	682	
10 mi	.n	596	10	min	674	
15 mi	n	554	15	min	640	
30 mi	.n	517	30	min	592	
60 mi	.n	498	60	min	584	
90 mi	.n	0.489	-90	min	578	
120 mi	n	487	120	min	569	
5 hr	`S	470	5	hrs	565	

3. 10^{-1} M C1⁻

4. $10^{-5} M C1^{-5}$

Time	Potential (Volts)	Time	Potential (Volts)
0	767	0	760
5 min	714	5 min	734
10 min	691	10 min	725
15 min	684	15 min	720
30 min	671	30 min	718
60 min	662	60 min	718
90 min	660	90 min	715
120 min	657	120 min	715
5 hrs	655	5 hrs	712
	₽		,

(f) "Potential Versus Time Measurements for Unpassivated Zinc at Different Chloride Ion Concentrations and 300 p.p.m. Chromic Oxide"

1. 10^{-3} M C1⁻

2. 10^{-2} M Ci⁻

Tim	e	Potential	(Volts)	Tin	ne	Potential	(Volts)
Q		930		0		933	•
5	min	917	•	5	min	920	
10	min	915		10	min	912	
15	min	900		15	min	905	
30	min	881		30	min	896	
60	min	866	· · ·	60	min	870	
90	min	838		90	min	847	
120	min	792		120	min	839	. , ,
5	hrs	670		5	hrs	760	

3.

3. 10^{-1} M C1⁻

4. 10^{-.5}M C1⁻

Tim	ne .	Potential (Vol	lts) <u>Tin</u>	ne I	Potential	(Volts)
0		937	0		938	
5	min	935	5	min	943	
10	min	933	10	min	945	
15	min	930	15	min	949	
30	min	· - .930	30	min	960	
60	min	928	60	min	962	
90	min	928	60	min	963	
120	min	927	120	min	967	
5	hrs	925	5	hrs	967	
		-				

(g) "Potential Versus Time Measurements for Passivated Zinc at Different Chloride Ion Concentrations and 70 p.p.m. Sodium Chromate"

1. 10^{-3} M C1⁻

2. 10^{-2} M C1⁻

Tin	ne	<u>Potential</u>	(Volts)	Tin	ne	Potential	(Volts)
0		429		0		427	•
5	min	412		5	min -	435	
10	min	404		10	min	430	
15	min	400		15	min	422	
30	min	392		30	min	410	
60	min	395		60	min	406	
90	min	390		90	min	404	
120	min	386	1	20	min	401	
5	hrs	379		5	hrs	400	

3. 10^{-1} M C1⁻

4. 10^{-.5}M C1⁻

Time	P	otential (Volts)	Tir	ne	Potential	(Volts)
0		439	0		432	
5 mi	n	452	5	min	467	
10 mi	n	463	10	min	469	
15 mi	n	467	15	min	472	
30 mi	n	471	30	min	475	
60 mi	n	469	60	min	477	
90 mi	n	471	90	min	481	
120 mi	n	473	120	min	487	
5 hr	s	476	5	hrs	491	

