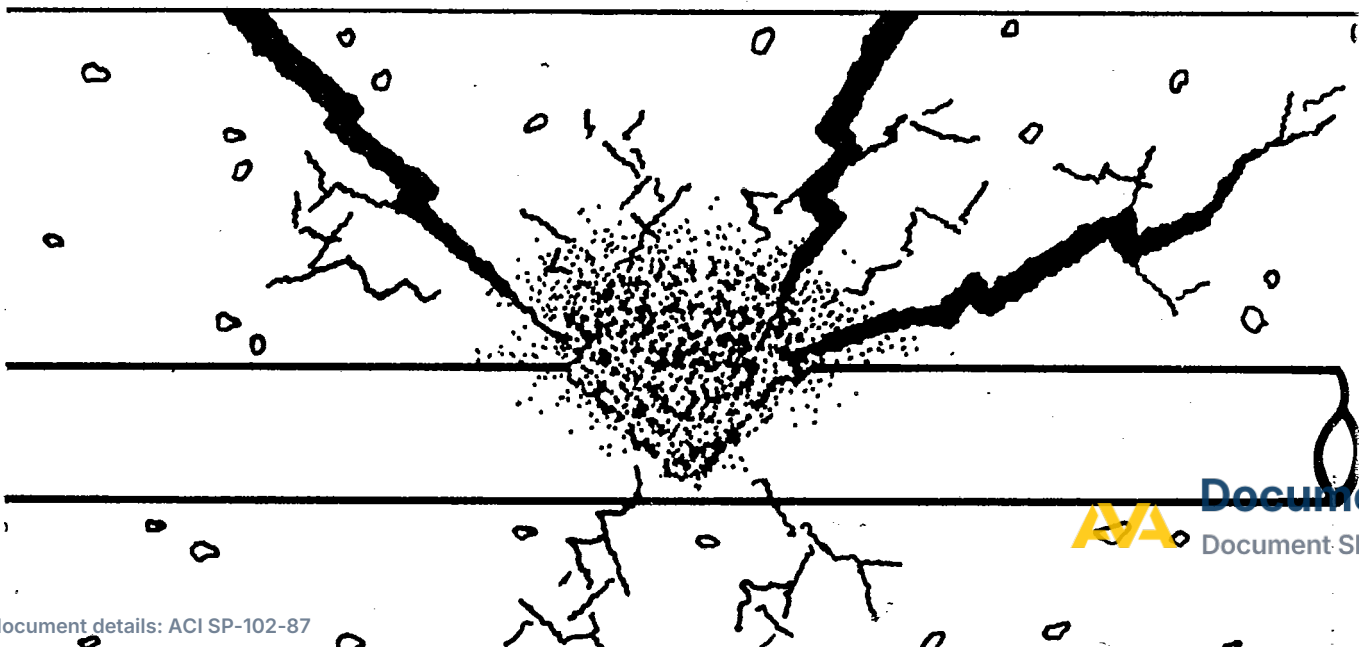


CORROSION, CONCRETE, AND CHLORIDES

Steel Corrosion in Concrete: Causes and Restraints

aci SP-102

Frances W. Gibson
Editor



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PREFACE

Corrosion of reinforcement in portland cement concrete is of major concern because it costs billions of dollars per year to stabilize and replace current construction, greatly increases construction costs to "protect" against the corrosion, and can result in safety hazards.

The corrosion phenomenon has always been of concern with structures exposed directly or indirectly to sea water. But it became of tremendous concern when extensive salting of bridges and highways began in the 1960s, with the tracking of chloride-containing deicing chemicals onto structures made with calcium chloride or other chloride-containing admixtures.

Since the onset of the nationwide corrosion problem with load-locked concrete, there have been extensive field and laboratory investigations into:

1. specific phenomena that induce corrosion,
2. methods for identifying the magnitude and extent of corrosion in structures,
3. techniques for stabilizing corrosion once it has begun, and
4. design of structures and concretes so that corrosion will not occur.

The industry and engineering concern about corrosion, and the need to disseminate state-of-the-art information about corrosion motivated the planning of three independent sessions related to corrosion of steel in concrete at the March 1985 ACI Convention. The three sessions were:

"The Chloride Issue -- the New Limits"
sponsored by ACI Committee 123

"Non-Chloride Accelerators" sponsored by
ACI Committee 212

"Chloride-Induced Corrosion of Steel in
Concrete" sponsored by ACI Committees
212 and 222.

This volume is a compilation of some of the papers presented at these sessions, plus an edited transcript of the Forum, and one additional paper solicited to round out the coverage of the subject.

The papers deal with a variety of aspects of corrosion. They include the marked influence of chloride in causing corrosion, the chemistry of corrosion as triggered by chloride that results in the internal electrical mechanism of corrosion, ways for controlling corrosion by using chloride-free accelerators (and their effects on the setting and strength of concrete), the reduction of chloride penetration through use of pozzolanic blast-furnace slag as an admixture in concrete, and the conductive coating aspects of cathodic protection.

The report on the Forum ranges over all of these topics, and more.

We thank the authors for sharing their knowledge. In addition, we thank the anonymous, but essential, reviewers for their helpful suggestions.

William F. Perenchio
Chairman, Session on "Non-
Chloride Accelerators"

Robert L. Henry
Chairman of Forum on "The
Chloride Issue -- The New
Limits"

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Some Chemical and Physical Aspects of Phenomena Associated with Chloride-Induced Corrosion

by W. Hime and B. Erlin

Synopsis: The wide variety of disciplines involved with the corrosion of steel in concrete has caused difficulties in communication. Each discipline has its own terminology; at times two disciplines use conflicting terms or explanations for the same phenomenon. This paper addresses some areas of such confusion, and presents chemical mechanisms to explain half-cell potentials and causes for chloride-induced corrosion. Examples of such corrosion are presented.

Keywords: admixtures; cathodic protection; chlorides; corrosion; half-cell potential; lightweight aggregates; reinforced concrete; reinforcing steels; sea water

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INTRODUCTION

The economic loss due to the corrosion of metals in portland cement systems has been estimated at billions of dollars per year. This magnitude would suggest the corresponding development of a body of literature and a corps of scientists and design engineers that could now adequately address the problem. Unfortunately, the science is so technical, and the art so confused, that many of the practicing engineers who must address a corrosion problem in the field are without clear, simple guidelines.

To illustrate, ACI committees still disagree as to the amount of chloride by weight of cement needed to promote corrosion^{1,2,3}, and some investigators report that steel doesn't corrode under seawater, while others cite specific instances of catastrophic failures.

Part of the problem is due to the relative newness of the corrosion problem. Prior to 1965, few investigations of the corrosion of metals in concrete were made. Now, with salting of bridges and highways, tracking of salt into parking structures, and aging of concrete structures made with calcium chloride admixtures, there may be few subjects of greater interest.

It is the purpose of this paper to simplify some of the basics of corrosion, to refute some "old-wives tales" that have become gospel, and to present examples from our studies that illustrate these aspects.

CORROSION CELL MODELThe Anode

Many readers are familiar with the classic metal:metal-ion half-cells that are illustrated in basic chemistry and physics texts. An example is a copper wire partially immersed in a solution of a copper salt. The copper metal atoms have a slight tendency to lose electrons and become copper ions, and the ions have a tendency to gain electrons and become copper metal atoms. This is illustrated by the equation:



For a single half-cell, after equilibrium is established there is no net reaction. Connection to a cathode (discussed later) can lead to substantial, continued reaction.

Confusion exists with respect to terms for this phenomenon: (1) chemists give the name "oxidation" to the reaction whereby an element becomes more positive (e.g. copper becoming copper ion), even though no oxygen is involved; and (2) some corrosion scientists (e.g. those involved with cathodic protection) refer to current flow as occurring in a direction opposite to electron flow, a concept foreign to many chemists and engineers, and one that will not be used herein.

To illustrate the metal:metal-ion half-cell, we note that many corrosion engineers employ copper:copper sulphate or calomel (mercury:mercury chloride) half-cell electrodes for determining corrosion of steel in concrete (ASTM C 876).

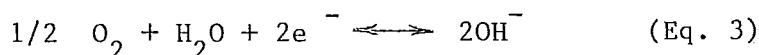
It is our purpose to consider the corrosion of steel in concrete to simply involve an iron:iron-ion half-cell, as illustrated by the left half of Figure 1. That is, it involves the reaction:



When the reaction goes left to right, oxidation occurs, and the electrode is defined as an anode. Thus, corrosion is at the anode. (For the above examples, the positively charged ions are called cations. Negatively charged ions are anions.)

The Cathode

Another electrode, a cathode, is needed to "take up" the electrons from the anodic reaction. For most of the usual steel corrosion reactions in reinforced concrete, the cathodic reaction is:



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The need for oxygen and water in this reaction leads to the common misconception that those substances produce rust; however, the corrosion product produced at an anode on a reinforcing bar does not incorporate the oxygen or water involved at the cathode. Indeed, red rust (Fe_2O_3) often occurs only after the iron corrosion product has, due to its relatively large volume compared to metallic iron, caused cracking of the concrete, allowing oxygen to penetrate and react with it.

Since water and oxygen can both exist in the gaseous form, and since even the best concrete is permeable to gases, cathodic reactions in reinforced concrete are very probable. However, the availability of oxygen at the cathode may be limited due to a low water-cement ratio paste, the presence of salt water (in which oxygen has a low solubility), or certain other oxygen-limiting or oxygen-destroying mechanisms.

Since, as detailed later, corrosion magnitude is primarily governed by the cathode "size" (a term implying area and availability of oxygen and water), methods of restricting the presence of oxygen and water at the surface of reinforcing steel are important considerations.

The Complete Cell

The complete corrosion cell usually involved in the corrosion of steel in concrete is illustrated figuratively in Figure 1 and practically in Figure 2. It consists of the anode and the cathode described above. The cathode metal (M) is usually, but not necessarily, iron (steel). To connect them, a metallic conductor for the electrons and an electrolyte conductor for the ions is required. A rebar usually provides the former, and the moist concrete the latter.

There are several important corollaries to our corrosion cell:

1. The anode and cathode are separated. The distance may be a micron (for a microcell), a meter, or a mile (for macrocells).
2. Oxygen is not involved at the site of the corrosion. Indeed, as described later, the presence of oxygen at the anode can limit or prevent corrosion.
3. Breaking the cell (stopping corrosion) can be accomplished by:
 - a. Cutting the metallic conductor between the anode and cathode.
 - b. Preventing oxygen from reaching the cathode.
 - c. Drying out the cell at any location between the cathode and the anode (water is required for the cathodic reaction, and to carry ions between the electrodes).

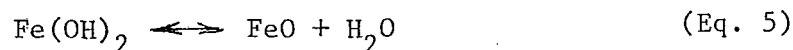
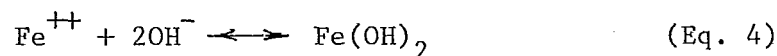
Most electrochemical corrosion situations present an almost unlimited anode as compared to the cathode, and are thus "cathodically" restricted. Unfortunately, a false understanding of the corrosion mechanism has caused some attempts at preventing corrosion to actually cause disastrous failures. For example, painting a portion of a potentially anodic area can increase the cathode:anode area ratio, promoting severe corrosion. Painting the cathodic area--where we wish to restrict oxygen and water--would be the proper procedure.

