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CORROSION OF STEEL REINFORCEMENT IN CONCRETE

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INTRODUCTION

Although corrosion is an important aspect to be considered in the design of reinforced concrete structures, corrosion in service is not a usual problem in the great majority of reinforced concrete applications. It is only in a limited number of cases, which usually have involved poor workmanship, improper construction practices, and inadequate design procedures as well as exposure to aggressive environments, that corrosion has been a problem.

The purpose of the paper is to present information on the nature and mechanics of corrosion of steel, information on the factors associated with the concrete and steel which will influence corrosion, and to discuss preventative methods to inhibit corrosion. The paper is primarily concerned with corrosion of reinforcing bars, however, information obtained from the use of prestressing wire has also been included because of the lesson which might be learned. The paper has been written for the engineer and not the scientist.

NATURE AND MECHANICS OF CORROSION OF STEEL

The current state of knowledge on the subject of corrosion has evolved rapidly over the past twenty years, however, there are still many aspects of the problem which are not fully understood. The corrosion mechanism, even when restricted to a single system, is extremely complex. This becomes evident when it is realized that the many factors which may influence the various reactions are not necessarily independent. Consequently, it comes as no surprise to find different theories that attempt to explain the corrosion phenomenon and that often conflict with one another. No attempt will be made in this report to enumerate all the various theories that have been presented by authorities in the field. However, there are certain facts pertaining to corrosion which have been well established by means of considerable study and research. The purpose of this section will be to incorporate these recognized facts into a discussion on the corrosion of reinforcement.

To fully understand the influence of the width of a crack with regard to corrosive attack on reinforcement it is necessary to first acquire a basic understanding of the general corrosion mechanism. In addition, a study of the various factors influencing the corrosion phenomenon must be made both in the general case and in the case of reinforcement embedded in concrete.

Mechanism of Corrosion

Corrosion may be defined as the deterioration or destruction of a metal due to chemical interaction with its environment. The reaction may be brought about by direct chemical attack, but more commonly, it is electro-chemical in nature. According to Evans, (1)* corrosion may be generally considered as any transformation whereby the metal goes from the elementary condition to the combined condition. In this aspect, it may be viewed as the opposite of the chemical process in which a metal is refined from its ore. No matter how the reaction is defined, it is a function of the metal, the chemical environment, and the mechanical and physical conditions existing in the system under consideration (2). By far the most common types of corrosive attack, including that on reinforcement embedded in concrete, are those produced by electro-chemical driving forces.

A review of the basic galvanic cell will aid in developing an understanding of the electro-chemical reaction on reinforcement in concrete. A galvanic cell is set up when two dissimilar electrodes, separated by an electrolyte, are electrically connected by a conductor. Perhaps the simplest type of galvanic cell is the flashlight battery as shown in Fig. 1a. Zinc, used in the battery case, serves as one electrode anode and the center carbon rod cathode serves as the other. The space between the electrodes is filled with an electrolyte which is an aqueous paste material.

Zinc enters into solution in the form of metallic ions. Hydrogen ions migrate through the electrolyte to the carbon rod where they are plated out as hydrogen gas.

A galvanic cell also exists when two similar metals are separated by dissimilar electrolytes as shown in Fig. 1b.

In any galvanic cell, the electrode at which the metallic ions enter into solution is known as the anode and eventually is deteriorated by continuous ionic flow. The other electrode is called the cathode.

The actual mechanism involved when reinforcement in concrete is subject to corrosive attack is similar to these basic galvanic cells, but much more complicated. Consequently, a more detailed discussion of the general electrochemical mechanism will ensue to enable a more complete understanding of the corrosion phenomenon.

* Numbers in parentheses refer to items in the list of references.

The electrochemical mechanism may be considered as providing an alternate path for the chemical reaction. In order for this to take place, there are three conditions which must exist: (a) there must be a potential difference between two metallic areas, (b) there must be a conduction path and (c) there must be an appropriate electrode reactions taking place (2). A difference in potential may arise from almost any conceivable heterogeneity of the system, that is, any assymetry of the metal, or the environment, or both. The various effects of such assymetries will be discussed in the section dealing with the influence of factors associated with the metal and the environment.

Typical Chemical Reactions

The tendency of a metal to oxidize to a metal ion in an aqueous solution of normal ionic activity at standard temperature is given in the electromotive force series. A normal hydrogen electrode is usually selected as an arbitrary reference. Any metal high in this series will have a greater tendency to corrode. Consequently, iron which is relatively high in the Electromotive Series will have a substantial tendency to enter into solution. As previously mentioned, the area where the metal ions go into solution becomes the anodic region. The ionization of the metal at the anode is often referred to as the first or primary stage of the corrosion reaction and may be represented by the following equation: (2,3).

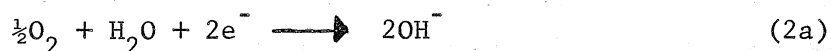


The anodic region of the metal now has an excess of electrons as indicated by Reaction (1). To maintain equilibrium of electric charges an equivalent quantity of hydrogen is plated out at adjacent surfaces of the metal. This results in a thin invisible film of hydrogen around the cathode and this protective film inhibits further progress of the reaction as shown in Fig. 2a. Consequently, any subsequent reaction will cease unless the hydrogen film is removed in some manner.

The destruction of the film may take place in one of two ways:

- (a) oxygen depolarization at the cathode, and (b) hydrogen evolved as a gas, (2, 3, 4) as shown in Fig. 2b.

(Cathodic reactions)



These cathodic reactions which are often called the secondary reactions are the controlling reactions on the rate of corrosion for iron or structural steels. Therefore, any environmental condition which influences these reactions will likewise influence the rate of corrosion. Corrosion processes characterized by the cathodic depolarization by oxygen (Reaction 2a) are probably of widest importance (4). Since this reaction is dependent on the concentration of dissolved oxygen next to the metal, it is influenced by the degree of aeration, temperature, salt concentration, etc. (3) Reaction (2b) generally isn't characteristic of the corrosion of steel in concrete; however, it should be mentioned that such reactions will take place in either acid solutions or concentrated alkaline solutions.