- (h) "Potential Versus Time Measurement for Passivated Zinc at Different Chloride Ion Concentrations and 70 p.p.m. Chromic Oxide"
- 1. 10^{-3} M C1⁻

```
2. 10^{-2} M C1<sup>-</sup>
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Time	e P	otential (Volts) Ti	me	Potential	(Volts)
			·			
0		751	0		768	
5 n	nin	759	5	min	756	
10 n	nin	743	. 10	min	754	
15 n	nin	734	15	min	752	
30 n	nin	694	30	min	748	
60 n	nin	635	60	min	710	
90 n	nin	607	90	min	623	
120 n	nin	592	120	min	617	
5 ł	nrs	577	5	hrs	607	

 $3.10^{-1} M Cl^{-1}$

,

4. 10^{-.5}M C1⁻

Ti	me	Potential (Volts)	Ti	me I	Potential	(Volts)
					1	· · · · · · · · · · · · · · · · · · ·
0		758	0		763	
5	min	792	5	min	798	
10	min	798	10	min	810	
15	min	821	15	min	822	
30	min	827	30	min	837	
60	min	834	60	min	857	
90	min	847	90	min	872	
120	min	854	120	min	902	
5	hrs	887	5	hrs	994	·

(i) " D S	(i) "Potential Versus Current Measurements for Zinc at Different Chloride Ion Concentrations and 70 p.p.m. Sodium Chromate"							
Current	10^{-3} M C1 ⁻	10^{-2} M CH	10 ⁻¹ M C1 ⁻	10 ⁵ M C1 ⁻				
(milli-	Potentia1	Potential	Potential	Potential				
amps)	(Volts)	(Volts)	(Volts)	(Volts)				
0	410	421	430	438				
.025	-1.009	-1.1011	-1.017	-1.027				
.050	-1.067	-1.071	-1.021	-1.075				
.075	-1.117	-1.121	-1.131	-1.157				
.100	-1.135	-1.129	-1.132	-1.163				
.125	-1.174	-1.130	-1.141	-1.212				
.150	-1.184	-1.139	-1.149	-1.231				
.175	-1.203	-1.207	-1.221	-1.257				
.200	-1.207	-1.213	-1.230	-1.260				
.225	-1.212	-1.220	-1.235	-1.266				
.250	-1.217	-1.229	-1.247	-1.273				
.300	-1.264	-1.273	-1.284	-1.291				
.350	-1.279	-1.289	-1.301	-1.301				
.400	-1.310	-1.315	-1.320	-1.329				
.450	-1.319	-1.322	-1.325	-1.334				
.500	-1.324	-1.326	-1.331	-1.340				
.550	-1.345	-1.348	-1.349	-1.352				
.600	-1.372	-1.379	-1.383	-1.391				
.650	-1.392	-1.399	-1.402	-1.417				
.700	-1.416	-1.424	-1.477	-1.431				
.750	-1.429	-1.431	-1.435	-1.437				
.800	-1.449	-1.452	-1.457	-1.461				
.850	-1.456	-1.459	-1.464	-1.470				
.900	-1.472	-1.482	-1.491	-1.492				
.950	-1.474	-1.486	-1.494	-1.497				
1.000	-1.484	-1.492	-1.496	-1.498				

(j)	(j) "Potential Versus Current Measurements for Zinc at						
	Different Chloride Ion Concentrations and 70 p.p.m.						
	Chromic Oxide"			•			
Current	10 ⁻³ M C1 ⁻	10 ⁻² M C1 ⁻	10^{-1} M C1 ⁻	10 ⁵ M C1			
(milli-	Potentia1	Potentia1	Potential	Potential			
amps)	(Volts)	(Volts)	(Volts)	(Volts)			
0	694	744	761	765			
.025	-1.128	-1.138	-1.147	-1.154			
.050	-1.174	-1.182	-1.184	-1.191			
.075	-1.187	-1.194	-1.195	-1.210			
.100	-1.191	-1.209	-1.212	-1.214			
.125	-1.199	-1.219	-1.236	-1.237			
.150	-1.203	-1.224	-1.242	-1.243			
.175	-1.208	-1.229	-1.252	-1.255			
.200	-1.214	-1.234	-1.262	-1.269			
.225	-1.219	-1.239	-1.270	-1.274			
.250	-1.230	-1.242	-1.274	-1.279			
. 300	-1.281	-1.286	-1.291	-1.300			
.350	-1.317	-1.321	-1.331	-1.334			
.400	-1.331	-1.347	-1.351	-1.359			
.450	-1.352	-1.361	-1.367	-1.371			
.500	-1.373	-1.390	-1.399	-1.402			
.550	-1.394	-1.397	-1.401	-1.403			
.600	-1.410	-1.411	-1.417	-1.421			
.650	-1.419	-1.422	-1.431	-1.435			
.700	-1.441	-1.447	-1.449	-1.451			
.750	-1.449	-1.453	-1.457	-1.471			
.800	-1.468	-1.472	-1.488	-1.489			
.850	-1.469	-1.473	-1.491	-1.492			
.900	-1.472	-1.478	-1.494	-1.496			
.950	-1.485	-1.491	-1.496	-1.496			
1.000	-1.498	-1.498	-1.499	-1.498			

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plotted on Figure 7.18. There are four plots, each of which was established by immersing a zinc electrode into a saturated calcium hydroxide solution with additions of 70 p.p.m. and 300 p.p.m. of sodium chromate and chromic oxide respectively. All plots show an increase in potential with time. Other interesting features of the four plots are that; as the amount of sodium chromate or chromic oxide increases, the potential of zinc also increases, and the potentials of zinc when the two additions of sodium chromate were made were higher than those when chromic oxide was added. It is important also to note that when sodium chromate was added a stable potential was reached while when chromic oxide was used the potential increased with prolonged times.

Figure 7.19 consists of two plots measuring potential with respect to current where current is measured in milliamps. 70 p.p.m. additions of sodium chromate and chromic oxide were made to the saturated calcium hydroxide solution respectively, and both zinc electrodes were passivated in their respective solutions as shown in Fig-There was an abrupt decrease in potential when ure 7.19. current was first applied. The potential when chromic oxide was added reached a value .2 volts lower than the potential when sodium chromate was added. As the current was increased, the potential of zinc when chromic oxide was added only decreased by .05 of a volt over a current range of .2 milliamps. Over the same current range the potential of zinc when sodium chromate was added continued to decrease, after which it too began to level off, but over a smaller current range than for the plot where chromic

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FIGURE 7.18 Measurements of potential with respect to time of zinc in a saturated calcium hydroxide solution with additions of different amounts of sodium chromate and chromic oxide.



FIGURE 7.19 Measurement of potential with respect to current of zinc in a saturated calcium hydroxide solution with additions; sodium chromate and chromic oxide.

oxide was used. At this stage the two plots were almost parallel.

7.2.2. <u>Passivation and Corrosion Characteristics of</u> <u>Zinc in the Presence of both Inhibitor Anions</u> and Aggressive Anions

A series of experiments involving the measurement of potential with respect to time and potential with respect to current of zinc in a saturated calcium hydroxide solution of a pH value of 12.5 were performed. Different concentrations of sodium chromate and chromic oxide were added respectively and to these different concentrations of chloride ions in the form of sodium chloride were also added. Both passivated and clean zinc electrodes were used. The purpose of these experiments was to obtain some information on the passivity and how different concentrations of aggressive anions affect the passivity of zinc in simulated concrete conditions in the presence of inhibitor anions.

Once again the potential of zinc was converted relative to a standard hydrogen electrode (Table 7.1).

Figure 7.20 shows a number of plots of potential with respect to time. A clean zinc electrode was used together with 70 p.p.m. of sodium chromate added to the calcium hydroxide solution. Chloride ion concentrations of 10^{-3} M, 10^{-2} M, 10^{-1} M and $10^{-.5}$ M were used. The plot showing the highest potential is the same one as in Figure 7.17. All plots show an initial increase in potential of zinc. For all chloride ion concentrations the potentials reach a consistent value. As the chloride ion con-