PASSIVITY

Our corrosion model has so far ignored a most important fact: the anodic steel corrosion reaction quickly stops in a highly alkaline medium such as portland cement mortar or concrete (that is, iron is passivated by the high-pH electrolyte), unless sufficient concentrations of a depassivating agent are present.

Passivation is described in most texts as due to the production of a minute protective layer of gamma iron oxide ($\gamma\text{Fe}_2\text{O}_3$) that prevents further corrosion. This is similar to the protection afforded to copper by a thin layer of cupric oxide, and to stainless steel by a chromic oxide layer. Figure 3 illustrates the rather uniform coating of the steel with a layer (magnified in the figure for illustration) of iron oxide. Here, a void, such as that which led to a cathode in Figure 2, has no effect on the bar.

Recent evidence suggests that this passivation explanation may not always be true. That is, passivation occurs, but may not involve a gamma iron oxide layer. In any case, it should be noted that passivation, not corrosion, can be fostered by the presence of oxygen at potential anodic sites; and that iron oxides can be, and usually are, formed without the need for gaseous oxygen, e.g.



The latter reaction produces water, and therefore the corrosion process itself generates the water necessary for the continued operation of the cell.

Passivation permits the successful use of millions of tons of reinforced mortar or concrete. Depassivation, the loss of passivation, usually occurs only under one of two conditions:

1. Neutralization of the portland cement paste system by atmospheric carbon dioxide, a process that occurs so slowly for low water-cement ratio concrete that the "neutral" (pH about 9) front progresses into concrete at most a few millimeters a year.

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For mortars or for lightweight-aggregate concrete, however, the carbonation rate can be much greater because they are generally more porous than ordinary concrete.

2. Overcoming the passivity by aggressive ions. Chloride and bromide are the only aggressive ions of normal concern.

Remarkably, corrosion scientists still do not agree on a mechanism for the depassivation reactions involving halides such as chloride and bromide. In our opinion, complex ion formation, as described later, is responsible.

Studies for the State of California, the Federal Highway Administration, and the Bureau of Standards have indicated that chloride ion concentrations of 0.2 percent by weight of cement cause depassivation in cement systems. However, those studies generally involved the non-uniform distribution of the chloride: more uniform distributions may require higher chloride concentrations to produce substantially the same corrosion current.

Some investigators have attributed the depassivation caused by chloride as due to a lowering of pH. This is not the case. Misunderstanding has developed because, unfortunately, it is impossible to simply add chloride ions to concrete. A cation must be added at the same time. Addition of, for example, aluminum chloride, does lower pH because the aluminum ion reacts with water to produce an acid. Addition of calcium chloride also reduces pH by the "common ion" effect of the calcium on the calcium hydroxide component of the cement paste. But addition of sodium chloride (the common deicer salt) causes no significant reduction of pH⁴.

Part of the confusion occurs because, in the neighborhood of a steel bar where a water-filled void exists, iron chlorides will hydrolyze to form hydrochloric acid. However, that acid is normally neutralized quickly by the enormous reserve of calcium hydroxide from the cement paste.

CASE ILLUSTRATIONS OF OUR CORROSION CELL MODEL

The literature abounds in conflicting information as to the corrosion of reinforcement in sea-water-exposed concrete. The non-corrosion of steel in some structures has been explained as due to the low solubility of oxygen in seawater. Other structures have apparently undergone extensive deterioration, for reasons not generally recognized:

- A. Figure 4 illustrates our explanation for at least some of the conflicting experience. The steel in the structure at the left is entirely below sea-level, and thus very little oxygen is present to create a cathode. The steel in the structure at the right is partially above sea-level where a cathode can form because of availability of oxygen.

flow and electrolytic conductance easily occur on the bar and in the wet concrete, respectively. The reinforcement in the underwater portion of the structure becomes anodic because of the presence of chloride and the relative absence of oxygen. Corrosion and cracking then result.

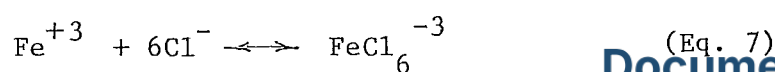
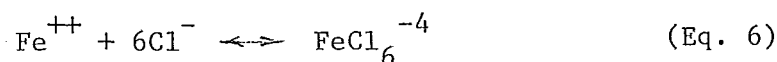
We have investigated a structure where steel extending to the ocean surface was corroding severely at 20 foot depths. An investigator removed some of the rust and carried it to the surface where it warmed his hand. The corrosion products were ferrous oxides (FeO) and hydroxides ($\text{Fe}(\text{OH})_2$), which readily "burned" in the oxygen of the air to form ferric products (e.g. Fe_2O_3 , $\text{Fe}(\text{OH})_3$, Fe_3O_4), elegantly demonstrating lack of oxygen, and the non-need of it, at the site of the corrosion.

- B. Figure 5 illustrates conditions present when concrete containing epoxy-coated steel is subjected to dynamic loads and salt solutions. Corrosion occurred at locations of lugs, but not at cracks. Quite obviously the cracks establish the cathode. The location of the anode may be due to local inhomogeneity of steel, perhaps occasioned by the presence of inclusions such as manganese sulfide.
- C. Recently floors in some areas of heated, air-conditioned, decade-old buildings have cracked due to corrosion of steel embedded in concrete containing admixed calcium chloride. Investigation revealed that the concrete had been made with a light-weight aggregate that held considerable water, and that severe corrosion occurred where the concrete could not dry out due to tiled surfaces. Carpeted areas evidenced no distress.

THE CHLORIDE PROBLEM

Chloride is probably responsible for all but a few percent of the economic loss due to corrosion of steel in concrete structures. Remarkably, there has been little interest shown in determining the mechanism for the depassivating action of chloride in concrete. (We have examined many general and inorganic chemistry texts and found most of them fail to discuss either chloride-caused corrosion or depassivation.) A knowledge of the mechanism could lead to methods for inhibition of the depassivation process.

In our view, and as proposed by others, complex formation could play a large role, according to such reactions as:

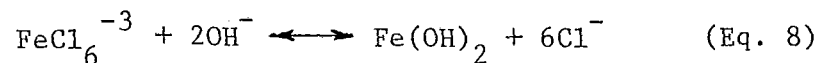


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A reaction such as Eq. 6 removes ferrous ions from the cathode area, allowing them to be deposited away (perhaps only a few microns) from the bar, through the reaction:



This reaction produces rust and releases chloride ion for further reaction with ferrous ion.

The complexation of the ferrous ion, in accordance with LeChatelier's Law and Eq. 2, causes more metallic iron to oxidize, leading to more rust. Further, the lowering of the ferrous ion concentration because of its reaction with chloride (Eq. 6) leads to a change in the half-cell potential of the iron:ferrous ion half-cell, which can be measured by the procedures of ASTM C 876. Thus, lower (toward a more negative value) half-cell potential does not indicate that "more rust is present" (an increased ferrous ion concentration) but actually dynamically demonstrates that a corrosion mechanism (decrease in ferrous ion concentration to force oxidation of the iron) is almost certainly in operation. This is why ASTM C 876 can state that half-cell measurements more negative than -0.35 volts (vs. the copper-copper sulfate electrode) are 90 percent certain of demonstrating that corrosion is occurring.

CONCENTRATION CELLS AND OTHER COMPLICATIONS

Our simplified model of the steel corrosion process as one involving an anode where iron atoms oxidize to form ferrous ions, and a cathode where oxygen is reduced and reacts with water to form hydroxyl ions, is insufficient to explain all of the causes for corrosion of steel in concrete, and the differences in corrosion current for apparently similar situations. These complications are due to mechanisms such as:

1. "Concentration cells" due to differences in chloride, oxygen, water, etc. concentration at different locations on a steel bar. Figure 6 illustrates that a cell may be set up simply by having two concentrations of ferrous ion (Fe^{++}) in contact with a steel bar. The different concentrations may be due to reactions of ferrous ion at one electrode with chloride or oxygen.
2. Local inhomogeneities in steel composition.
3. Galvanic effects, due to contact between dissimilar metals.

A more complete discussion of these phenomena is outside the scope of this paper.

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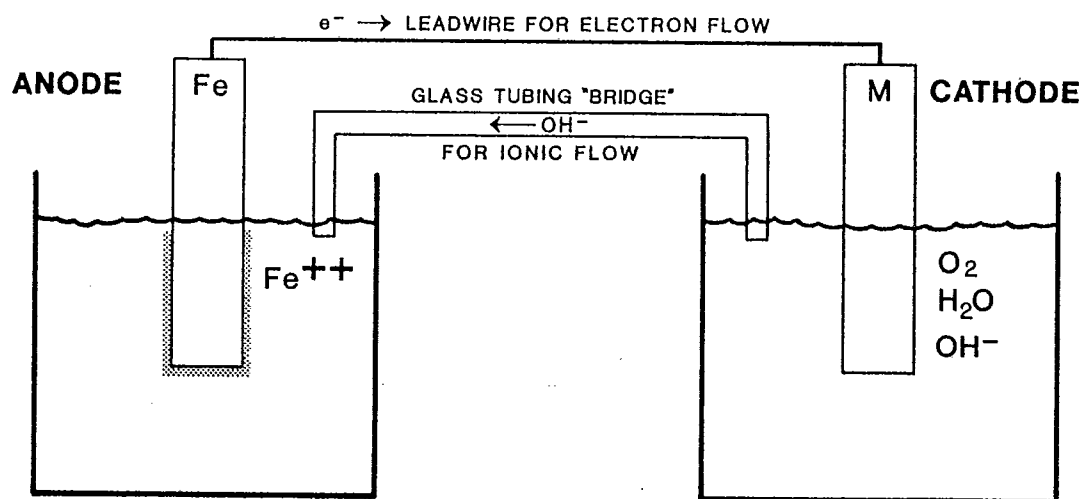