The secondary reactions permit the primary reaction to proceed with the accumulation in the solution of ferrous ions, Fe^{++} , which in the presence of water and oxygen are oxidized and precipitated as rust. Two states of oxidation may exist depending mainly on the availability of oxygen (1, 3, 5). The first state, ferrous hydroxide, is more soluble than the second, hydrated ferric hydroxide. The first is usually formed directly at the metal surface and is converted to the latter at a little distance away from the surface where it is in contact with more oxygen as shown in Fig. 3. If the supply of oxygen is limited, the product may be green hydrated magnetite or black anhydrous magnetite, but these products are relatively uncommon. In between the two layers of ferrous hydroxide and ferric hydroxide there may exist combinations of the two compounds.

The structure and composition of the rust varies considerably with the conditions prevailing during its formation and the structure plays an important role in the subsequent corrosion process (3, 5). If the rust layer is hard, dry, and fairly adherent to the metal surface, then it may retard corrosion by forming a protective coating. On the other hand, if the layer is spongy and readily detachable it will absorb oxygen and moisture from the surrounding media and consequently will add to further activity.

In summary, electrochemical corrosion brings about a combination of iron with oxygen and water, yielding an oxide which may exist in two states

depending on the amount of available oxygen. This process differs from direct oxidation in that the iron goes into solution at one place (the anode), oxygen is taken up at a second (the cathode) allowing the first reaction to proceed and resulting in the formation of the oxide. The oxide product may either accelerate or retard further reaction depending on its physical condition.

If a process comprises two or more reactions, as in the case of electrochemical corrosion, then the rate of the process is determined by the rate of the slowest of these reactions under the particular conditions (3). In most cases, the primary reaction is much faster than the secondary reactions and since the dominant influence on the latter is the oxygen concentration of the media, then it is likewise the dominant influence on the rate of the overall corrosion process. However, there are other factors which may also enter the picture. If the cathode is large and consequently exposed to a greater amount of oxygen, then the cell current may be quite strong in relation to the size of the anode (3). This intensifies the attack and results in a greater rate of penetration at the anodic region.

It should be pointed out that the magnitude of the electrochemical potential determines the tendency of the reaction to proceed, whereas the rate of corrosion is determined mainly by resistance to the continued process set up by certain of the corrosion by-products. There are three conditions which may exist that will tend to resist the continued reaction (2): (a) the supply of electrons at the metal surface takes places much more rapidly than the supply of retractable particles from the media, (b) the corrosion product serves as a protective coating as previously mentioned and retards the rate of corrosion, and (c) the discharge reaction is retarded even though there are sufficient electrons and solution particles available at the metal-solution interface. This third condition is a general problem of electrode kinetics which is still not perfectly understood. When any of the above conditions exist, the electrode potential changes and the electrode is said to be polarized. If the slope of either the cathode or anode polarization curve is increased, the local cell current is reduced and consequently the corrosion rate is reduced. Conversely, a reduction of the slope increases the corrosion rate. Such reduction in slope of the polarization curve is termed "depolarization" and may be brought about by increasing the electrode area or by introducing chemicals which aid the electrode reaction.

CORROSION OF STEEL REINFORCEMENT EMBEDDED IN CONCRETE

Now that the general corrosion mechanism has been considered, the discussion can proceed into the subject of primary interest, that is, the corrosion of reinforcement in concrete.

Even in the simplest cases, the corrosion process is extremely complicated and is greatly and diversely influenced by numerous factors, both external and internal. Often it is found that the effect of a single factor may not be difficult to determine, but it is a different matter when having to estimate the net effect of several factors working in conjunction with each other. Therefore, the discussion to follow will consist mainly of a study of each of the variables and their singular effect on the corrosion reaction.

It is quite difficult to make a general classification of the various factors and several different schemes have been employed. In the section on the corrosion mechanism, it was pointed out that the contact of a metal and an electrolyte in the presence of potential differences at the metal surface is the necessary condition for corrosion. These local differences are caused by factors inherent in the metal and/or by factors associated with the electrolyte (6). The factors associated with the electrolyte, the concrete in our case, is usually characterized by local differences in chemical composition. However, this is not the only scheme that may be used. Speller (3), for instance, separates the factors which govern this tendency of the corrosion reaction to proceed from those which influence the rate of reaction. In this report the former classification will be used.

Factors Associated with the Steel

If the metal surface consists of any heterogeneities, there will be differences of effective potential thus establishing probable corrosion cells. Non-homogeneities may be caused by differences of chemical composition over the surface, discontinuous surface layers, or differences in texture (3). Differences in chemical composition may be due to any heterogeneity characterized by impurities, grain boundaries, or a variation in corrosion resistance of the micro-structure (2).

Carbon is an effective alloying element for increasing the strength of the steel, but is undesirable with regard to intergranular corrosion. Excessive percentages of carbon alloyed with iron may produce metallic phases, such as ferrite (alpha iron) and cementite (Fe_3C). The metal is, therefore, more susceptible to corrosion due to the weakened resistance along the existing

phase boundaries. This effect is best explained by energy considerations of the crystalline structure. Less work is needed to dislodge an atom at the boundary of two differently oriented crystals than to dislodge an atom in a crystal interior having all its neighbors similarly oriented; thus corrosion often starts at intergranular boundaries (11). Alloying elements such as carbon in steel do not markedly affect the total corrosion if the reaction is of the oxygen depolarization type (4) as given by Reaction 2a. Their effect is to create weak points in the surface film thus increasing the corrosion probability.

In the case of steel embedded in concrete, the presence of a broken layer of mill scale is one of the main sources of potential differences (6). Discontinuities in the mill scale expose areas of the metal surface to chemicals which may be absorbed by a permeable concrete thereby perpetuating localized corrosion. The seriousness of this condition is obviously dependent on the chemical composition of the electrolyte. Here, then, is a good example of the interdependence of the many influencing factors.

From what has been said, it is seen that there is always some characteristic of the metal structure, some degree of segregation, or some presence of impurities which is sufficient to produce varying potentials. These factors inherent in the metal tend to increase the probability of corrosion and, additionally, may tend to localize the action. From the standpoint of total corrosion, however, these factors are not as important as the external conditions which may exist (3).