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centration increased, the initial increased in potential of zinc decreased, and so did the constant potential value reached.

Figure /.21 shows a number of plots of potential with respect to time. All conditions are the same as those used to obtain the plots in Figure 7.20 except that for these plots, 70 p.p.m. of chromic oxide was added to the calcium hydroxide solution. The plot showing the highest potentials is the same one as in Figure 7.18 ; the most outstanding feature of these plots is that the presence of small amounts of chloride ions changes the shape of the plots quite considerably.

The plots in Figure 7.22 show a number of plots of potential versus time. All conditions used for obtaining these plots were the same as those used to obtain the plots in Figure 7.19 except that here, 300 p.p.m. of sodium chromate was added to the calcium hydroxide solutions. The plots obtained in this figure are similar to those obtained for Figure 7.20, the main difference being that slightly higher potentials were obtained for all chloride on concentrations when a solution having 300 p.p.m. of sodium chromate was used.

Figure 7.23 consists of a number of plots of potential versus time, and all conditions used for obtaining these plots are the same as those used to obtain all the plots in Figure 7.21, except that here 300 p.p.m. of chromic oxide was added. Once again the plots in Figure 7.23 are very similar to those of Figure 7.21. The only difference being that at a chloride ion concentration of 10^{-1} M the potential of zinc was higher than for the corresponding chloride ion concentration in Figure 7.21.

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FIGURE 7.20

Measurements of potential with respect to time of zinc in a saturated calcium hydroxide solution with a 70 p.p.m. addition of sodium chromate and different additions of sodium chloride.





Measurements of potential with respect to time of zinc in a saturated calcium hydroxide solution with a 70 p.p.m. addition of chromic oxide and different additions of sodium chloride.



Measurements of potential with respect to time of zinc in a saturated calcium hydroxide solution with FIGURE 7.22 300 p.p.m. addition of sodium chromate and different additions of sodium chloride.

Time



FIGURE 7.23

Measurements of potential with respect to time of zinc in a saturated calcium hydroxide solution with 300p.p.m. additons of chromic oxide and different additions of sodium chloride.

Figure 7.24 consists of a series of plots of potential versus time. The conditions under which these plots were obtained were similar to those from which the plots in Figure 7.20 were obtained. The only difference here is that the zinc electrode used to obtain the plots for Figure 7.24 was already passivated. The zinc electrode was allowed to passivate for 5 hours in a calcium hydroxide solution of a pH value of 12.5 containing 70 p.p.m. sodium chromate. It is believed that the passive film hardens with age, and care was taken not to allow this to occur. The potentials of zinc for all chloride ion concentrations and all times are considerably higher than the corresponding potentials in Figure 7.20. The plots for chloride ion concentrations of 10^{-3} M and 10^{-2} M show an initial increase in potential. The plots for chloride ion concentrations of 10^{-1} M and 10^{-5} M show an initial decrease in potential.

Figure 7.25 also consists of a series of plots of potential versus time. These plots were obtained under the same conditions used to obtain the plots in Figure 7.21, but once again an already passivated zinc electrode was used. This time the zinc electrode was passivated in a calcium hydroxide solution of pH of 12.5 with a chromic oxide content of 70 p.p.m. The zinc was allowed to passivate for five (5) hours and care was taken not to allow the passive film to age harden. The potentials of zinc for all chloride ion concentrations and at all times were higher than the potentials in the corresponding plot in Figure 7.21

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Measurements of potential with respect to time of passivated zinc in a saturated calcium hydroxide solution with 70 p.p.m. addition of sodium chromate and different additions of sodium chloride.



FIGURE

7.25

Measurements of potential with respect to time of passivated zinc in a saturated calcium hydroxide solution with 70 p.p.m. addition of chromic oxide and different additions of sodium chloride.

Figures 7.26 and 7.27 show series of plots of potential measured with respect to correctfor different chloride ion concentrations in a calcium hydroxide solution of a pH value of 12.5 with 70 p.p.m. of sodium chromate and 70 p.p.m. of chromic oxide added respectively.



FIGURE 7.26

Measurements of potential with respect to current of zinc in a saturated calcium hydroxide solution with 70 p.p.m. of sodium chromate and different additions of sodium chloride.



FIGURE 7.27 Measurements of potential with respect to current of zinc in a saturated calcium hydroxide solution with 70 p.p.m. of chromic oxide and different additions of sodium chloride.

8. DISCUSSION

8.1 CORROSION OF GALVANIZED REINFORCEMENT IN CONCRETE

A common result in all the accelerated corrosion tests was that iron oxide stains appeared earlier on beams reinforced with black reinforcing bars. The results obtained from the tests on the cylindrical beams where high current density was used cannot be extended to give a quantitative comparison on the life of concrete beams reinforced with black and galvanized reinforcing bars since a high current density was used. A lower impressed current density, such as used for the larger reinforced concrete beams, correlated more closely to a real life situation, but nevertheless, it was far removed from all service condition. These tests were only concerned with the behaviour of the reinforcing bars as anodes and therefore the zinc coating was unable to hinder the initiation of corrosion. However, the zinc coating corroded in preference to the steel and corrosion occurred over a much larger area of the reinforcing bar and was not as localized as the corrosion of the black bar.

8.1.1. <u>Corrosion Characteristics of the Cylindrical</u> <u>Concrete Beams</u>