Fig. 1--Electrochemical corrosion cell

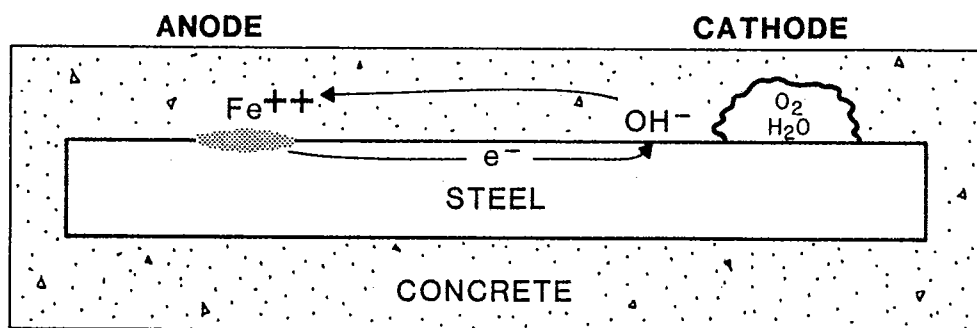


Fig. 2--Corrosion cell in reinforced concrete

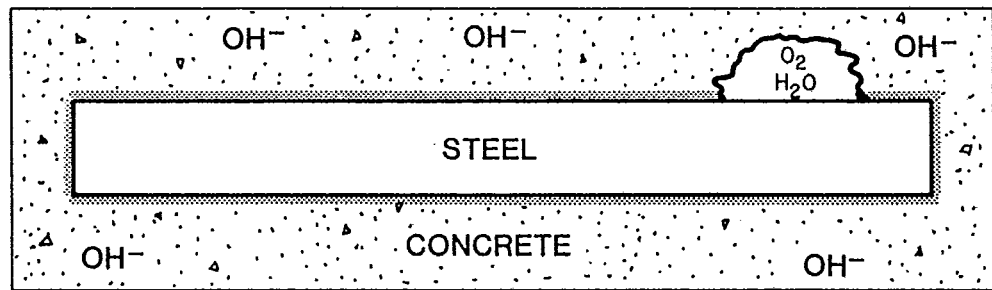


Fig. 3--Passivated steel in concrete

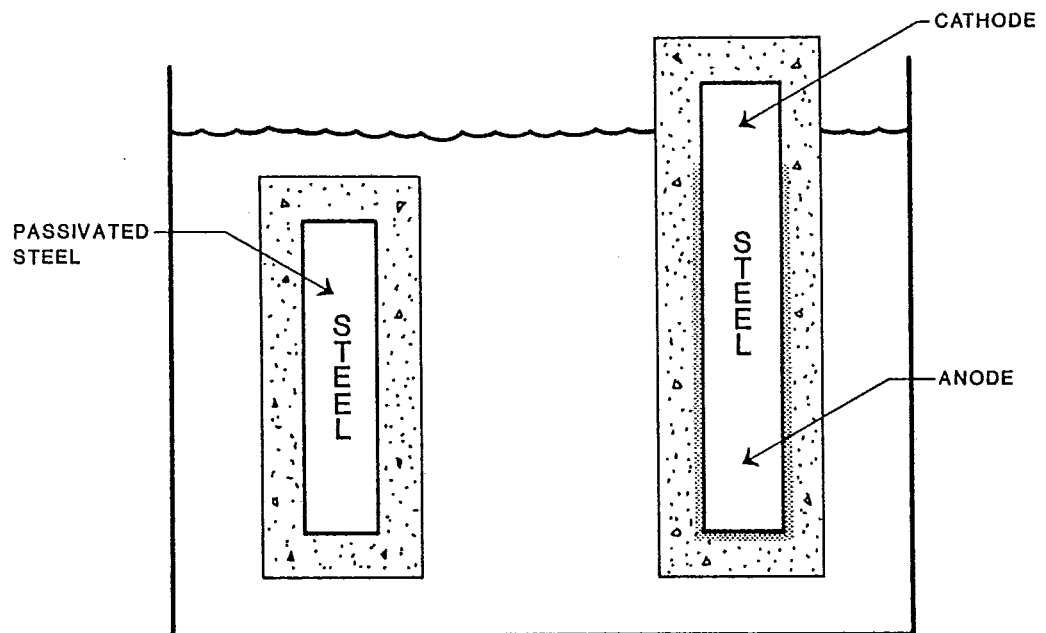


Fig. 4--Examples of steel in concrete completely and partially immersed in sea water

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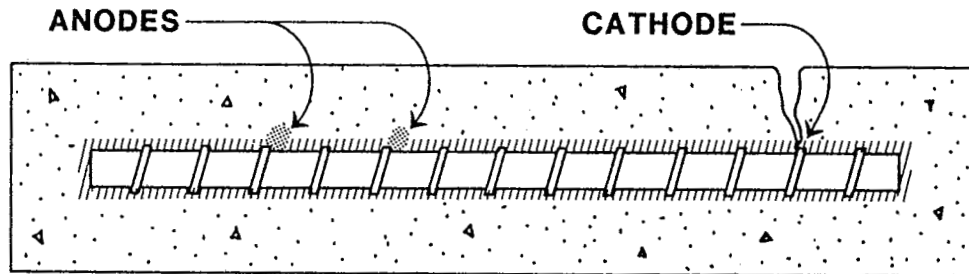


Fig. 5--Dotted areas represent corrosion of epoxy-coated steel in cracked concrete

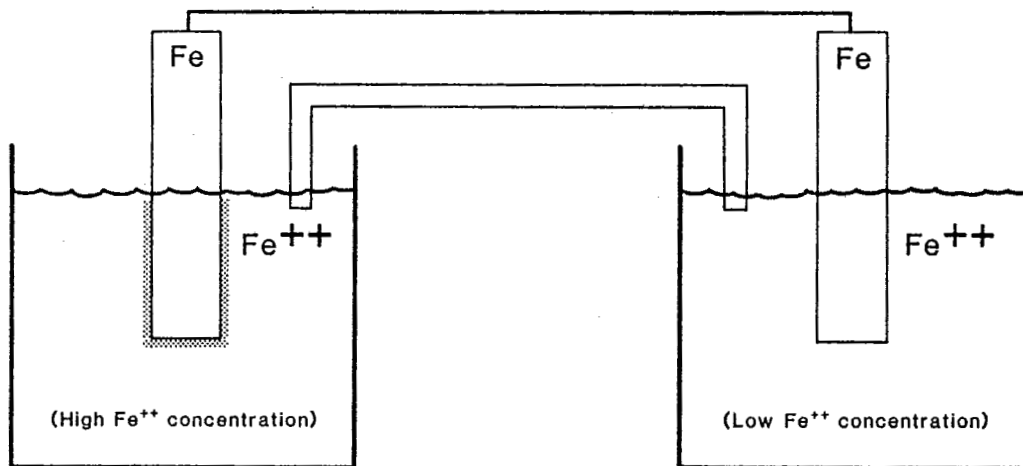


Fig. 6--A "concentration" cell

A Review of Electrochemical Principles as Applied to Corrosion of Steel in a Concrete or Grout Environment

By J. Fraczek

Synopsis: Corrosion of steel in concrete proceeds at a far greater rate in the presence of chloride ions.

Most researchers agree that chloride ions act as an essential part of the corrosion cell by

1) lowering the pH of the concrete pore water in contact with the steel, thereby dissolving the passive oxide film on the steel surface, or

2) penetrating the film to react with and transport the metallic iron into the electrolyte.

In the latter process, the resulting iron chloride complex ion combines with hydroxyl ions to form ferrous hydroxide in solution and lower the pH. This, in turn, thins out the oxide film and speeds penetration of chloride ions. Eventually the continuing corrosive action results in a pit.

To initiate corrosion, a threshold concentration of chloride is needed in excess of the amount immobilized by reaction with tricalcium aluminate in the cement. Investigation of the chloride ion content in concrete adjacent to corroding reinforcing steel shows the concentration to be 1.0 to 1.4 lb of chloride ion per cubic yard of concrete (0.59-0.83 kg/m³).

Keywords: chlorides; corrosion; electrolysis; galvanic corrosion; pH; reinforced concrete; reinforcing steels

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INTRODUCTION

The phenomenon of corrosion of steel in concrete has been studied extensively since 1960. Various investigations prior to 1960 identified the basic correlation between chloride ions and the corrosion of steel in concrete (1, 2). The nature of the interaction, however, was not clearly understood. Most research in the 1960's concentrated on the corrosion of mild steel reinforcement in bridges. The corrosion potential of prestressing steel was also recognized, however, and researchers eventually realized that the principles governing chloride-induced corrosion of mild steel in concrete apply to prestressing steel as well.

The following is a brief review of the principles governing chloride-induced corrosion of steel in concrete. It is intended to provide the engineer having little or no knowledge of the corrosion process with sufficient background and understanding to comprehend the functioning of various corrosion protection measures.

PRINCIPLES OF CORROSION

For purposes of this discussion, corrosion will be divided into two categories: stray current and

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galvanic. Stray current corrosion is caused by the discharge of stray direct current from the surface of a metal, and is not a common problem in concrete structures. Galvanic corrosion, in the strict sense, is caused by the potential differences developed when two dissimilar metals are electrically connected. In the broad sense, however, the term has also been applied to corrosion resulting from dissimilar surface conditions, differences in oxygen concentration or differences in environment around a structure (3).

The Basic Corrosion Cell

The basic principles of electrochemical corrosion can be traced to the components of the electrolytic cell which must be established for corrosion to occur. Three basic components comprise the cell: the anode, the cathode and an electrolyte. For corrosion to occur, the anode and cathode must be connected in a manner that permits electron flow.

Anode and Cathode -- The site where metal corrodes is termed the anode. In the anodic reaction, a metal atom loses electrons in a reaction with the corroding medium. These electrons are consumed at the cathode, typically through oxygen reduction. In acidic media, hydrogen evolution is a common cathodic reaction. The two reactions are coupled by a migration of ions into the electrolyte at the anode and out of the electrolyte at the cathode.

The orientation of the anodic and cathodic sites can be viewed on two scales. In the microscopic view, a tiny anode may be surrounded by the cathode. On a macro-cell scale, the anode and cathode can be separated by a finite distance measured in inches, feet, or yards. Generally, the surface area of the anode is small relative to that of the cathode, and the corrosion cell consists of a combination of many micro- and macro-electrolytic cell interactions.

Electrolyte -- The current which drives the anodic and cathodic reactions flows through a medium termed the electrolyte. The electrolyte conducts current primarily through ionic diffusion, and thus must have a specific minimum ion content and a minimum water content to allow the flow of ions.

Corrosion Potential and Corrosion Rate -- The electrolytic or galvanic cell operates as a circuit. Current flows around this circuit between the anode and the cathode, flowing one way through the metal and returning through the electrolytic medium. The



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driving force producing current flow is called the electromotive force, or emf, and results from the chemical reactions taking place at the anode and cathode. The value of the emf is measured as a potential difference, in units of volts, between these two sites.

The value of the emf is not an indication of the rate of corrosion, but only of the force or potential energy pushing the reaction in a particular direction. The corrosion rate depends on the amount of current actually flowing, as calculated by Faraday's Law:

$$W = k I t \quad (\text{Eq. 1})$$

where W is the weight of the metal corroded, k is the electrochemical equivalent, I is the current, and t is the time.

Corrosion Cells

Generally, any nonuniformity within the electrolyte or between the anode and cathode can produce a cell with different potentials (an emf). Examples of such nonuniformities include dissimilar metals, oxygen concentrations and temperature differentials. Coupling dissimilar metals will cause the more active metal to corrode while the more noble metal acts as the cathode. This activity can occur on a microscopic or macroscopic scale. A corrosion cell can also be produced by differential concentrations of either oxygen or metallic ions at the electrodes. A potential develops due to the greater availability of the reacting ion at one location than at the other. Differential oxygen concentrations can occur in many ways within a given electrolyte. Even a temperature gradient in a metal adjacent to an electrolyte can result in a corrosion cell.