Another source of differences in potential is due to stress either static or cyclic, in the reinforcement. Borgmann views this as simply a modification of the bimetallic couple problem; the crystalline structure in the strained areas having a somewhat different configuration from that in the unstrained areas (4). The rearrangement is such that the strained regions become negative or anodic to the unstrained regions thereby setting up electrochemical couples (5). Generally, it is tension stresses which cause trouble in corrosion. Tension stresses exert a force on the grain boundaries at the metal surface and if corrosion sets in along these boundaries, the stresses will open the grooves produced between the grains. This effect exposes the boundaries to further corrosive attack and at the same time creates stress concentrations which disrupt protective surface films and predisposes the metal to continued attack (1, 2).

In the case of static stresses, the corrosion is usually intergranular. In the case of cyclic stresses, the attack is generally transgranular and tends to follow those planes so situated that the resolved shear stresses are maximum. If the range of alternating stresses exceeds a certain value defined as the "fatigue limit", any crack originating at the metal surface will propagate through the cross-section until fracture occurs. Below the fatigue limit failure will never occur, no matter how many cycles are applied, provided that corrosive influences are absent. If corrosive conditions are present the metal structure, being unstable, will deteriorate at the crack boundaries and the crack will extend no matter how low the stress range (1).

This mechanism is not believed to be of great importance in reinforcing bars but it does occur in prestressing steels. The stresses in bars for ordinary reinforced concrete are generally much lower than for prestressing steels. Certainly in prestressed concrete structures and in structures subjected to fatigue loading, precautions must be made to protect the concrete from a corrosive environment. In instances where such precautions were not taken severe effects have been observed and in certain cases failure of the entire structure occurred. (7, 8, 9).

Another factor inherent in the metal is the tendency of the metal to form a protective film. This is commonly referred to as the passivity of the metal. Passivity is the ability of a metal to become abnormally inactive in a given environment; in other words, a passivated metal is characterized by a more noble potential under certain environmental conditions. It should be mentioned that although passivity is due to a protective film on the metal surface, it is still associated with the properties of the metal itself. The passivity of a metal is affected by environmental factors--these factors dictating the duration of the transitory passive state (5). It follows, then, that the behavior of a passivated metal is controlled by either physical or chemical changes in the surface film and these changes are generally brought about by various environmental factors.

Various theories of passivity have been suggested over the past years. A fairly thorough discussion of these theories is presented by Pollitt (5).

Factors Associated with the Concrete

In the basic concrete-steel system, electrochemical cells are in most cases set up by heterogeneities of the concrete media. Two types of corrosion cells may exist depending on the prevailing conditions (10). The first type, often called the micro-cell, is characterized by microscopic distances separating the anodic and cathodic regions. Such cells are set up when moisture containing oxygen, carbon dioxide, and chloride salts penetrates the concrete surface and migrates to the reinforcement. Under these conditions the so-called "micro-environment" is no longer inhibitive of corrosive action and numerous micro-cells will operate. Most common among this type are the mill scale cell and the differential aeration cell. The second type commonly known as the macro-cell operates when the concrete permeability varies from place to place on a macro-scale. Reaction variables which influence macro-cell corrosion are the moisture content, chloride content, pH at the concrete-steel interface, and the amount of available oxygen. The basic galvanic cells described earlier fall in the macro-cell class and are the easiest to visualize.

Before investigating these environmental factors and their influence on the corrosion reaction it may be well to list the constituents of the concrete media. Hardened concrete made from portland cement, sand, gravel, and ordinary tap water will contain the following (10):

1. Sand and gravel, usually considered inert.
2. Particles of unground cement clinker, also considered inert.
3. Calcium hydroxide and small amounts of other alkalies.
4. Hydrated cement minerals (calcium silicates, calcium aluminates, and calcium alumino ferrites)
5. Varying amounts of uncombined water.
6. Calcium carbonate and calcium sulphates.

When moisture is present the concrete medium becomes an electrolyte containing mainly calcium hydroxide. The various ions present which could influence the corrosion reactions are hydroxyl, calcium, sodium, potassium, carbonate and sulphate ions.

Effect of pH: Speller (3) simply states that corrosion in acid solutions tends to be more rapid than in neutral solutions ($\text{pH} = 7$) and the latter is more rapid than in alkaline solutions ($\text{pH} > 7$). It follows then, that the influence of alkalies on the corrosion reaction is inhibitive. Metzger (11)

has shown with the use of the Pourbaix Diagram that corrosion will occur for Fe-H₂O at 25°C for pH values between 0 and 10 and for pH values greater than 12. These values are dependent on the electrical potential.

It has been shown by Mayne and Menter (12) that steel becomes passive in sodium and calcium hydroxide solutions due to the formation of an impervious layer of ferric products on the steel surface. Weak areas in the initial rust layer are first repaired by the formation of ferrous hydroxide which then reacts with oxygen to form Fe₃O₄ (magnetite) and Fe₂O₃ (ferric oxide). Later repair may occur by direct electrochemical production of ferric oxide. If, for some reason, the hydroxyl ion concentration is reduced, the protective layer would be disrupted and corrosion would proceed.

Influence of oxygen--differential aeration: Oxygen may be considered not only as an essential factor to corrosion, but as the one primarily responsible for the progress and rate of corrosion (3, 5, 6, 10). Oxygen acts as a depolarizer at the cathode as indicated by Reaction (2a), and consequently tends to increase the velocity of corrosion. Dissolved oxygen alone will accelerate corrosion in acid, neutral, or slightly alkaline electrolytes. All things being equal, the rate of corrosion in a neutral solution is almost directly proportional to the oxygen concentration (3). The influence of dissolved oxygen on the corrosion process is illustrated by the qualitative curves shown in Fig. 4. These curves, obtained from experiments by Mayne, Menter and Pryor (12) are representative of iron specimens immersed in sodium hydroxide solutions. Curve I represents the corrosion rate in a de-aerated solution; the sharp break in the curve takes place at time X when air was admitted into the solution. Curve II represents the corrosion rate in a similar solution except that the system was in contact with air throughout the entire experiment.