The only meaningful discussion which can be made of the results obtained from the series of accelerated corrosion tests performed on the cylindrical concrete beams is a qualitative one. A comparative analysis can be made of the results which showed a trend in the corrosion characteristics of the reinforced beams with different degrees of protection (protection here means that the reinforcing bar was passivated by a film, or it was galvanized, or it had

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millscale, or the combination of these) of reinforcing bar.

The trend shown was that, as the protection of the bar increased, so did the uniformity of corrosion of the bar and the time taken for the bar to corrode. This trend was also apparent in the corrosion of the reinforced concrete beams which had a lower current density and constant depth of concrete cover.

The trials were conducted on a comparative basis. The first beam to show rust stains on the concrete surface was reinforced with a 16 mm cold twisted deformed 410C black Excessive corrosion occurred in a few isolated areas bar. (Figure 7.1). During the pouring of the concrete, discontinuities on the bar concrete interface were formed which readily set up differential pH cells and differential aeration cells. Millscale was broken during the twisting process but in many cases did not completely flake off, and this caused further discontinuities. The concrete beam, which had the sodium chromate addition, showed more uniform corrosion on the bar surface, and it took longer for the rust stains to reach the concrete surface. The chromates contained in the concrete were reduced to form a chromic oxide film which was shown in the infra red spectroscopy analysis, but severe corrosion sites were present on the reinforcing bar where the passive film had been broken or not established (Figure 7.2). The beam reinforced with the deformed structural 230 S bar showed more uniform corrosion (Figure 7.4). This bar had the added protection of millscale and corrosion was more uniform. The high impressed current density could not destroy this film as easily as it did the hydrated ferric oxide film. The trend continued in this way. As the amount of protection of the

reinforcing bar surface increased, so did the uniformity of corrosion and time for rust stains to reach the surface. This is demonstrated in figure 7.5 where uniform corrosion sites are shown on the ridges of deformation on the 230 S black reinforcing bar. These ridges could be sites for differential aeration cells where corrosion would have initiated. The galvanized reinforcing bars showed even more uniform corrosion. After 21 days of testing, no rust stains appeared on the surface of the concrete, and the reinforcing bars showed an even layer of white corrosion product (Figure 7.6). The reinforcing bar embedded in the concrete, where sodium chromate was added to the cement, showed white corrosion products where the passive film was broken (Figure 7.8). The white layer could be attributed to the reaction of the zinc with calcium hydroxide which forms calcium hydroxo-zincate. The grey layer which was formed over the white corrosion products could be a combination of zinc chromate, chromic oxide, and calcium hydroxo-zincate.

When a reinforcing bar had little protection differential pH cells and differential aeration cells were set up by discontinuities in the concrete opposite the reinforcing bar. The areas on which the cells formed were oxide free regions at the bottom of accelerated cells, and during an impressed current test, passage of electrons from the impressed current was concentrated at these points and thus caused localized corrosion at these sites. Since the impressed current was constant, the current density was extremely high through these points and corrosion occurred quickly and was highly localized. As the protection of the reinforcing bar increased, these points became less apparent

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because the added protection over the reinforcing bar eliminated the effect of discontinuities in the concrete. That is, if a film exists on the steel surface of the reinforcing bar, a barrier existed between the differential pH and oxygen concentrations cells and the steel surface, thus there was a resistance to the passage of ions and electrons to the steel surface along the length of the bar and corrosion was less localized. In the case of the 410C black bar in the concrete which contained sodium chromate, the film could have formed on the steel surface during the application of the concrete, and thus the differential pH and differential aeration cells were set up during and after the application of the concrete. This means that the points of weakness were still apparent, but not to the same degree as in the case of the cold twisted 410C bar where no sodium chromate was present in the concrete. Thus, these points of weakness were not apparent to the steel surface and hence corrosion was more uniform. It also took longer for rust stains to appear on the surface of beams reinforced with galvanized steels because there were less sites of high current densities. The galvanized bars had the greatest amount of protection and consequently corroded uniformly.

The three concrete blocks, which were reinforced with 16 mm deformed structural 230 S galvanized bar, had different additions made to the concrete. The first had neither sodium chromate nor chromic oxide, the second had 70 p.p.m. of chromic oxide, and the third had 70 p.p.m. sodium chromate. The concrete surface opposite the reinforcing bars was studied. The concrete with neither sodium chromate nor chromic oxide was the most porous

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(Figure 7.11). This porosity was thought to be due to the evolution of hydrogen on the zinc surface. Hydrogen was evolved by the cathodic reduction of water in the concrete. The concrete with 70 p.p.m. of chromic oxide was the next most porous (Figure 7.9) and less hydrogen evolution This was because there were some chromates occurred here. present in the concrete which were reduced instead of water, but water was still reduced to form hydrogen gas. The concrete with 70 p.p.m. of sodium chromate was the least porous of them all (Figure 7.10) and little hydrogen was evolved. The reduction reaction which predominated was the reduction of chromates. This hypothesis is valid since the Pourbaix equilibrium diagram (5) allows for oxidation of zinc and reduction of water at a pH value of 12.

8.1.2. Corrosion Characteristics of Concrete Beams