Factors Affecting Corrosion Activity

Many factors affect the activity of a corrosion cell. In general they include 1) the ratio between the surface areas of the anodic and cathodic regions, 2) polarization, and 3) resistivity of the electrolyte.

1. Area Ratio -- The corrosion rate is related to the density of the current flowing in the cell (4). For a given current, the current density decreases at the anode as the anodic area increases with respect to the cathodic area. The decrease in current density denotes a decrease of the corrosion rate.

2. Polarization -- Electrochemical polarization, or the change of potential of an electrode resulting from current flow, can be divided into activation and concentration polarization. Activation polarization refers to electrochemical processes which are controlled by the reaction sequence at the metal-electrolyte interface. Concentration polarization refers to reactions which are controlled by the diffusion of ions in the electrolyte. Both activation and concentration polarization usually occur at an electrode. Activation polarization usually controls at low reaction rates, while concentration polarization becomes controlling at higher rates. The total polarization of an electrode is the sum of the activation and concentration polarization contributions (5, pp. 308-313).

Passivation is a special case of activation polarization caused by the formation of a thin passive, or nonconducting, layer on the metal surface. It is estimated that the film is only approximately 30 angstroms or less in thickness. When the layer becomes thick enough at either the anode or cathode to partially or fully block the flow of current, corrosion activity slows or comes to a halt and the cell is considered to be passivated. Formation and breakdown of the passive layer depends on a number of factors, including the ionic concentrations and pH level within the electrolyte.

3. Electrolyte Resistance -- Another major factor affecting the corrosion rate is the electrical resistance of the electrolyte. This factor depends on temperature, moisture and ionic content, since the corrosion current flows through the electrolyte by ionic conduction. The potential corrosion rate is inversely proportional to the resistance of the electrolyte.

CORROSION OF STEEL IN CONCRETE

The surface of steel reinforcement in concrete has been studied extensively in the recent past (6-8). Evidence exists that a passive iron oxide film is present on the steel surface and that this film normally protects the steel substrate against corrosion through a form of activation polarization. The film prevents iron cations (Fe^{++}) from entering into solution in the electrolyte and acts as a barrier to prevent oxygen anions (O^{-2}) from contacting the steel surface.

There is also an initial basicity of the electrolyte surrounding the steel due to the presence of a saturated lime solution in the cement gel. The

pH of moist concrete typically remains above 12, maintaining the passive oxide film in a stable condition. However, the film breaks down (depasivates) if the pH of the surrounding environment falls below approximately 10-11, or if the chloride ion concentration becomes sufficiently high, and corrosion can result.

Reduction in pH can occur in one of three ways: 1) by carbonation of the concrete, 2) by water leaching associated with cracking, or 3) due to other chemical reactions within the cement matrix. Carbonation involves a reaction of atmospheric carbon dioxide with the Ca(OH)_2 in the cement gel to form insoluble CaCO_3 and water. This reaction results in a significant reduction in pH of the electrolyte due to removal of hydroxyl ions from the pore water solution (9, p. 190). Although carbonation is normally not a significant concern because it proceeds at a very slow rate, significant corrosion damage resulting from carbonation of lightweight concrete has been reported (10). Similarly, properly designed concrete does not normally crack enough to cause significant leaching. Other chemical reactions that result in pH reduction are typically due to certain aggressive environments -- for example acid rain, or the presence of halides such as chloride, or sulfide.

The Role of Chloride in the Corrosion Process

Corrosion of steel in concrete proceeds at a far greater rate in the presence of chloride ions. Almost all researchers agree that the chloride ion acts as an essential catalyst in the corrosion reaction. The precise role which the chloride ion plays in the reactions, however, is not necessarily agreed upon.

Effect on Conductivity of the Electrolyte -- Concrete, acting as an electrolyte, has a wide variation in its electrical resistivity characteristics. Resistivity values ranging from about 10,000 to 10,000,000 ohm-cm have been reported by researchers studying concrete with different moisture and induced ionic contents. An increase in temperature or addition of moisture and ions, such as chloride ions, to cured concrete results in a large drop in resistivity. High water-cement ratio, chloride-bearing, saturated concrete provides the lowest resistivity to current -- while low water-cement ratio, well cured, air-dry concrete provides the highest. Condensed silica fume, an admixture described as an extremely active pozzolan, dramatically increases the resistivity of concrete.

Chemical Reactions Involved in Corrosion -- To demonstrate the ways in which the chloride ion may af-

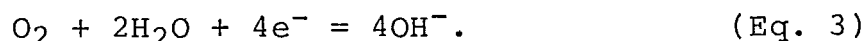


fect the corrosion reaction, it is helpful to discuss the basic chemical reactions taking place within the galvanic corrosion cell. The actual physical reactions are much more complex, but result in the fundamental process described below.

At the anode, metallic iron goes into solution by oxidation (loss of electrons):

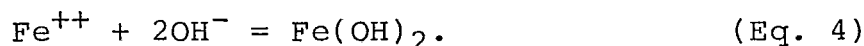


At the cathode, dissolved oxygen in the pore water which has diffused to the steel surface is reduced by electrons supplied by the anode reaction to form hydroxyl ions:



The current completes the circuit back to the anode through the concrete electrolyte in the form of the negative hydroxyl ions. The rate of this transfer depends on the temperature, moisture content, ion concentration and permeability of the concrete. This is an ionic diffusion process, but it can still be equivalently modeled by Ohm's Law relating the driving force (emf), current, and resistance of the electrolyte (6, p. 1138).

The OH^{-} ions at the anode can then combine with the Fe^{++} cation to form a fairly soluble ferrous hydroxide, $\text{Fe}(\text{OH})_2$:



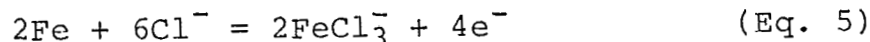
Given sufficient oxygen, this product can be further oxidized to form insoluble hydrated red rust. Unless the concrete is cracked, however, oxygen usually cannot diffuse quickly enough at an active anode site to support this reaction and the iron remains in the ferrous state.

General Effect of Chloride -- Most researchers believe that the chloride ion initiates the corrosion reaction by depassivating the natural oxide film on the steel surface, allowing the iron to go into solution. However, the depassivation does not necessarily occur through a direct reduction of alkalinity in the electrolyte by the chloride-induced reaction. Some researchers now believe that the chloride ion also acts directly by migrating through the film, as first proposed by Hoar (11). The actual mechanism of migration, however, is not well understood or agreed upon. Ogura and Ohama recently suggested that nucleation

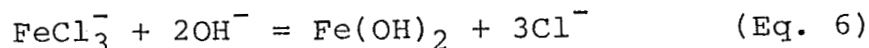
sites are related to microscopic inclusions and grain boundaries on the metal surface (12). Other theories include the effects of chloride ion concentration (13; 14, p. 78) and localized concentrations of lower pH at the film-electrolyte interface due to reduction of the iron oxide film (8, p. 491-492).

Chloride ions also result in a shift of potential of the steel. Non-uniform penetration of chloride ions to the level of the steel thus produces differences in potential and leads to the formation of "macro" corrosion cells. Non-uniform penetration is a general occurrence, and results from such factors as uneven salt distribution, variations in concrete cover and local differences in concrete quality.

Specific Effect of Chloride Ion -- On reaching the iron substrate, the chloride ion acts as a catalyst for the oxidation of the iron by taking an active part in the reaction. According to Uhlig (5, p. 75), it oxidizes the iron to form the complex ion FeCl_3 and draws this unstable ion into solution, where it reacts with the available hydroxyl ions to form $\text{Fe}(\text{OH})_2$. This releases the Cl^- ions back into solution and consumes hydroxyl ions, as seen in the following reactions:



followed by:



The electrons released in the oxidation reaction (Eq. 5) flow through the steel to the cathode surface. This process would result in a concentration of chloride ion and a reduction of the pH at the points of corrosion initiation, probably accounting for the process of pitting corrosion. The lowered pH at these sites contributes to the continual breakdown of the passive oxide film (15).

Threshold Chloride Concentrations -- The tricalcium aluminate (C_3A) content in portland cement is usually large enough to combine with a significant amount of chloride ion, forming an insoluble calcium chloroaluminate (9, p. 193). Larger quantities of chloride ion appear to be immobilized when the concrete is in a plastic state than when in a hardened state. Because of this reaction with tricalcium aluminate, a threshold concentration of chloride ions in the concrete mass must be present above which localized chloride concentrations can be effective in des-

destroying the passive film surface (6, p. 1138). It is possible that these localized concentrations occur primarily in voids in the concrete matrix that are in direct contact with the oxide film (13).

Investigation of the chloride ion content in concrete adjacent to corroding reinforcing steel has found it to be in the range of 1.0 to 1.4 lb of chloride ion per cubic yard (0.59-0.83 kg/m³) (16). At the present time, a commonly accepted value for the corrosion threshold is 0.20 percent total chloride ion by weight of cement (17). This represents the minimum quantity of total chloride ion necessary to initiate corrosion in portland cement concrete when sufficient moisture, oxygen and other requisite factors are present. Using this value, a typical 7-sack (660 lb/yd³ or 390 kg/m³) bridge deck concrete would have a corrosion threshold of approximately 1.3 lb of chloride ion per cubic yard (0.77 kg/m³).

Factors Affecting Pitting Corrosion -- There appears to be an initial threshold potential, called the pitting potential, above which pitting corrosion can be initiated on an otherwise passive surface. The overall galvanic potential generally drops when corrosion current begins to flow through a localized anode or pit. This potential drop essentially repassivates the remaining, non-pitted steel surface. Since hydrolysis has taken place within the pit, however, the lower pH of that solution allows continuation of the reaction at the available potential level. The very small anode-cathode area ratio in pitting corrosion also results in a high current density within the pit because of the relatively large cathodic area available for distributing excess electrons to the electrolyte. This area effect helps to reinforce the corrosion cell action until the pit surface area is sufficiently large for the chloride ion concentration at that location to maintain the reaction (18).

Researchers have found evidence supporting this phenomenon utilizing small-scale equipotential mapping of a corroding steel surface (19). They have found that generally many small pits initiate simultaneously at an early stage, and then all but a few repassivate. Their current is then channeled into the remaining few pits, causing an increase in the corrosion rates at those locations.

SUMMARY

Chloride and oxygen ions, when present, diffuse through concrete at a rate that depends on the quality and integrity of the concrete. The galvanic corrosion cell, which provides the driving force behind the corrosion process, is established mainly by the development of differential concentrations of oxygen or chloride anions along electrically continuous steel surfaces. The electric potential differential that builds up between an anode and cathode on these surfaces is the measure of the force driving the corrosion cell. Although the potential differential provides a measure of corrosion activity, rate of metal loss is proportional to current flow in the cell.