The chief action of oxygen is as a depolarizer at the cathode, but at the anode it may lead to the formation of protective layers (4, 6). This is specially important in the case of steel where the formation of insoluble ferric hydrates influences the rate and probability of corrosion. Thus, oxygen may play a dual role: as a depolarizing agent, it tends to enhance corrosion; on the other hand it may produce protective layers over the anodic regions prohibiting further reaction. It has been shown that as the oxygen availability is increased, the probability of corrosion is decreased, whereas the intensity of attack is increased (4).

Differential aeration, that is, the unequal distribution of oxygen over the steel surface, will set up anodic and cathodic regions (1, 3, 4). Regions of the metal least accessible to oxygen become anodic, and regions readily accessible to oxygen becomes cathodic. Thus, the presence of oxygen in varying concentrations along the reinforcement will tend to increase the probability of corrosion. The influence of differential aeration emphasizes the deleterious effects of cracking and of porous concrete; two conditions which allow the penetration of oxygen to local areas of the reinforcement.

Influence of moisture--differential moisture contents: As mentioned previously, the corrosion reactions will occur only if moisture is present. Therefore all corrosive factors become ineffective in the absence of moisture (10). Additionally, moisture penetration is the means whereby any exterior substances such as chloride salts, carbon dioxide, and dissolved oxygen may gain access to the reinforcement. Corrosion macro-cells may be set up by differential moisture contents along the reinforcement--the regions having the greatest moisture content being anodic (13).

Influence of chloride ion concentration: The influence of chloride ions is not as readily predictable as the influence of pH. However, it is well known that the presence of salts may be expected to increase the corrosion rate if only because it is conducive to ionic activity (2, 3, 5, 14). Salts, derived from the combination of strong acids and weak bases, will hydrolyze in a solution giving a definite concentration of hydrogen ions (5).

However, the presence of salts provides two opposing effects: (a) it increases the conductivity of the electrolyte thus raising the corrosion rate, and (b) at high concentrations it diminishes the solubility of oxygen and thereby may lower the corrosion rate. Consequently, as the salt concentration of the electrolyte is increased, a maximum corrosion rate would be expected as shown in Fig. 5 (2, 3, 5). Thus, the influence of salts depends chiefly on their concentrations.

The inhibiting influence of salts present, in high concentrations, is not entirely due to the subsequent decrease in oxygen solubility. Experiments have shown that the reduction of the corrosion rate in saline solutions is not proportional to the reduction of oxygen solubility. It is, in fact, much more rapid as shown in Fig. 6(5). It is believed that the precipitating action of the negative salt radicals comes into play when the critical concentration is exceeded, and the corrosion rate is thereby retarded. Further

increases in salt concentration will continue to retard corrosion and a concentration may be reached at which complete prohibition occurs (5).

Therefore, the effect exhibited by the various salts depends not only on their concentration, but also by their negative ion valencies which reflect their precipitating power. The relative precipitating powers of various negative ions have been investigated and found to have the following ratios (5).

Chromates and Bichromates	1000
Sulphates	670
Chlorides and Nitrates	3

Since chlorides exhibit a low precipitating power as shown in the above table, a relatively high concentration of such salts is required for corrosion to be retarded. Therefore, the influence of sodium chloride and other such salts is usually to enhance the corrosion process unless they are present in abnormally high concentrations.

To ascertain the effect of sodium chloride and sea salts on the pH value of an alkaline media, Shalon and Raphael (14) conducted a series of tests in which steel bars were immersed in calcium hydroxide solutions of various concentrations. The pH values were reduced proportionally with salt concentration as shown in Fig. 7. A schematic presentation of the effect of both salt concentration and pH in a $\text{Ca}(\text{OH})_2$ solution is illustrated in Fig. 8 also taken from Shalon and Raphael's report (14). As the concentration of salt increases, the protection afforded by the higher alkaline solution (pH = 12.6) is reduced and rust development takes place at an increased rate. Past the critical salt concentration, the inhibitive influence of the negative salt ions comes into play. Therefore, when water containing soluble chloride salts penetrates the concrete, the margin of safety derived from the alkalinity of the concrete is markedly reduced. The investigators concluded that "the alkalinity of air-exposed concrete penetrated by saline water is insufficient for complete inhibition of corrosion of the reinforcement" (14).

Different salt concentrations at various regions of the reinforcement tend to produce corrosion micro-cells and thus increases the corrosion probability. Differential salt concentrations, therefore have an effect similar to that of differential aeration and differential moisture contents.

Influence of carbonation: If carbon dioxide is absorbed into the concrete, the calcium hydroxide will be converted to calcium carbonate thereby reducing the pH and, consequently, the protective value of the concrete (6, 7, 10, 15). Values of pH of 10 and lower may result, especially if sulphur dioxide is also present. Enough evidence has been accumulated, however, to prove that in a concrete of high quality (low permeability) atmospheric carbonation isn't likely to proceed beyond a few millimeters, thus the pH in the region of the reinforcement is not affected (14). Carbonation also tends to increase the shrinkage of concrete and thus promotes the development of cracks (15). Shrinkage cracks will increase the porosity of the concrete hence allowing the penetration of moisture and other external chemicals which may promote corrosion.

Quality of concrete: The permeability of concrete is probably the most important single factor affecting the corrosion of the reinforcement (10, 15). Concrete of high permeability will have a high electrical conductivity and will allow the penetration of deleterious substances to the reinforcement. Concrete permeability depends on numerous factors, some of which are: water-cement ratio, richness of mix, aggregate size, aggregate grading, methods of compaction, curing, etc. A detailed discussion of the more significant factors which govern concrete permeability is presented later.

Low quality concrete is also characterized by voids of appreciable size adjacent to the reinforcement. In prestressed concrete the dimensions of the voids may be in the order of the reinforcement (9). High moisture contents may exist in such voids thereby setting up macro-cells perpetuating rapid corrosive attack (10).

Influence of storing conditions: Corrosion has been found to be greater when concrete is stored under moist conditions than when stored under dry conditions. If the atmosphere in the region of the concrete member has a relative humidity of 50 per cent or less, corrosive action may be reduced to zero (16). Likewise, structures permanently immersed in water will exhibit little or no corrosion of the reinforcement. The concrete of submerged structures generally maintains a high pH value and a uniform salt concentration thus reducing the occurrence of corrosion cells (14). Probably the main reason why submerged members are protected, however, is that oxygen starvation takes place, i.e., no air is available at the concrete surface and thus can not penetrate to the reinforcement.