The accelerated corrosion tests performed on the concrete beams gave comparative results on the life of a concrete beam reinforced with either black or galvanized steel. The main purpose of these tests was to obtain some information on how the geometry and concrete depth of cover affect the life of a concrete beam reinforced with black and galvanized steel.

All tests were carried out under the same conditions and the same impressed current density of .114 amps/m^2 . Time for corrosion of the beams to occur was determined by the time taken for red iron oxide stains to appear on the exposed surface of the beams. This was the time required for a certain amount of corrosion product to be formed to produce the required pressure necessary to crack the concrete cover over the reinforcing bar, plus the time for the iron oxide to diffuse through these cracks to the surface of the concrete beams. When the cracks were formed in the concrete, the corrosion rate was further increased by allowing the sodium chloride solution to penetrate through the cracks to the reinforcing bar surface. This caused the corrosion rate of the reinforcing bars to increase for a number of reasons: firstly, the chloride ions broke down the passivity of the film on the bar surface, secondly, the conductivity of the concrete increased due to the presence of chloride ions in the concrete, and thirdly, differential aeration cells, differential pH cells, and differential salt water concentrations were set up. The rate of corrosion of nonuniformly corroded bars increased more than it did for uniformly corroded bars because cracks formed in isolated areas, and those corrosion cells set up by the salt water had higher current densities at those sites.

Another limitation in the study of accelerated corrosion cells was that the zinc did not provide complete cathodic protection to the steel. Only the zinc coating on the bars facing the exposed concrete face provided sacrificial protection as the zinc coating behind the bar was not subjected to the impressed current.

The results obtained were comparative. For concrete beams with the same concrete cover over the same diameter reinforcing bars, the results can be discussed in terms of corrosion of the reinforcing bar. In cases where different diameter bars and different depths of cover were used, results are discussed in terms of corrosion of the concrete beams.

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It was shown that it took twice as long for rust stains to appear on the concrete surface of a beam reinforced with a 16 mm cold twisted deformed 410C galvanized bar with 10 mm of concrete cover than it did with the corresponding black bar. A factor affecting this result may be the Bedworth-Pilling ratios of iron and zinc, where the ratio of iron is 1.30 times greater than that of zinc. Another factor affecting this result could have been that the corrosion products of zinc have slightly higher diffusion rates than those of iron, although the hydrated ionic radii of both zinc and iron are .74Å (106) this is a valid point since the volume of the corrosion products of zinc are smaller than those of iron for the same amount of corrosion, of the parent materials. Thus it is reasonable to say that the size of the zinc corrosion product particles are smaller than those of iron corrosion product particles, and the zinc corrosion products would be able to diffuse through the concrete at a faster rate than the corrosion products of iron. These two factors affected the pressure produced by the corrosion products where the pressure produced by zinc corrosion products must have been considerably smaller than the pressure produced by iron corrosion products by the same amount of current. Another important factor lies in the appearance of the rust stains on the concrete The rust stains on the concrete reinforced with surface. galvanized reinforcing were much more uniform than those formed on the concrete reinforced with black reinforcing (Figure 7.14 and Figure 7.15). As in the case of the cylindrical concrete beams, the uniformity of staining

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increased with the amount of protection of the steel. With non-uniform stains, small isolated corrosion cells were set up on the reinforcing bar surface even before the accelerated corrosion tests were commenced, and a high current density initiated regions of high corrosion rates.

Before rust stains appeared on the surface of the concrete beams reinforced with galvanized steel, a white residue was first formed on the concrete; this residue was initially first thought to be zinc hydroxide, but because of the fast rate of deposition on the concrete surface it was believed to be calcium carbonate leached from the concrete. Such leaching would lower the pH of the concrete with a resultant decrease in the corrosion resistance of the galvanized reinforcing bar. The high rate of leaching in these experiments could have been caused by the impressed current, and in a field situation, leaching of calcium hydroxide from the concrete would occur at a much lower rate.

The concrete beams reinforced with the various bars and different depths of concrete cover exhibited rust stains in the sequence shown in Figure 7.14. The most apparent result was that the concrete beams with 10 mm of concrete cover showed rust stains before the beams with 20 mm of concrete cover for identical reinforcing bars. The reasons for this are as follows:

> <u>firstly</u>, the corrosion products had to diffuse a larger distance to reach the concrete surface and thus a lower concentration gradient of corrosion products existed in the concrete, and <u>secondly</u>, the increase in concrete cover increased

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the resistance to spalling of the concrete. Although it has been proposed by Magee (75) that increasing concrete cover does not eliminate or reduce the cracking of concrete, in a real life situation, an increase in concrete cover would improve the life of the reinforced beam because a low pH carbonated layer would take much longer to penetrate through the thicker cover and, in the absence of aggressive anions, corrosion would not take place until the pH had dropped in value.

Another feature of the results was that the concrete beams reinforced with 16 mm reinforcing bars showed rust stains on the surface before the beams reinforced with corresponding 20 mm reinforcing bars with the same concrete cover. A deviation from this phenomena was that the concrete beam reinforced with a 28 mm reinforcing bar showed rust stains before its corresponding beam reinforced with a 20 mm bar. Although the ratio of the surface areas (1.25 for 20 mm bar: 10 mm bar) is greater than the ratio of volume of concrete of a cylinder with wall thickness of 10 mm and height of the concrete beam (1.15 for 20 mm bar: 10 mm bar for 10 mm of concrete cover), a possible explanation for the concrete beams reinforced with the 10 mm bars showing rust stains before the beams reinforced with the 20 mm bars could be that the beams with the smaller bars had a higher stress gradient. The beam reinforced with the 28 mm bar showed rust stain before the beam reinforced with the 20 mm bar because the surface area ratio was greater than the volume areas ratio. The results shown in Figure 7.14