The chloride ion acts as an essential part of the corrosion cell in one of two ways. It either lowers the pH of the concrete pore water in contact with the steel, dissolving the passive oxide film on the steel surface, or it attacks the passive film directly by penetrating through the film surface to react with and transport the metallic iron into the electrolyte. The resulting iron chloride complex ion then combines with hydroxyl ions to form $\text{Fe}(\text{OH})_2$ in solution and lower the pH. This, in turn, thins out the oxide film and allows easier penetration of chloride ions, allowing continued corrosion in the newly initiated pit.

Regardless of the method by which chloride ions act in initiating corrosion, it has been shown that a minimum threshold concentration of chloride is needed in excess of the amount immobilized by reaction with tricalcium aluminate. This concentration may take place initially in voids of the cement matrix in contact with steel surfaces. A currently commonly accepted value for the corrosion threshold is 0.2 percent total chloride ion by weight of cement.

The rate of corrosion activity is affected by the ionic concentrations within the concrete electrolyte. These concentrations affect not only the resistivity of the electrolyte, but also the availability of the reactants. As an example, if oxygen is inhibited from reaching the cathodic steel, either by dense concrete, moisture saturation or impermeable coatings on the concrete surfaces, the galvanic cell will be stifled since hydroxyl anions will not be produced. (As a practical matter, however, this is rarely achieved.) Similarly, a depletion of the chloride ion or concrete pore water, or a reversal of the electromotive force

(as with cathodic protection), can stop the active corrosion cell.

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Effects of Two Non-Chloride Accelerating Agents on Setting Characteristics of Portland Cement Mortars

by P. Smith

Synopsis: Effects of two non-chloride accelerating agents -- sodium thiocyanate and calcium nitrate -- on time to achieve initial set of two brands of Type I cement were determined at 70 F (21 C) and 40 F (4 C).

Results with these two non-chloride accelerators were compared with results with calcium chloride, the conventional accelerator.

Tests show:

- Low or moderate dosages of the two non-chloride accelerators can reduce time to achieve initial set by 1-2 hr.
- Any one of the three accelerators may be more effective with one cement than with another cement having similar setting characteristics without accelerators.
- In general, all three of the accelerators are more effective at 40 F than at 70 F.

Keywords: accelerating agents; calcium chlorides; calcium nitrates; mortars (material); setting (hardening); sodium thiocyanates

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INTRODUCTION

A major consideration in choosing an accelerator to be used in concrete must, of course, be its effectiveness in accelerating setting. That is the characteristic studied in this investigation. Other characteristics that should be considered in choosing an accelerator include:

- cost
- influence on corrosion of steel reinforcement and other metal embedments, and
- enhancement of compressive strength of concrete.

It is well known that non-chloride accelerators are more expensive than chloride accelerators. Sodium thiocyanate is the most expensive of the three chemicals used as accelerators in this test program. Calcium nitrate is somewhat less expensive. Both are far costlier per ounce than calcium chloride.

It is well known also that chloride accelerators can contribute to corrosion of steel reinforcement. However, non-chloride accelerators are not necessarily noncorrosive. A particular non-chloride accelerator may or may not contribute to corrosion.

This investigation did not cover effects of the accelerators on corrosivity or concrete compressive strength. Nor did it cover all of the many possible non-chloride accelerators. As Chapter 3 of ACI 212.1R states, "Studies have shown that a wide range of soluble inorganic salts, such as chlorides, bromides, fluorides, carbonates, nitrates, thiosulfates, silicates, aluminates, and alkali hydroxides, will accelerate the setting and early hardening of portland ce-

ment." ACI 212.1R also discusses organic accelerators such as triethanolamine, which are used in admixtures with water-reducing constituents to counteract their retarding effects. Triethanolamine could also be used with other non-chloride or chloride accelerators. But it is costly and of limited effectiveness. Calcium formate and other inorganic accelerating admixtures are discussed by Roskopf, Linton, and Peppler (1975).

ACCELERATORS STUDIED

In the study, a 55% aqueous solution of sodium thiocyanate was prepared in the laboratory by dissolving sodium thiocyanate technical grade crystals in distilled deionized water. The calcium nitrate solution used was 66% tetrahydrate, 45.9% active. The 35% aqueous solution of calcium chloride was prepared from anhydrous calcium chloride, 94-97% pure, dissolved in distilled deionized water. The concentration solutions prepared in the laboratory were based on the total weight of the solids introduced into the distilled deionized water. These concentrations are as high as is practical for general field use.

The dosage rate of these accelerating solutions is reported in liquid ounces at the stated concentration per 100 lb of cement.

TEST METHOD

The initial setting times of mortars were determined in accordance with ASTM C 403-80 with the following exceptions:

1. A concrete mixture was proportioned in the laboratory using 470 lb of cement per cubic yard of concrete (279 kg/m^3) -- which is a "five sack" mixture -- to yield a 5-in. slump. Mortars from this mix were then separated from the concrete and a flow determined in accordance with ASTM C 230-83 (flow table dropped five times). For this mixture, it was determined that the 5-in. slump concrete would produce a mortar with a flow of 96%.

2. The mortars used in these series of tests were then prepared using the same cement, sand, and water ratio as used in the test mixture, and the flows were maintained between 90 and 100% using the aforementioned method for determining flows.



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The volume of the total liquid content was kept approximately the same, regardless of the dosage rate of accelerator. The non-water-reducing aspects of these accelerators allowed us to accomplish this and still maintain a consistency of mortar between 90 and 100% flow.

In this test program, one set of samples was stored at 70 F, about the highest temperature at which accelerators are used. A second set was stored at 40 F, the minimum placing and curing temperature allowed in most specifications. One hour after initial contact between cement and mixing water was made, and at intervals of $\frac{1}{2}$ -hr thereafter, the resistance of the mortar to penetration by a standard needle was measured.

Mortars were maintained at the selected test temperature during mixing, placing, and testing.

MATERIALS

The two cements used were from different regions of the United States, but had similar setting characteristics without accelerators, as shown in Table 1.

For each accelerator dosage in the test program, three batches of mortar were prepared using the same proportions of cement, fine aggregate, and water; flows were maintained between 90 and 100%. Mortars were mixed in accordance with ASTM C 305-82. Then initial setting time was determined according to ASTM C 403-85.

RESULTS AND CONCLUSIONS

Figs. 1-4, which appeared in Concrete Products for October 1985, compare the data obtained.

Fig. 1 shows the effects of a range of dosages of the three accelerators on Cements A and B at 70 F ambient temperature. Fig. 2 presents similar information for 40 F.

Figs. 3 and 4 present the same data plotted in Figs. 1 and 2. But Fig. 3 presents the effects of the three accelerators on Cement A at 70 F and 40 F. Fig. 4 presents similar information for Cement B.

In Fig. 1, with calcium nitrate Cement A appears to set about $\frac{1}{4}$ hr sooner than Cement B over the range of working dosage rates. With sodium thiocyanate at 16 oz/100 lb of cement, Cement A appears to set about $\frac{3}{4}$ hr sooner than Cement B. However, with calcium chloride, Cement B sets sooner than Cement A.

In Fig. 2, with calcium nitrate the difference in setting times for Cements A and B is even more pronounced; over much of the dosage range Cement A sets about $\frac{3}{4}$ hr sooner. With sodium thiocyanate, Cement B consistently sets somewhat sooner than Cement A. However, with calcium chloride, Cement A sets about $\frac{1}{2}$ to $1\frac{1}{2}$ hr sooner than Cement B and the difference is wider at 16-32 oz/100 lb of cement than at 48-64 oz per 100 lb.

Figs. 3 and 4 demonstrate that, as might be expected, for both Cement A and Cement B all three accelerators are more effective in hastening setting at 40 F than at 70 F. With sodium thiocyanate, the difference is more pronounced for Cement B than for Cement A. However, for calcium chloride the difference is more pronounced for Cement A than for Cement B.

When interpreting Figs. 3 and 4, one should note that, as Table 1 shows: 1) Cement A mortar at 40 F with no admixture took 2 hr 47 min longer than did the same mortar at 70 F to reach initial set. 2) Cement B mortar at 40 F took 2 hr 37 min longer than did the same mortar at 70 F to reach initial set. Therefore, in order for the mortars at 40 F to have the same setting characteristics as the mortars at 70 F, they would have to have demonstrated an acceleration over that of the 70 F mortar of approximately 2 hr 40 min.

Also, it should be remembered that ounce for ounce, sodium thiocyanate is the most expensive, calcium nitrate somewhat less expensive, and calcium chloride far less expensive.

From the test data and cost data, it appears that the most effective dosage rates in terms of cost are for sodium thiocyanate approximately 2-8 oz/100 lb of cement and for calcium nitrate 12-40 oz/100 lb.

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- C 230-183 Specification for Flow Table for Use in Tests of Hydraulic Cement
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- C 403-85 Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance

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TABLE 1--TIME OF INITIAL SETTING OF CEMENTS A AND B

	<u>At 70 F (21 C)</u>	<u>At 40 F (4 C)</u>
	hr:min	hr:min
Cement A	4:45	7:32
Cement B	4:50	7:27