Effect of temperature: The corrosion of concrete reinforcement is not greatly influenced by temperature (either curing temperatures or environmental temperature gradients); therefore, this factor will only be briefly discussed. A rise in temperature may result in a two-fold effect: (a) the reaction rates are generally increased and (b) the oxygen solubility is decreased, hence, reducing the rate of corrosion (2, 5). An extreme rise in temperature, however, will accentuate the effects of the other reaction variables previously mentioned and may bring into action factors which otherwise would be negligible.

Effects of Corrosion

In most cases, the corrosion rate is extremely slow and the normal life span of a structure is not largely affected. However, if the external and internal conditions are such that a corrosive environment exists, a destructive action may take place at an increased rate and create serious problems.

Intensified corrosive action produces deep pitting and a severe loss of cross-section of the reinforcement. This is particularly serious if the reinforcement is subjected to high stresses as in the case of prestressed beams or structures carrying large loads. A combination of high stress and intense corrosion will produce stress concentrations that may result in rupture of the reinforcement.

Corrosion cracking is another problem which may occur under intensified corrosive attack on the reinforcement. Severe corrosion of the reinforcement usually results in cracking of the concrete in a direction parallel to that of the reinforcement. These cracks result from internal pressures created by the oxide rust products which occupy a greater volume than the deteriorated metal. In advanced cases, entire sections of the concrete are spalled off thereby exposing the reinforcement to the atmosphere. Corrosion cracks usually progress most rapidly where shearing stresses are the greatest and where slipping occurs due to loss of bond (17).

As the corrosion reaction progresses with continued destruction of the reinforcement at the anodic regions, a migration of alkali ions to the cathodic areas takes place. If the corrosion cell potential is sufficiently high, alkaline compounds will precipitate out on the reinforcement and cause a subsequent loss in bond strength (13). However, such a reaction is usually predominant only when external EMF's are applied to the system and, therefore, is not characteristic of natural corrosion.

The Protective Properties of Concrete

Under most conditions, portland cement concrete provides the reinforcement with good protection from corrosion. The protective value of concrete is derived from its high alkalinity and from its low electrical conductivity in atmospheric exposure (9, 15). Shalon and Raphael (14) found the average pH of mortar mixed with tap water to be about 12.8. By means of further investigation they concluded that complete inhibition of corrosion apparently occurs when the pH is equal to or greater than 12.

This passivation process associated with high alkalinity is best explained by a brief description of the mechanism of protection given by Unz (18), and Mayne and Mentor (19). The galvanic conditions produce anodic and cathodic regions. In the anodic zones ferrous ions go into solution and are oxidized forming a soluble ferrous hydroxide. In the presence of oxygen and alkali, however, the solubility of ferrous hydroxide is diminished, and instead of passing into solution it is converted to a hydrated ferric oxide ($\gamma - \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) in physical contact with the reinforcement. It is suggested, then, that this oxide arises from the oxidation of ferrous hydroxide produced by an anodic discharge of hydroxyl ions on the metal surface. As this process continues, the half-cell (open-circuit) potential becomes more noble and with subsequent reaction this "cement skin" of insoluble ferric oxide becomes stronger. The electrical resistance of this coating rises up to an asymptotic maximum value and a state of equilibrium is eventually reached. If, however, there are serious breaks in the coating, such as large voids adjacent to the reinforcement, the equilibrium state breaks down and corrosion ensues.

Dry concrete is almost a perfect electrical insulator, however, the smallest amount of humidity gives it considerable conductivity (18). As the concrete dries with aging the resistivity increases thereby inhibiting macro-cell reactions.

PREVENTION OF CORROSION

Since the corrosion of reinforcement is primarily due to the penetration of deleterious materials, prevention methods should either eliminate this penetration or render the reinforcement passive in the presence of these materials (10). Over the past years, several methods of prevention have been introduced: some with success and others which either proved ineffective or too costly for economic use. This section is devoted to a brief discussion of the more widely used prevention methods which are as

follows:

1. Structural design -- adequate amount of cover
2. High quality mix
3. Non-reactive materials
4. Cathodic protection
5. Surface coatings
6. Oxygen starvation
7. Anodic inhibitors
8. Construction techniques

Structural Design -- Adequate Amount of Cover

In the design of structures care should be taken to avoid dangerous features which may lead to corrosive condition; such as poor draining systems which allow collected water to flow over the concrete instead of being thrown clear. Pools of rainwater on roof slabs or bridge decks can leach out the hydroxides from the concrete and collections of saline water can make salt available for penetrations. In structures located in a corrosive environment, reinforcement should be held to a minimum in members not subject to high loading such as hand rails, balustrading, curbs, walkways, and the like.

Probably, one of the more important factors associated with structural design is the amount of cover. This factor must obviously be considered with permeability (i.e. the quality of the concrete mix) since 2 inches of permeable concrete may afford less protection to the reinforcement than 1/4 inch of impermeable concrete. The required thickness of cover also depends on the environment and exposure of the structure. Because of this, various requirements have been suggested depending on the environmental conditions and the quality of concrete used.

In marine environments, Lewis and Copenhagen (10) suggest a minimum cover of 3 inches and state that 2 inches is essential. The Port of Los Angeles sets a minimum of 3 inches for marine exposure. AREA specifies a 3 inch cover from plane and curved surfaces and a 4 inch cover at corners. AASHO specifies a 4 inch cover in all cases except for prestressed concrete piles where a minimum of 3 inches is allowable. However, a number of state highway departments have reduced the required cover of prestressed concrete to 2½ inches.

The exposure of concrete on inland structures generally does not present a corrosion problem. However, in locations where de-icing materials

are often used, AASHO recommends 2 inches of cover in roadway decks and adjacent appertenances such as curbs, sidewalks, and railings.

Some investigators who have studied the problem of adequate cover concluded that increasing the depth of cover is not as effective as one might suspect. Pletta, Massie, and Robins (16), for example, state that the rate of corrosion decreases with an increase in cover up to about $\frac{1}{2}$ inch; thereafter, little change is noticeable. Kinnemann, (20) observed that $\frac{1}{2}$ inch of high quality concrete will completely protect the reinforcement from salt water corrosion. Therefore, adequate depth of cover can not be recommended unless specifications are set on the quality of the concrete.