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show the same trend as the results for the smaller cylindrical beams showed and that is, as the amount of protection of the reinforcing bar increased, so did the uniformity of stains and the time required for rust to reach the concrete surface. This can be seen in Figures 7.15, 7.16 and 7.17.

The highly alkaline content of the concrete was not a significant factor in determining the life of the concrete beams in the impressed current experiments since it had no effect in hindering the initiation of corrosion in the impressed current experiments. The sodium chromate additions, moreover, only played a role during the initial curing part of the programme when a passive film was established on the zinc surface of the galvanized reinforcing bars. The passive films formed during curing together with the zinc coatings made the heterogeneity of the concrete reinforcing bar interface less apparent but did not hinder initiation of corrosion; it only affected the location and uniformity of initiation.

The heterogeneity on the reinforcing bar sets up points of weakness where the impressed current densities were the highest. Contributing factors to the heterogeneity were aggregates in contact with the reinforcing bars surface. Such areas were initially points of low pH and low sodium chromate content and thus did not allow a passive film to form, while differential aeration and differential pH cells were also formed on the surface

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of the bar. Moreover, cracks in the concrete cover created differential salt water concentration cells. Other discontinuities such as air voids on the reinforcing bar's surface produced the same effects. Cold twisting also produced heterogeneity on the bar surface by creating points of high and low surface stress.

The exposed end of the 16 mm diameter deformed structural 230 S galvanized reinforcing bar, which was subjected to a natural corrosion environment for 16 weeks, had, after 6 weeks, a large deposit of rust in the centre of the bar while there was no rust on the perimeter (Figure 7.12). During this time, dust and rain water fell onto the end of the bar. The dust particles created differential aeration cells while the rain water, which contained impurities, acted as an electrolyte and the steel corroded. This region was too far from the zinc coating for the zinc to provide sacrificial The steel near the perimeter of the protection. bar was exposed to the same conditions, but no signs of rust appeared because the zinc was able to provide sacrificial protection. With time, the rust particles spread with more rainfall and more differential aeration cells were set up. After 16 weeks, the rust grew in area and spread to the perimeter of the bar. On the perimeter, a white residue of zinc corrosion product had also formed (Figure 7.13). As time progressed, the zinc itself, by providing sacrificial protection, corroded.

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Consequently, no zinc remained to protect the steel and thus the steel adjacent to the perimeter also corroded.

8.2 <u>PASSIVATION AND CORROSION CHARACTERISTICS OF</u> ZINC

These experiments on the passivity of zinc were performed, using both sodium chromate and chromic oxide in a calcium hydroxide solution with the intention of comparing the efficacy of the different inhibitor solutions. Chromic oxide is used together with sodium hydroxide (83) to prevent evolution of hydrogen gas on the surface of galvanized steel reinforcement before the concrete is poured, while sodium chromate is used in the concrete to passivate zinc and stop the evolution of hydrogen at the zinc surface. Chromates are reduced in preference to water to stop the evolution of hydrogen.

Chloride ions were added at different concentrations to study the effects of chloride ions on both passivated and clean zinc electrodes in the presence of inhibitor anions. The results obtained are discussed in terms of relative passivity created or destroyed.

In these experiments, potential measurement gave an indication of the passivity of the zinc. As the potential increased, it became more difficult for zinc ions to go into solution, whereas when the potential decreased, it became easier for zinc ions to go into solution. It must be noted at this point that at high potentials pitting corrosion can occur in the presence of aggressive anions and thus increase in potential at high potentials does not necessarily indicate the passivity of the zinc even at high pH values. (107)

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8.2.1. Passivation and Corrosion Characteristics of Zinc in the Presence of Inhibitor Anions

Figure 7.18 shows that all the zinc electrodes were rendered initially passive. The degree of protection obtained with sodium chromate was higher than with chromic oxide in the calcium hydroxide solution. After approximately 120 minutes, the zinc stabilized when sodium chromate was used, while the potential of zinc when chromic oxide was used did not stabilize and corrosion resistance continued to increase, but at a much slower rate. The zinc became more passive with sodium chromate than it did with chromic oxide, and the corrosion resistance increased with increased amounts of both sodium chromate and chromic oxide.

Figure 7.19 shows the two plots of potential measured with respect to current. Zinc electrodes were passivated in the calcium hydroxide solution where additions of 70 p.p.m. sodium chromate and 70 p.p.m. chromic acid were made respectively and measurements were recorded. Both plots show a sharp decrease in potential when a current was first applied. In the solution containing chromic oxide, there was a greater loss of protection of zinc than in the solution containing sodium chromate. The passivity of zinc when chromic oxide was used became quite stable on further increases in the current. The potential of zinc when sodium chromate was used continued to decrease until it too became stable but over a smaller current range. Further increases in current caused the zinc to become more active on both electrodes and the two plots remained parallel. The initial decrease in potential