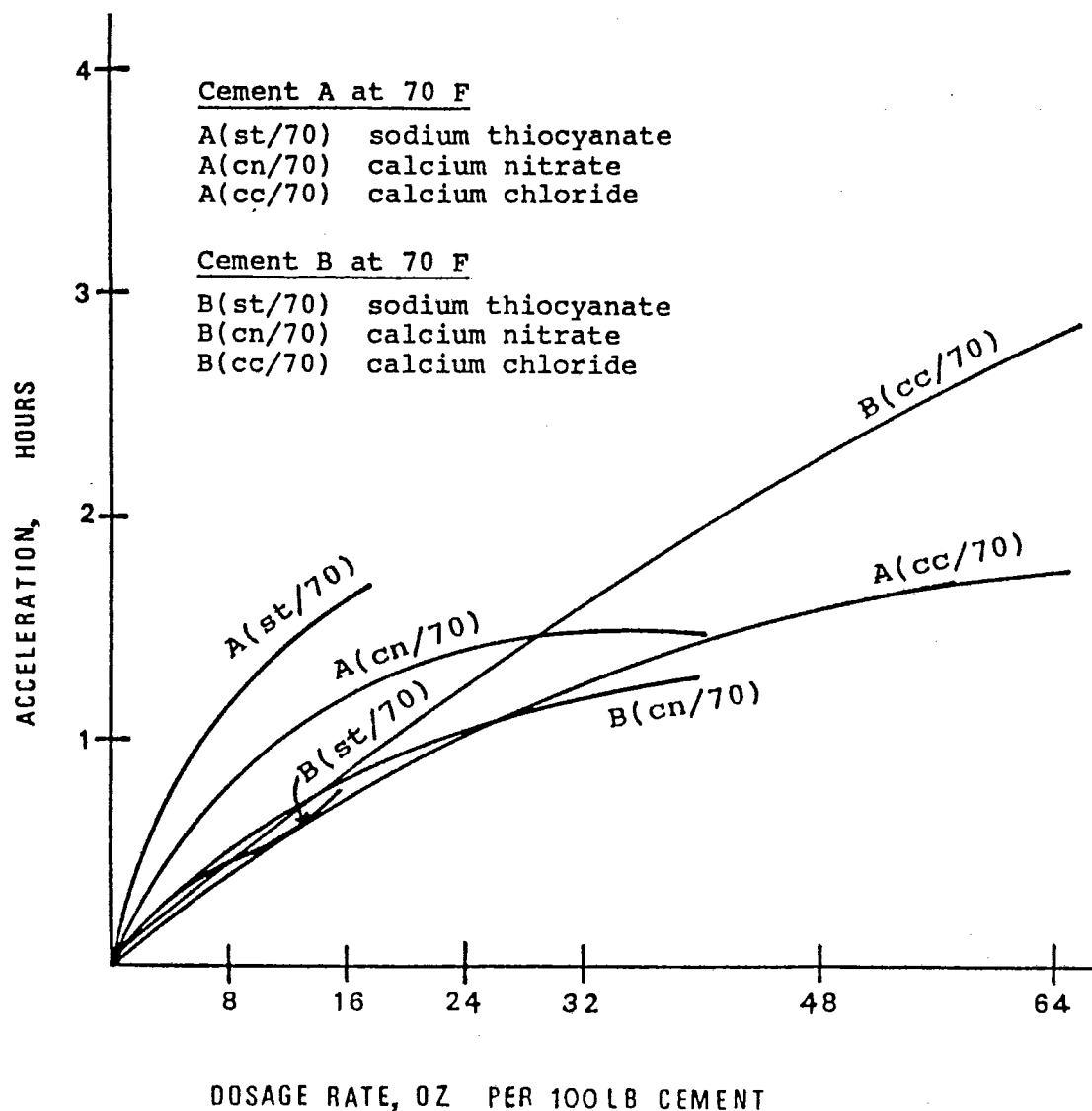


Fig. 1--For Cements A and B at 70 F, effect of dosage rate on time to set for three accelerators

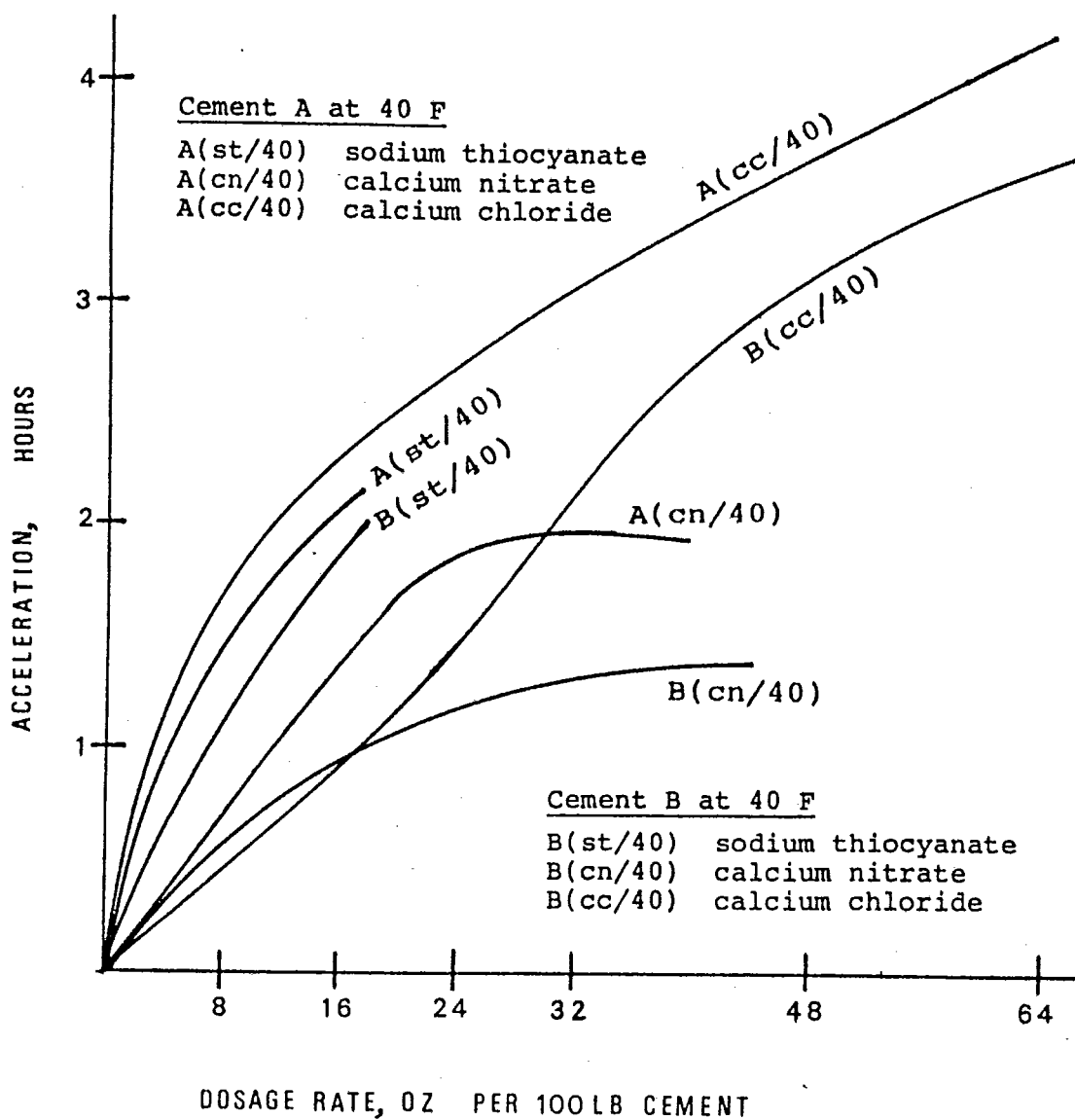


Fig. 2--For Cements A and B at 40 F, effect of dosage rate on time to set for three accelerators

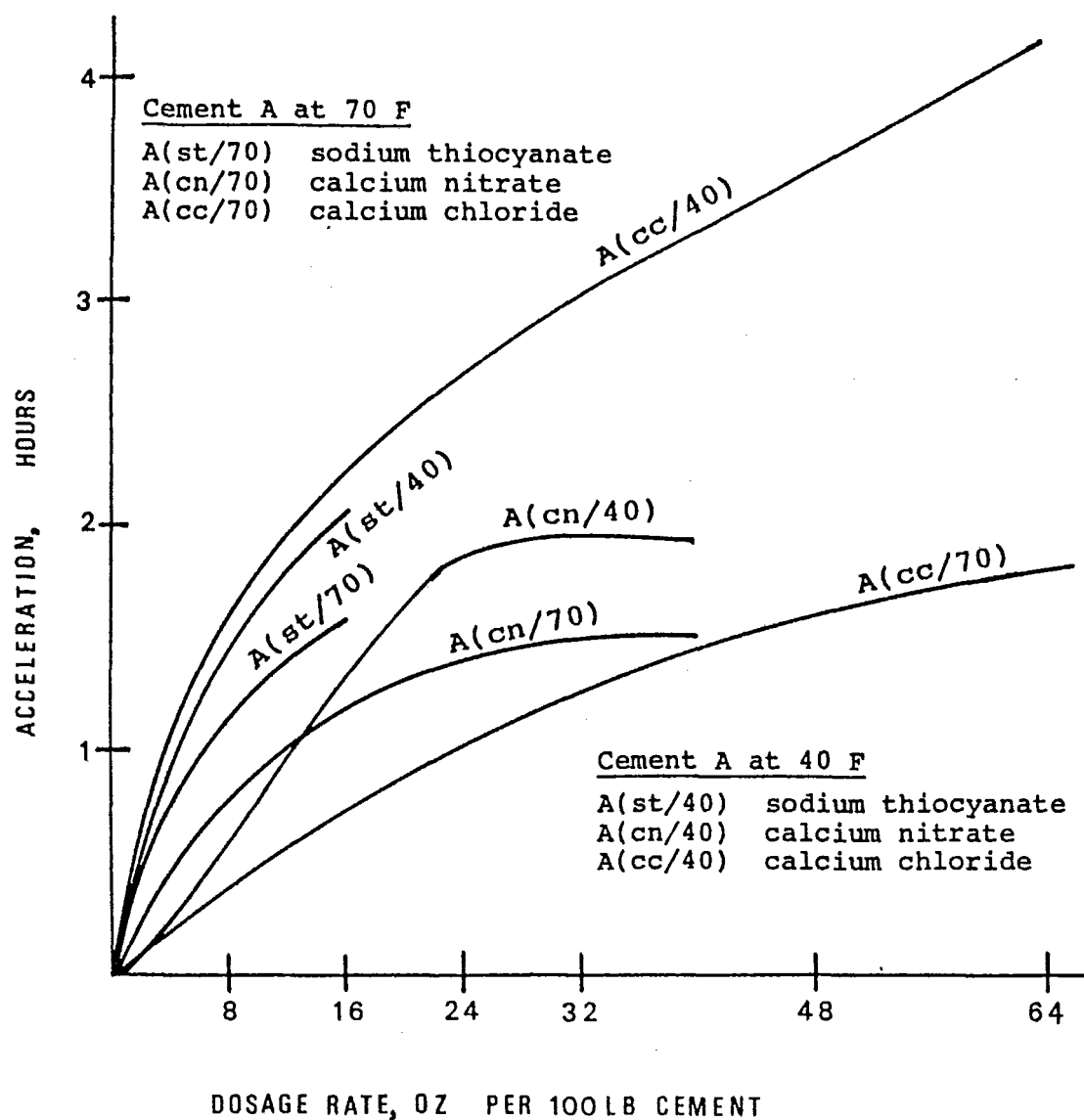


Fig. 3--For Cement A at 70 F and 40 F, effect of dosage rate on time to set for three accelerators