High Quality Concrete Mixture

For a given thickness of cover, the permeability of the concrete will determine the degree of penetration for a given environment. By means of modern concrete technology, it is possible to design a high quality, impermeable concrete which will greatly sustain the life of a structure in a corrosive environment. Concrete permeability has been found to rely on numerous factors, the more important ones being: water-cement ratio, cement-aggregate ratio, aggregate grading, and consistency (10). Shalon and Raphael (14) give the following definition for a high quality concrete: "The kind of concrete which can be achieved only by close attention to every detail in connection with the selection of materials, proportioning of the mix to produce a truly plastic concrete having a relatively low water-cement ratio, and thorough consolidation of the concrete as placed".

Tyler (21) found that, in general, a concrete mix having a low water-cement ratio afforded better protection than a mix of similar consistency having a high water-cement ratio. Low water-cement ratios require higher cement factors than normally needed for strength requirements. For marine construction, the Port of Los Angeles recommends a cement factor of 7 sacks/cu. yard. AASHO and AREA suggest a minimum cement factor of 6.

A specification on the water-cement ratio, however, is not valid unless the mix consistency is also considered. The consistency of concrete has a pronounced effect on the corrosion rate which is not governed only by the water-cement ratio or the cement content (22). In general, the rate of corrosion is greater for very dry and very wet mixes than it is for mixes of plastic consistency. There appears to be an optimum consistency at which the amount of corrosion is almost completely diminished. This is illustrated

by the qualitative curve shown in Fig. 9 (22) drawn up from data obtained from specimens exposed to moist-air for 2 years. The results of these tests indicate that consistency has a marked influence on the protective value of concrete and that water-cement ratio does not in itself control the corrosion rate of the reinforcement (22).

Varying the cement-aggregate ratio likewise has an effect on the corrosion rate as indicated in Fig. 10 (22). The results of this series are questionable because one cannot be sure if moist air storage is a reliable index for outdoor exposure. In any event the results do show that a lean mix affords little protection as indicated by the time-rust curve for a 1:10 cement aggregate ratio.

Aggregate gradation is another factor which should be considered for high quality concrete. Well-graded aggregate is an important requisite for low permeable concrete (16, 22). Data taken by Friedland (22) indicated that coarser grading enhances the protective quality of concrete; however, the spread of data was too great to warrant definite conclusions.

Due to the influence of these various factors it is possible to increase the protective qualities of concrete by means of proper proportioning of the materials. A high quality, impermeable concrete is perhaps the most effective means of corrosion prevention. However, it should be pointed out that no matter how precisely the mix specifications are prepared, careful supervision and site control is required to insure that proper mixing and placing techniques are followed (10).

Non-reactive Materials

To maintain the protective properties of a well proportioned concrete, care should be taken to avoid the use of materials which are reactive or otherwise undesirable from the corrosion point of view. Water and additives containing salts, particularly chlorides, should not be used. The use of aggregates which contain high salt contents should be avoided. As an additional precaution, any salt deposits that may have formed on the reinforcement should be washed off before it is placed.

Some lightweight aggregates and other types of aggregates exhibit high permeabilities and shrinkage characteristics and should not be used for structures in a corrosive environment. Preliminary tests have shown that the protection afforded to reinforcement may be less for concrete made with lightweight aggregates than for a comparable concrete made with natural aggregates (23).

Since portland blast-furnace slag cement lowers the passivity of the reinforcement it has been suggested that such a cement may promote an intensified corrosive attack (18), however this has not been shown to be the case. Tests reported by Mather (25) indicated that rusting of reinforcing steel was significantly less in concrete made with two portland blast-furnace slag cements than in a concrete made with a type 2 portland cement. However little corrosion was noted for any of the cements tested even for unreported tests where the specimens were exposed to sea water.

Cathodic Protection

The general principle involved in cathodic protection is to make the reinforcement cathodic to some exterior anode. Two methods of cathodic protection have been introduced (15). In one method the anode is a sacrificial metal, such as zinc, in which case the flow of current is induced by galvanic means. This system requires that the anodes be replaced as they are deteriorated. The second and most common method is one in which a current is impressed between the reinforcement and an exterior anode (usually carbon) which need not be sacrificial in nature.

The use of cathodic protection on the San Mateo-Hayward Causeway has indicated apparent satisfactory results as judged by lack of stray current corrosion and lack of further spalling (13).

Although this method has proven effective, there are many problems involved in applying its use to reinforced concrete structures. One of the problems, for example, is that the entire system of reinforcement must be electrically continuous for effective protection. A lack of complete electrical connection of one or more bars would set up isolated corrosion systems causing intensified attack under the action of impressed current (15). Also, the cathodic metallic circuit should have a low, uniform sensitivity so that large potentials are not required to provide adequate currents (10). It is doubtful, then, if cathodic protection could be used more economically than a program of routine repair of the structure as corrosion defects appear (10, 15).

Surface Coatings

The purpose of impervious surface coatings is to prevent the absorption of exterior salts and other aggressive substances into the concrete. They are also used to equalize moisture contents by reducing evaporation or absorption of moisture which occurs with each weather change (13). There are

many types of surface coatings being investigated; some of the more common ones being: paints, coal tars, cutback asphalts, and asphalt emulsions.

Bituminous coatings are usually not effective unless they are preceded by applications of some kind of primer coat. Penetrating primers such as coal tar or asphalt base impregnate the pores and hairline cracks. A bituminous solution or a hot bituminous membrane is then applied over the primer followed by a coat of white wash for thermal protection (18). Cutback asphalts are also used for primers, however, they require suitable solvents for proper penetration.

Asphalt emulsions have been used for wet concrete surfaces, after curing or in rainy weather, but such emulsions appear to have smaller insulating resistances.

Resistivity tests on coated specimens have been conducted to obtain a practical evaluation of the insulating properties of the various bituminous coatings (18). The following resistance ratios were obtained with respect to uncoated specimens made of the same mortar batch:

Coal tar paint with filler	5-10
Cutback asphalt	3-5
Asphalt emulsion with filler	1-2
Uncoated mortar specimens	1

Although impervious surface coatings have displayed a certain degree of effectiveness, they have a tendency to maintain high moisture contents within the concrete and thereby reduce the electrical resistivity (15). These coatings also seem to somehow increase the ratio of cathodic areas to anodic areas and as a result, localize and intensify corrosion (13). Therefore, the effectiveness of surface coatings is certainly questionable and in many cases may do more harm than good.