of the zinc electrodes indicates that the passive film formed in sodium chromate was more stable than the one formed in chromic oxide. This could either mean that two different films were formed, or that one film was more adherent to the zinc surface than the other.

The reduction of chromates produces chromic oxide, and when zinc is oxidized, zinc-chromate also Tests showed a small amount of chromate ions forms. present in a calcium hydroxide solution containing both 70 p.p.m. and 300 p.p.m. of chromic oxide. Thus, on both zinc electrodes, it was expected that a passive layer composed of chromic oxide and zinc chromate would be formed, but because of the smaller concentration of chromate present in the solution where chromic oxide was added, the passive film there would be weaker and thus the zinc would become active. Duval et al (95) and Rehm et al (104) showed that zinc is passivated in a calcium hydroxide solution by the formation of calcium hydroxo-zincate on the surface. This could be the case with the zinc where chromic oxide was used, and as this calcium hydroxo-zincate formed, chromic oxide particles could be incorporated into the film to increase the corrosion resistance of the zinc. Both Figure 7.18 and Figure 7.19 support this analysis. Figure 7.18 shows initial formations of passive films which form at the same rates in both solutions. This could indicate the formation of a film composed of zinc-chromate and chromic oxide. The zinc passivated in sodium chromate became more stable since a greater concentration of chromate was present where a stronger passive film was

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formed. The zinc passivated in the solution containing chromic oxide was not as stable and a calcium hydroxozincate layer continued to grow. The breakdown in passivity, as demonstrated in Figure 7.19, shows that the passive film formed in the solution containing sodium chromate is the stronger of the two. The stable regions in both plots indicates that the same type of film is being disrupted. This film could be the zinc-chromate, chromic oxide film.

8.2.2. Passivation and Corrosion Characteristics of Zinc in the Presence of Both Inhibitor Anions and Aggressive Anions

In Figure 7.20, the plots show that a passive film still forms in the presence of chloride ion concentrations, but the degree of passivity obtained decreases with increasing chloride ion concentrations. Since 70 p.p.m. of sodium chromate was used, a large chromate ion concentration was present, and with a chloride ion concentration of 10^{-.5}M the zinc was passivated but only to a small degree. At the chloride ion concentration of 10^{-3} M and 10^{-2} M, it took 170 minutes for the zinc to stabilize while for chloride ion concentrations of 10^{-1} M and 10^{-.5}M, the zinc stabilized after 15 minutes. This indicates that there was a competition between inhibitor anions and aggressive anions for the zinc surface. At low chloride ion concentration, the inhibitor anions are able to form a passive film, but chloride ions hinder this formation. After some time, the chromate ion concentration is lowered and the chloride ions hinder any further passivation of zinc. As the chloride ion concentration increased, the passivity decreased. The

time for a stable passive layer to form also decreased since the increases in chloride ion concentrations further hinder the formation of a passive film. Gouda et al (28) proposed that a critical concentration of inhibitor anions exists that can tolerate a range of concentrations of the aggressive anions. In the case of Figure 7.20, 70 p.p.m. of sodium chromate provided a concentration of chromate ions greater than the critical concentration for the range of concentrations of chloride ions.

Figure 7.21 shows that at low chloride ion concentrations, the potential of zinc electrode increased at a low rate and the zinc became passive, while at high chloride ion concentrations, the zinc became more active with increase in time. This indicates that the zinc chromate, chromic oxide film does not form at all and that the concentration of chromate ions in the solution containing 70 p.p.m. of chromic oxide is lower than the critical concentration for all concentrations of chloride The increase in passivity at low chloride ion ions. concentrations could only be attributed to the formation of a calcium hydroxo-zincate film. The increase in activity at chloride ion concentrations of 10^{-1} M and 10^{-5} M indicates that there exists a critical concentration of chloride ions above which zinc will not become passive in a calcium hydroxide solution of a certain pH or that there exists a critical pH that can tolerate a range of concentrations of chloride ions.

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Figure 7.22 shows the same as Figure 7.20 except that in Figure 7.22 it is shown that higher degrees of passivity were obtained. This is because much higher concentrations of chromates were present and the effects of the chloride ions were lowered. The passivity at this higher sodium chromate content did not increase to a much higher degree when compared to the passivities obtained in Figure 7.20. This is due to the fact that the concentration of chromate ions was higher than the critical concentration for the range of chloride ion concentrations when the sodium chromate content was 70 p.p.m.

Figure 7.23 is very similar to Figure 7.21, because the chromate concentration was still lower than the critical concentration from the chloride ion concentration of 10^{-3} M, and the pH of the solution containing 300 p.p.m. of chromic oxide was the same as the pH of solution containing 70 p.p.m. chromic oxide.

A linear double logarithmic relationship (28-33) exists between the concentration of an inhibitive anion and the maximum tolerated concentration of an aggressive anion. This relationship resembles a linear relationship between the pH of an alkaline solution and the highest concentration of sodium chloride that can be tolerated.

Figure 7.24 shows that at chloride ion concentrations of 10^{-3} M and 10^{-2} M the corrosion resistance already established increased, while for chloride ion concentrations of 10^{-1} M and $10^{-.5}$ M some passivity was