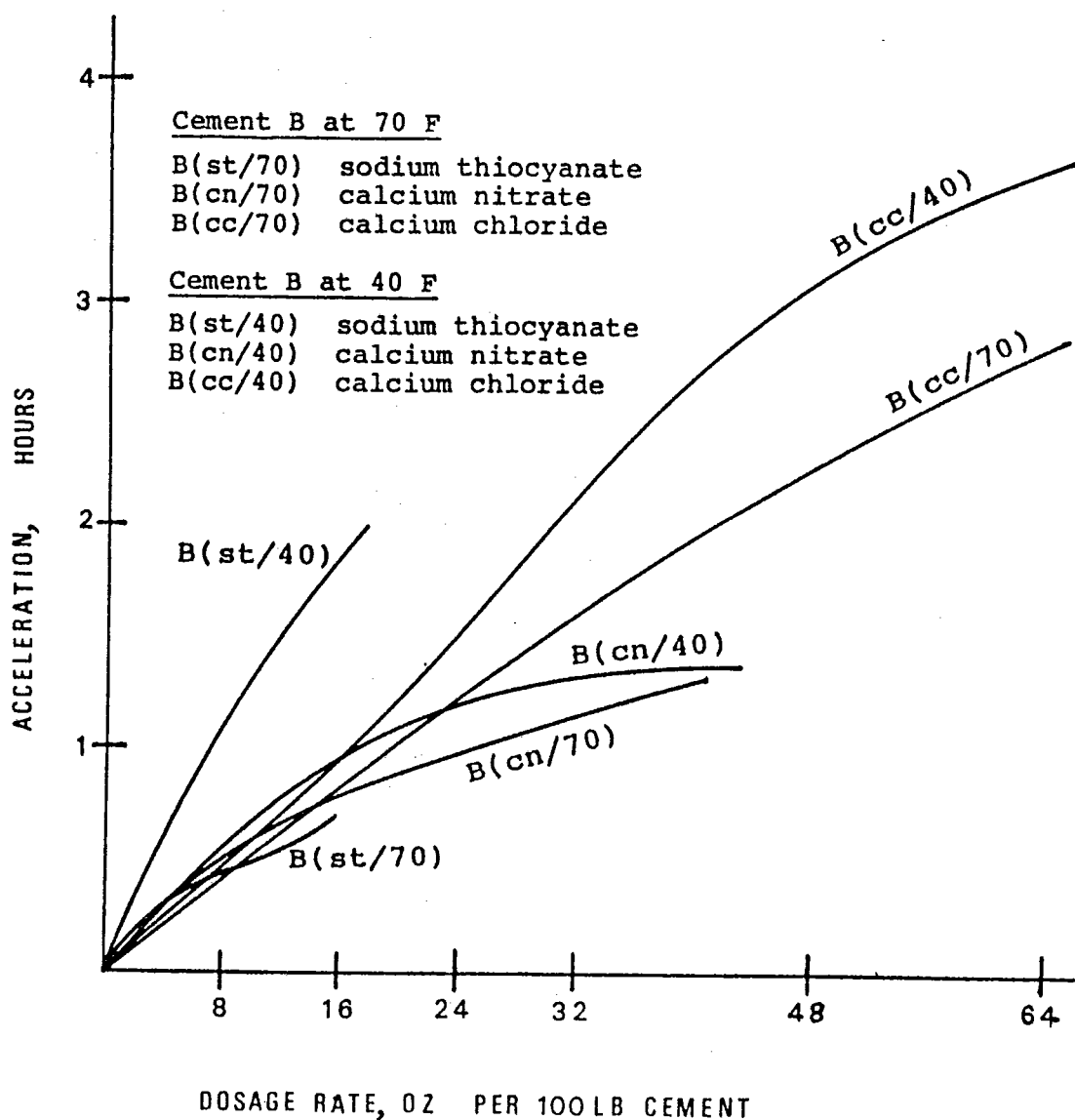


Fig. 4--For Cement B at 70 F and 40 F, effect of dosage rate on time to set for three accelerators

Comparison of the Corrosion Potential of Calcium Chloride and a Calcium Nitrate Based Non-Chloride Accelerator— a Macro-Cell Corrosion Approach

by J. Holm

Synopsis:

A method for evaluation of the corrosion potential of chemical admixtures is presented. The method allows the direct measurement of the macrocell corrosion current between two layers of electrically connected reinforcing bars embedded in concrete. By ponding the specimens with chloride-free water, the potential of the chemical admixture to instigate corrosion can be evaluated. By using a chloride-containing ponding solution, in particular a 15% NaCl solution, it may be possible to assess the potential corrosion inhibiting effects of certain chemical admixtures.

The test method was used to compare the corrosion activity in reinforced concrete slabs containing a normal dosage rate of calcium chloride, plain concrete and concrete containing two dosage rates of a multicomponent calcium nitrate based non-chloride accelerator. Only the slabs containing calcium chloride exhibited corrosion when ponded with tap water. When subjected to cyclic ponding with the salt solution, both the plain concrete and the concrete slabs containing the two dosage rates of the non-chloride accelerator exhibited corrosion. However, the slab containing the higher dosage rate of the non-chloride accelerator exhibited only 25% of the corrosion activity of the other two slabs. It is speculated that this reduction may be the result of corrosion-inhibiting effects of the non-chloride accelerator when it is added at sufficient rates.

Keywords: accelerating agents; calcium chlorides; calcium nitrates; concrete slabs; corrosion; corrosion tests; reinforced concrete

36 Holm

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INTRODUCTION

The growing concern about chloride-induced corrosion of reinforcing bars embedded in portland cement concrete has led to the development of a number of chloride-free admixtures. Particular attention has been given to the formulation of chloride-free set-accelerating admixtures to replace the widely used calcium chloride accelerator. Some of these non-chloride accelerators (NCA) are based partially on chemical compounds which are believed to have corrosion-inhibiting properties.

This paper presents a method for studying the influence of admixtures on the rate of corrosion of reinforcing bars embedded in concrete, both with respect to possible corrosion-promoting and corrosion-inhibiting effects. This method utilizes direct measurement of the macrocell corrosion current between two layers of electrically connected reinforcement embedded in concrete.

The method was used in this study to compare the corrosion potential of calcium chloride and a multicomponent calcium nitrate based accelerator. In addition, the ability of this accelerator to act as a corrosion inhibitor was assessed.

CONCLUSIONS

The results of the work presented in this paper indicate that for the non-chloride accelerating admixture used in this study:

1. The addition of the non-chloride accelerator at dosage rates of 25 or 40 oz per 100 lbs of cement did not result in corrosion of reinforcing bars embedded in concrete which was continually exposed to essentially chloride-free water. This behavior is similar to that of plain concrete.
2. The addition of calcium chloride to concrete at a rate of 1.8% by weight of cement caused an initially very high corrosion rate which subsequently subsided to a relatively low level, when the concrete was exposed to continuous ponding with essentially chloride-free water.

3. While the addition of 25 oz per 100 lbs of cement of the non-chloride accelerator had no effect on the corrosion rate of the reinforcement in concrete exposed to cyclic ponding with a salt solution, there was a marked reduction in corrosion activity in the concrete containing 40 oz of non-chloride accelerator per 100 lbs of cement.

RECOMMENDATIONS

The use of the non-chloride accelerator which was used in this test program does not cause increased corrosion activity in reinforced concrete, either when exposed to moisture alone or when exposed to externally introduced chloride ion, and should therefore from a corrosion standpoint be a recommended admixture, provided its ability to accelerate the setting of concrete is adequate for the given application.

The test method which was used in this study is recommended for use as an accelerated method for evaluating the corrosion potential of chemical admixtures. Because of the number of corrosion related parameters which can be measured, this method may provide more extensive information than the hitherto quite widely used "lollipop" (1) procedure with regard to corrosion of reinforced concrete members such as bridgedecks, where chloride ion predominantly enters the concrete from one surface.

The results of this work do, however, indicate that there is a need to learn more about the influence of admixed calcium chloride on the corrosion rate of reinforcement embedded in concrete which is not exposed to external chloride. Similarly, there is a need for additional work to evaluate the effects of the calcium nitrate alone as well as in combination with other compounds which are commonly present in non-chloride accelerating admixtures on the corrosion rate of rebars in concrete exposed to external chlorides.

DISCUSSION

The chemical reactions involved in electrolytic corrosion of reinforcing bars in concrete, an explanation of the differences between micro and macro corrosion cells and details concerning test specimens and testing procedure are presented in the Appendix. Tables and graphs listing the acquired data are likewise included in the Appendix. The geometry of the test specimens used in this study is shown in Fig. 1.

A test method which can be modified to evaluate the corrosion potential of a chemical admixtures has been reported by Spellman and Stratfull (1). This method relies on the assessment of corrosion activity by measurement of the electrical potential of a reinforcing bar embedded in concrete containing the chemical admixture. These measurements are typically made with reference to either a saturated calomel half cell (SCE) or a copper-copper sulfate half cell (CSE). ACI 222 and ASTM C876 suggest that

active corrosion is likely for measured CSE potentials more negative than -0.35 volts. This same value has been frequently used as a threshold value in studies of the influence of admixtures on corrosion of rebar.

However, unpublished data from ongoing corrosion studies conducted by Wiss, Janney Elstner Associates, Inc. (WJE) for the Federal Highway Administration (FHWA) have shown that active corrosion cells may be associated with CSE potentials as high as -0.25 volts; see Fig. 2. The test method used to develop the relationship shown in Fig. 2 is an accelerated test setup which simulates field exposure of reinforced concrete. This was the same test method as the one used in the study presented in this paper.

Continuous Ponding

The development of the corrosion currents in the specimens containing calcium chloride while ponded continuously with tap water is interesting. As can be seen from the data in Table 3, the corrosion activity was quite high for the first 6 - 8 weeks, after which time it subsided considerably. This phenomenon may have resulted because the ponding water which entered the concrete from the top surface could migrate through the specimen and escape as vapor from the bottom surface thereby causing a disturbance of the presumably originally uniform distribution of the water-soluble chloride ion. The results of acid-soluble and water-soluble chloride content analyses throughout the depth of one of the calcium chloride containing slabs are listed in Table 4 and presented in graphical form in Fig. 3. The chloride data indicate that the water-soluble chloride ion concentration in the concrete at the bottom layer of steel had become 50 percent higher than at the top layer of reinforcing. Considering these data and the discussion of electrolytic corrosion presented in the Appendix, there appear to be two primary reasons for the subsidence in the corrosion activity in the slabs containing calcium chloride: (1) The tendency of moisture to move down through the specimens causes a reduction in the available oxygen at the bottom (cathodic) layer of steel (oxygen starvation); (2) The displacement of water-soluble chloride ion towards the bottom layer of bars puts these bars in a more corrosive environment than the top bars. The top bars are, however, prevented from becoming cathodic because practically no oxygen is available, and because, according to Le Chatelier's principle, the cathodic reactions which produce water will be resisted by the abundant presence of moisture in the top, saturated concrete.

At the time of termination of this portion of the test program, one slab from each of the four test conditions was destroyed and the reinforcing bars were examined for corrosion products. All bars embedded in the plain concrete and the concrete containing the two dosage rates of non-chloride accelerator were free of corrosion products. The top bars embedded in the concrete containing calcium chloride exhibited

considerable pitting but no broad areas of corrosion. The bottom bars contained only a few pits.

Cyclic Ponding

The corrosion current data in Table 5 indicate that the plain concrete and the concrete containing 25 oz/cwt of cement of the non-chloride accelerator show similar corrosion activity when exposed to cyclic ponding with a 15% NaCl solution. Considerably less corrosion took place in the slab containing 40 oz/cwt of cement of the NCA. The amount of iron which passes into solution (corrodes) at the anode is proportional to the amount of charge which passes through the resistor. Since current is defined as the amount of charge which passes through a given conductor per unit time, the areas under the curves in Fig. 4 are proportional to the amount of corrosion products which have been produced in the slabs by the macro cell. From the graphs it appears that the slab containing the higher dosage rate of NCA showed a reduction in corrosion activity by about 75 percent compared with the other two systems. It is speculated that this reduction in corrosion activity could be the result of the presence of proprietary chemical(s) in the NCA. The data presented in Fig. 5 resulted from cyclic testing of slabs containing calcium nitrite as a corrosion inhibitor, as part of the previously mentioned test program for FHWA. Although the measured corrosion currents are substantially higher in this case, presumably because cyclic ponding was started immediately after completion of the 25 day drying period, the tendency of the calcium nitrite to reduce the rate of macrocell corrosion during the test period is evident.