Oxygen Starvation

Depolarization of corrosion cells set up by various environmental conditions may be prevented by reducing the access of oxygen to the reinforcement in cathodic areas (15). If a concrete specimen containing two steel electrodes is immersed in water, thereby reducing the accessibility of oxygen to the steel, the electrochemical currents due to differential salt contents will be greatly lowered (13).

This type of cathodic starvation was attempted on a section of the San Mateo-Hayward Bridge in California (24). A metal trough containing water

was attached to a portion of the bridge deck which was found to be the chief part of the cathodic region. The procedure, however, was found to be costly, difficult to maintain, and its effectiveness was questionable.

Anodic Inhibitors

Anodic inhibitors contain materials such as alkalies, phosphates and chromates which form either iron salts or a ferric oxide film on the anodic surface thus preventing ferrous ions from entering the solution (10). Such anodic inhibitors are effective only in high concentrations. If they are added in insufficient quantities, the corrosion reaction may be locally intensified. On the other hand, high concentrations may adversely affect the concrete. Therefore, the use of conventional anodic inhibitors can not be recommended until more complete and fundamental investigations have been conducted.

Construction Techniques

There are many operations in construction that could perpetuate serious difficulties if carried out improperly or contrary to known good practices. First class workmanship is of major importance for structures in environments which may cause corrosion problems.

The concrete, when placed, should be thoroughly vibrated and compacted to insure against excessive voids in the concrete. Large voids adjacent to the reinforcement may contain high moisture contents, thus allowing the possibility of macro-cell corrosion to take place.

The concrete should be placed such that the thickness of cover is uniform throughout. Evenness of cover over the reinforcement plays an important role in protection against corrosion. In many cases it has proven to be more decisive than the quality of the concrete (14).

The reinforcement should not come in contact with soil, bricks, wood and other porous non-alkaline material.

A helpful operation suggested by Unz (18) is to place a priming coat of pure portland cement slurry over the reinforcement immediately followed by the concrete. This method, if carried out properly, will create a continuous, cement skin which may do much to protect the reinforcement from corrosion.

There are numerous other techniques that should be followed which will not be listed here. Most of these have varying degrees of importance depending on the type of structure and the environmental conditions. It is

highly important that the specification of these operations be followed up by careful on site supervision and inspection.

SUMMARY

The corrosion of reinforcement in concrete is known to be brought about by electrochemical driving forces. Irregularities in the reinforcing bars and in the surrounding concrete produce potential differences between anodic and cathodic regions on the reinforcement thereby creating corrosion cells. The steel combines with oxygen and water at the anodes to yield an oxide usually existing in two states depending on the available oxygen. Although the steel does not deteriorate at the cathodes, the cathodic reactions control the rate of corrosion; therefore, any factors which control the cathodic reactions will likewise control the overall corrosion process.

Heterogeneities of the steel reinforcement which may create corrosion cells are caused by alloying elements, discontinuous layers of mill scale, and static or cyclic stresses. Irregularities in the concrete usually exist in the form of differential aeration, differential moisture contents, differential salt concentrations, large voids adjacent to the steel and cracks.

The corrosion reaction is greatly influenced by the penetration of moisture containing chemicals such as dissolved oxygen, salts, and carbon dioxide. Although concrete exhibits remarkable protective qualities, the degree of protection afforded to the reinforcement is severely reduced by the penetration of these materials. Therefore prevention methods must either eliminate this penetration or render the reinforcement passive in the presence of harmful substances.

The most effective method of prevention is the use of a high quality, impermeable concrete. Such concrete is achieved by proper selection of materials and proportioning of the mix followed by thorough consolidation of the concrete as it is placed. Other methods which have been incorporated to reinforced concrete structures with questionable results are cathodic protection, surface coatings, oxygen starvation, and anodic inhibitors.

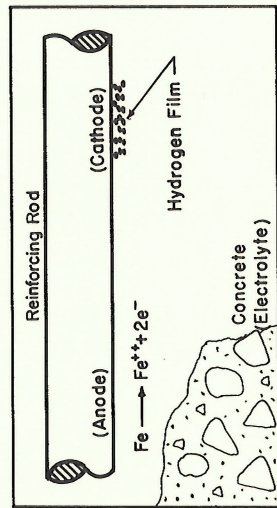
Although the influence of cracks in the concrete is not discussed in this report, it should be briefly mentioned that cracking predisposes reinforced concrete structures to corrosive attack. Cracks of sufficient dimensions will allow direct access of deleterious materials to the reinforcement. Every effort should be made, therefore, to keep the size and occurrence of cracks to a minimum in a structure exposed to a corrosive environment.

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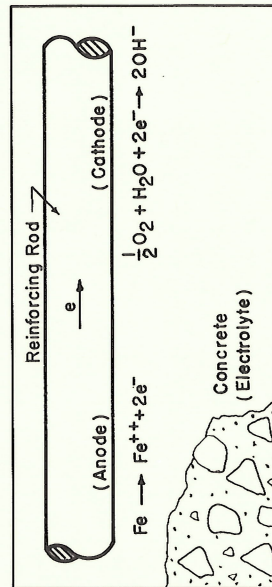
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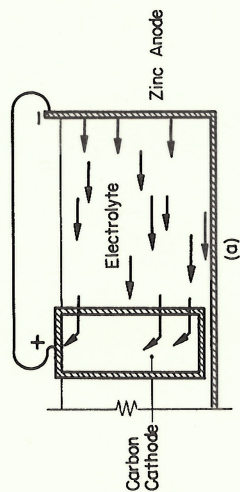


(a) Primary Reaction - Formation of Hydrogen Film at the Cathode which Inhibits Subsequent Reaction.