destroyed. For all chloride ion concentrations, the zinc became stable after the initial effect of the presence of chloride ions. In the case of chloride ion concentrations at 10^{-3} M and 10^{-2} , the potential of zinc increased slightly and a higher degree of passivity was reached than is the case of a clean zinc electrode in the solution containing the same quantity of sodium chromate and having the same concentration of chloride ions. In the case of chloride ion concentrations of 10^{-1} M and $10^{-.5}$ M, less adherent layers of passive film were quickly destroyed or disrupted and a stable condition was soon obtained. Once again, the degree of passivity obtained at those chloride ion concentrations was greater than for the corresponding clean zinc electrodes in the same chloride ion concentrations.

In Figure 7.25, increases in potential of zinc are shown for chloride ion concentrations of 10^{-3} M and 10^{-2} M, while decreases in passivity of zinc are shown in chloride ion concentrations of 10^{-1} M and $10^{-.5}$ M. In the case of chloride ion concentrations of 10^{-3} M and 10^{-2} M, higher degrees of passivity were obtained than those corresponding to the clean zinc electrodes with the same chloride ion concentrations. While in the case of chloride ion concentrations at 10^{-1} M and $10^{-.5}$ M, the loss in passivity caused these zinc electrodes to become active. This once again indicates that either a critical pH exists which can tolerate a certain chloride ion concentration, or a critical chloride ion concentration exists which can destroy or prevent a passive film from forming.

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The plots in Figure 7.26 show that, as the chloride ion concentration was increased, so did the ease with which the passive film could be destroyed. The region of the plot where zinc established a stable state became less apparent with increasing chloride ion concentrations. This indicates that the thin zinc chromate, chromic oxide film formed during passivation is quite readily destroyed by increasing chloride ion concentrations.

A number of theories exist on how chloride ions destroy the passivity of a metal surface. Since passive films of a different nature were observed to have formed, let us consider each film individually. The passive film formed when the zinc was exposed to the calcium hydroxide solution containing sodium chloride was a zinc-chromate chromic oxide film. When it formed in the presence of chloride ions, there was a competition between the two species of anions for the zinc surface. Since the concentration of chromate ions was higher than the critical concentration for all chloride ion concentrations, the film was able to form. Passivity decreased because either some chloride ions were incorporated into the passive film and reduced its protective properties, or the chromate ion concentration near the zinc surface decreased due to reduction The chloride ions could have then of chromates. prevented further formation of the film. When chloride ions were exposed to an already formed passive film, at higher concentrations of chloride ions, loosely

bound film could have been destroyed by the action of the chloride ions. The passive film formed when the zinc was exposed to the calcium hydroxide solution containing chromic oxide had a thin layer of zincchromate and chromic oxide, but the greater proportion of the film was composed of calcium-hydroxo-zincate. When low concentrations of chloride ions were present, they prevented the formation of zinc chromate because of the low concentration of chromate ions, and passivity was reduced by the incorporation of chloride ions into the passive film. At high chloride ion concentrations, the zinc became active because of the high number of chloride ions becoming incorporated in the passive film.

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9. CONCLUSION

The corrosion resistance of reinforcement embedded in concrete at depths of cover from 10 mm and 20 mm when subjected to impressed current improved when the reinforcing bar was galvanized and when the diameter of the bar was increased.

The galvanized bar increased the corrosion resistance by firstly providing sacrificial protection and by also eliminating the effect of discontinuities on the reinforcing bar surface. Discontinuities on the reinforcing bar surface set up sites of high impressed current densities, and the effect of these was assessed or eliminated by increasing the protection of the reinforcing bar.

Increase in the diameter of the bar increased the **beam life** by producing a lower stress gradient produced by the corrosion product. On the other hand, the ratio of the surface areas is greater than the ratio of concrete volumes for a larger and smaller bar diameter, but this factor is insignificant under service conditions, and thus it would be reasonable to say that the life of a beam reinforced with a larger galvanized bar would be longer than one reinforced with a smaller bar.

Zinc was passivated in calcium hydroxide solution by the formation of calcium hydroxo-zincate film. Zinc was

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found to passivate in calcium hydroxide solution containing sodium chromate and chromic oxide respectively. In a calcium hydroxide solution containing sodium chromate, chromate ions were reduced, thus eliminating the reduction of water which produced hydrogen gas. A passive film consisting of zinc chromate and chromic oxide passivated the zinc. In a calcium hydroxide solution containing chromic oxide, small concentration of chromate ions was present and these decreased the degree of reduction of water, and passivated the zinc to a smaller degree by the formation of a zinc chromate and chromic oxide film. Calcium hydroxozincate was also produced which helped in passivating the zinc surface.

Chloride ions in the presence of chromate ions will compete for the zinc surface. It was found that a calcium hydroxide solution containing 70 p.p.m. of sodium chromate had a chromate ion concentration greater than the critical concentration for a chloride on concentration of 10^{-.5}M. In the case of 70 p.p.m. and 300 p.p.m additions of chromic oxide to the calcium hydroxide solution the chromate ion concentration was less than the critical concentration for a chloride ion concentration of 10^{-3} M. and passivity was due to the formation of a calcium hydroxo-zincate film . In both cases where chromic oxide additions of 70 p.p.m. and 300 p.p.m. were made to the calcium hydroxide solution, zinc passivated at chloride ion concentrations of less than 10^{-1} M and zinc became active at chloride ion concentrations of 10^{-1} M and greater. Thus it is reasonable to assume that a crit-

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ical pH exists which can tolerate a certain range of chloride ion concentrations.

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