Upon termination of the cyclic ponding test the three specimens were broken and the bars were examined. In all three cases the bottom bars were free of corrosion. By contrast, the top bars in all slabs exhibited corrosion. The amount of corrosion product on the bars from the plain concrete and the concrete with 25 oz/cwt of the non-chloride accelerator contained similar amounts of corrosion products when examined visually. However, the bars from the slab with the higher dosage rate of the non-chloride accelerator exhibited only about a fourth of the corrosion products as did the aforementioned slabs. These observations of actual corrosion product formation correlate well with the measurements of macrocell corrosion currents.

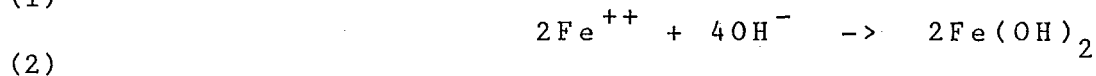
ACKNOWLEDGMENTS

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APPENDIX

Electrolytic Corrosion of Reinforcing Steel in Concrete

Corrosion of reinforcing steel in non-carbonated concrete can occur in the presence of oxygen, moisture and halide ion (typically chloride ion). This form of corrosion is termed "electrolytic corrosion" because it requires the presence of an electrolyte. The corrosion current passes through the electrolyte from anodic to cathodic regions of the reinforcement. The iron passes into solution (corrodes) at the anode and the electrons released during the conversion of free iron to ferrous ions are consumed at the cathode. The net chemical redox reactions which take place can be summarized as follows:



In the absence of chloride (or other halide) ion, the high alkalinity of the concrete pore solution causes the above reactions to reach an equilibrium; the reinforcing steel becomes "passivated". However, when chloride ions are introduced in sufficient amounts, the equilibrium is disturbed and the reinforcement corrodes at the anode. The driving force in the electrolytic corrosion cell is the difference in nonpolarized potentials between the anode and the cathode.

It is characteristic of electrolytic corrosion that oxygen is required for the chemical reactions at the cathode only. In fact, the rate of corrosion is often determined by the availability of oxygen to the cathode. This is why electrolytic corrosion does not take place in reinforced concrete structures which are fully submerged in sea water.

Microcell Versus Macrocell Corrosion Cells

The main difference between microcell and macrocell corrosion is illustrated in Fig. 6. In microcell (or pitting) corrosion, the anode is immediately adjacent to the cathode. In a macrocell, the anode and the cathode are separated by some distance. The anode/cathode pair in a macrocell can occur on one and the same rebar or as is often the case in parking decks or bridge decks, one layer of reinforcement becomes anodic while the other layer becomes cathodic. In the macrocell shown in Fig. 7, chloride and moisture enter the concrete from the top surface and promote corrosion of the top layer of reinforcement. The bottom layer of reinforcement, being drier and therefore having more access to oxygen, acts as the cathode, supporting corrosion at the top layer anode.

Test Specimens

An isometric sketch of the test specimens used in this study is shown in Fig. 1. The specimens were 12 in. by 12 in. by 7 in. in dimensions. Two layers of #4 reinforcing bars were incorporated in each specimen, both with 1 in. clear cover. The bottom layer consisted of four bars, while the top layer contained two bars. All rebars within each layer were electrically connected. The two layers of bars were electrically connected via a resistor.

Four pairs of test slabs were fabricated. These pairs of slabs represented the following four conditions:

1. Control slabs. No accelerating admixtures
2. Anhydrous CaCl_2 @ 1.8 percent by weight of cement
3. Non Chloride Accelerator @ 25 oz/cwt of cement
4. Non Chloride Accelerator @ 40 oz/cwt of cement

The main properties of the non-chloride accelerator used in this study are given in Table 1. All concrete was batched according to the mix design given in Table 2. Eau Claire sand and gravel was used since this is a chloride-free aggregate source.

The ends of the bars were given a thick epoxy coat. The epoxy left 11 in. of bar uncoated, so that the outer 0.5 in. of the bar embedded in concrete was coated. The slabs were cast upside down to eliminate top surface variations due to finishing and were cured for three days in plastic bags followed by 25 days of air-drying in the laboratory.

During the period of air-drying the slabs were instrumented. Plexiglass dikes, 1 in. high, were mounted on the top surface of the slab. The sides of the slabs were given two coats of a commercially available two-component epoxy concrete sealer. The bars within each of the two layers of reinforcement were electrically connected and the two layers of bars were connected via a known resistor. All exposed surfaces of the bars were subsequently coated with epoxy.

Testing Procedure

Testing of the slabs began at the age of 28 days. Initial measurements of the corrosion current were taken by measuring the voltage drop over the resistor. Although this was not made a part of this study, the test setup also permits measurement of the following parameters:

- Instant-Off Potential: Measured between the two layers of bars 16 milliseconds after breaking contact. This is close to the true non-polarized potential difference.
- Half-Cell Readings: Copper-copper sulfate half-cell measurements can be made over the top bars.
- Concrete Resistance: The electric resistance between the two layers of bars can be measured with an ohmmeter.

The top surfaces of the slabs were subsequently ponded with tap water and stored under a canopy at 90-110 °F. Corrosion readings were subsequently taken at regular intervals. After 35 weeks of continuous ponding, one slab each from the pairs containing NCA and the pair containing calcium chloride were exposed to cyclic ponding with a 15% solution of NaCl in water. The cycles consisted of 4 days of ponding at laboratory temperature and 3 days of drying under a heated canopy.

The results of all corrosion readings are presented in Tables 3 and 4. The results of the cyclic ponding tests are presented graphically in Fig. 4.

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TABLE 1--MAIN PROPERTIES OF THE NON-CHLORIDE ACCELERATOR

ASTM C494 Classification	Type C - Accelerating Admixture Type E - Water Reducing and Accelerating Admixture
Major Constituents	Calcium Nitrate, $\text{Ca}(\text{NO}_3)_2$ Proprietary Modifiers
Range in Dosage Rate	10-40 oz per 100 lbs of Cement 0.65-2.60 ℓ per 100 kg of Cement

TABLE 2--CONCRETE MIX PROPORTIONS AND TEST DATA

Cement	432 lb/yd ³ (4.6 bags/yd ³) 257 kg/m ³
Aggregate	Eau Claire Sand and Gravel (Chloride-free)
Slump	3 $\pm$ 1 in. 75 $\pm$ 25 mm
Water-Cement Ratio	0.46-0.51
Compressive Strength	5000 psi @ 28 days 35 MPa @ 28 days

TABLE 3--CORROSION CURRENTS DURING CONTINUOUS PONDING

Weeks of Continuous Ponding	Corrosion Current (10^{-6} Amperes)			
	Plain (no accelerator)	1.8% CaCl_2	25 oz/cwt *	40 oz/cwt *
0	0	2	0	0
2	1	295	0	0
4	0	220	0	0
6	0	70	0	1
9	0	19	0	0
11	0	18	0	0
13	0	10	0	0
19	0	4	0	0
24	0	6	0	0
64	0	4	0	0

* Dosage rate of non-chloride accelerator, per 100 lbs of cement

TABLE 4--CHLORIDE ANALYSIS TEST RESULTS FOR SLAB CONTAINING CALCIUM CHLORIDE

Sampling Depth from Top Surface, in.	Cl^- , Percent by Weight of Concrete	
	Acid Soluble	Water Soluble
0 - 1/2	0.075	0.033
1/2 - 1 1/2	0.097	0.043
1 1/2 - 2 1/2	0.115	0.054
2 1/2 - 3 1/2	0.112	0.058
3 1/2 - 4 1/2	0.103	0.060
4 1/2 - 5 1/2	0.105	0.060
5 1/2 - 6 1/2	0.109	0.065
6 1/2 - 7	0.117	0.091

TABLE 5--CORROSION CURRENTS DURING CONTINUOUS PONDING

Weeks of Cyclic Ponding	Corrosion Current (10^{-6} Amperes)		
	Plain (no accelerator)	25 oz/cwt *	40 oz/cwt *
0	0	0	0
3	0	0	0
6	0	50	0
8	100	110	0
11	120	120	3
13	130	120	24
16	130	120	22
20	130	130	35
23	130	120	33
26	100	120	27
29	80	110	28
32	80	110	28
35	80	100	42

* Dosage rate of non-chloride accelerator, per 100 lbs of cement

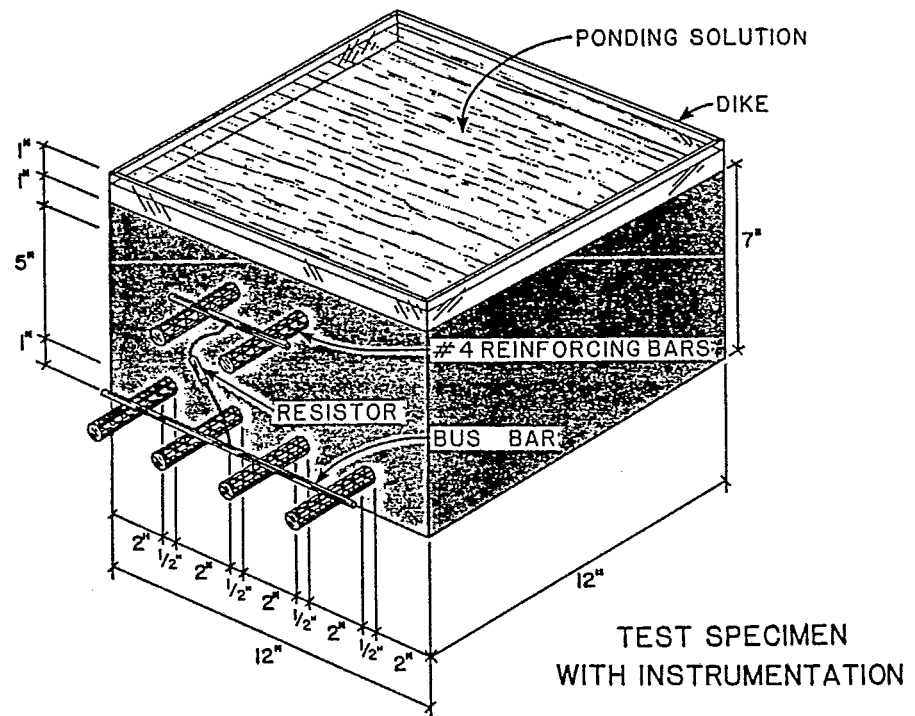


Fig. 1--Geometry of the test specimens