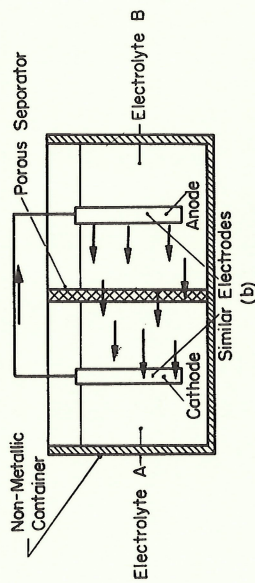


(b) Secondary Reactions - Break down of the Hydrogen Film Thus Allowing the Corrosion Process to continue.

Fig. 2 Typical Chemical Reactions



Dissimilar Metals, Separated by an Electrolyte



Similar Metals, Surrounded by Dissimilar Electrolytes

Fig. 1 Galvanic Cells

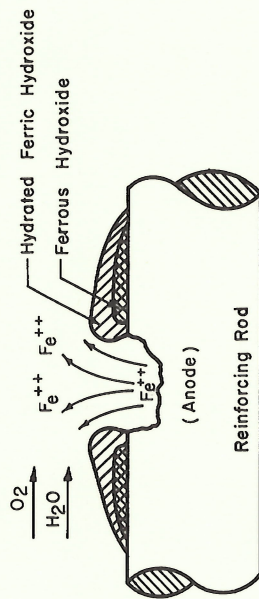


Fig.3 Formation of Rust at the Anodic Region - Two States of Oxidation May Exist Depending on Availability of Oxygen.

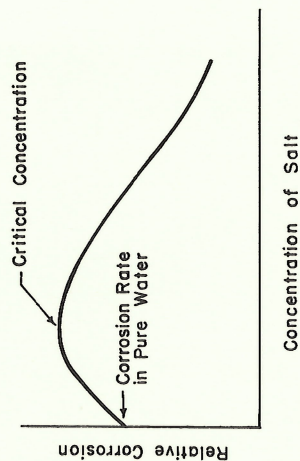


Fig.5 Influence of Salt Concentration on the Rate of Corrosion.

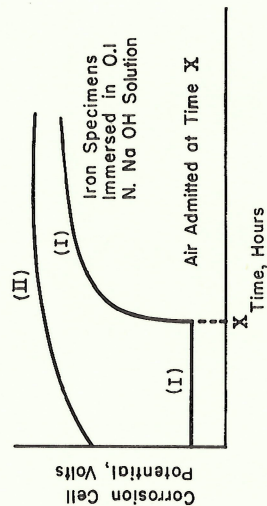


Fig.4 Influence of Dissolved Oxygen

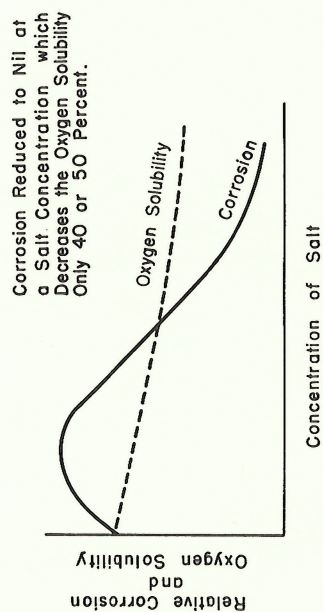


Fig.6 Effect of Salt Concentration on Corrosion Rate and Oxygen Solubility.

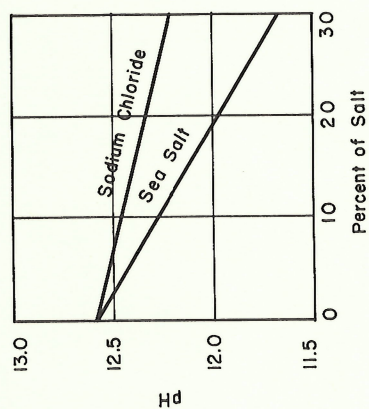


Fig. 7 Effect of Salt Concentration on pH Values

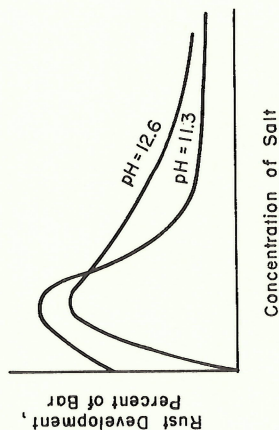


Fig. 8 Schematic Presentation of the Effect of Salt Concentration and pH in $\text{Ca}(\text{OH})_2$ Solution

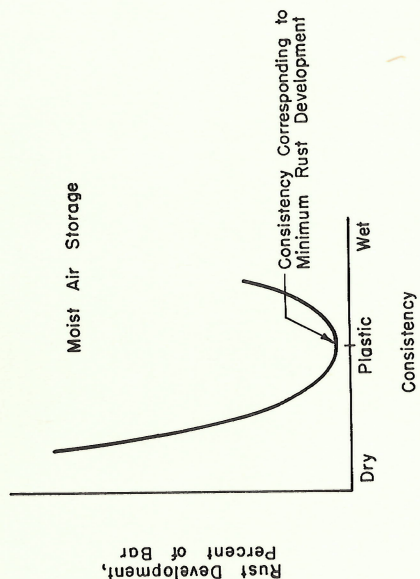


Fig. 9 Relation Between Consistency of Concrete and Rusting of Reinforcement After 2 Years.

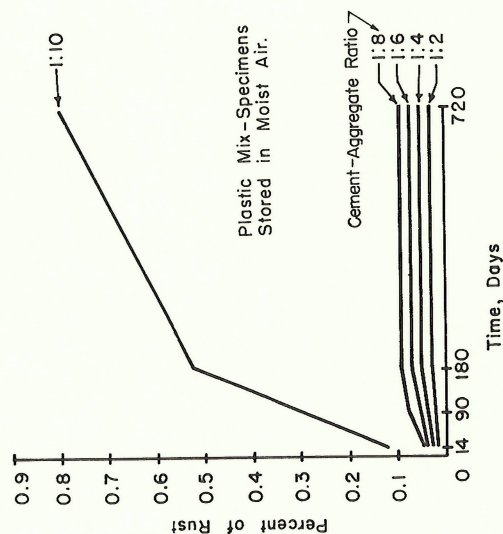


Fig. 10 Time-Rust Relationship in Concrete Showing Effect of Varying the Cement-Aggregate Ratio.