

SP 49-1

CONTROL OF STEEL CORROSION IN CONCRETE SEA STRUCTURES

By

Odd E. GjØrv

Synopsis: Under the combined effects of exposure to ocean environments and heavy structural loading there are a number of deteriorating processes taking place. Experiences from the field have shown, however, that it is the electrochemical corrosion of the reinforcing steel which represents the greatest problem to the durability of concrete sea structures. Experiences have also shown that it may take a long time before any practical problems due to steel corrosion occur. When the problems do occur, however, the most susceptible parts of the structures are those parts which are the most exposed to intermittent wetting and drying in the splashing zone. A brief survey of protective methods indicates that it may be difficult to find a general method to inhibit this corrosion. However, if the steel corrosion is detected at a very early stage by a regular monitoring of steel potentials along the concrete surface, it should be possible to choke down and control the corrosion by application of a proper surface coating. In the long term the most direct way to reduce the problem of steel corrosion would be to develop new types of reinforcing materials which are less subjected to corrosion.

Keywords: admixtures; cathodic protection; chlorides; concrete durability; concretes; corrosion; corrosion resistance; deterioration; loads (forces); marine atmospheres; permeability; protective coatings; reinforcing materials; reinforcing steels; sea water; structural analysis.

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INTRODUCTION

All the literature on durability of concrete in sea water makes up a comprehensive, interesting and fascinating chapter in the long history of concrete technology. Concrete in sea water is a topic which has concerned professional people, committees, and national authorities through generations. A number of papers have been presented to international meetings such as The International Association for Testing Materials in Copenhagen 1909, New York 1912, and Amsterdam 1927, and the Permanent International Association of Navigation Congresses (PIANC) in London 1923, Cairo 1926, Venezia 1931, and Lisbon 1949. In more recent years there has been the meetings of The International Union of Testing and Research Laboratories for Materials and Structures (RILEM) in Pragh in 1961 and 1969, and the RILEM-PIANC meeting in Palermo in 1965.

As early as 1923 Atwood and Johnsen (1) had assembled a list of approximately three thousand references, and even today the discussion continues on the mechanism of deterioration of cement pastes in sea water (2). However, with the concrete technology of today it should not be the disintegration of the concrete itself which represents the greatest problem to the durability, but rather the electrochemical corrosion of the reinforcing steel (3). In the following, therefore, a brief survey will be given of various means to control this corrosion.

CORROSION OF REINFORCING STEEL

Concrete normally provides to embedded steel a high degree of protection against corrosion. This is because steel in concrete is polarized anodically, and a thin protective film of gamma iron oxide is formed on the steel surface. However, this passivating film is disrupted when the pH-value of the moisture in equilibrium with the concrete is reduced by carbonation, or when sufficient salt (chloride ions) has penetrated to the steel surface. The relationship between the rate of steel corrosion and the alkalinity and chloride concentration in the environment has not been completely elucidated. However, the works of Shalon and Raphael (4) and Hausmann (5) suggest that there is a threshold concentration of chloride ions which must be exceeded before any corrosion occurs. This threshold concentration of chloride ions depends on the pH-value.

It is a well known phenomenon that even very small concentrations of chloride ions are able of breaking the passivating film. Bäumel and Engell (6) have shown that if a saturated calcium hydroxide solution substitutes the concrete, chloride concentrations even smaller than 0,0035 per cent have some effect on the passivity.

That the passivity of the steel becomes partly or completely broken only means that the electrochemical potential locally becomes more negative (anodic areas), while other portions of the steel still having the passivated potential intact thereby will act as cathodes and catchment areas for oxygen. Since moist concrete is a good electrolyte a rather complicated system of galvanic cell activity can develop along the steel. The electromotive force in these galvanic cells depends mainly on the pH-value and chloride concentration in the moisture next to the steel and on the transfer of dissolved oxygen through the concrete cover.

Depending on exposure, thickness of concrete cover, and age of concrete the following conditions may exist along the embedded steel:

- Moisture in equilibrium with uncarbonated concrete without any chlorides.
- Moisture in equilibrium with carbonated concrete without any chlorides.
- Moisture in equilibrium with uncarbonated concrete contaminated with chlorides.

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- Moisture in equilibrium with concrete being both contaminated with chlorides and having low pH.

Normally, carbonation of concrete is not a problem unless cracking of the concrete has occurred or the concrete cover is defective. In high chlorine environments such as ocean environments, however, investigations on existing structures (7, 8) as well as on laboratory specimens (9) indicate that chloride ions can penetrate even into high-quality concrete to greater depths than what is normally prescribed as the thickness of concrete cover. However, this does not necessarily mean that a severe steel corrosion will occur. When steel corrodes in concrete this is normally a process controlled by the rate at which dissolved oxygen can reach the steel. Thus, if the concrete cover is sufficiently thick or if the concrete is completely water saturated, this may slow down the transfer of oxygen and hence the rate of corrosion.

Even though some degree of steel corrosion has been reported on concrete piles continuously submerged (7) comprehensive observations in the field indicate that corrosion normally becomes more negligible if the concrete is continuously water saturated (8). The most susceptible parts of the structures are those parts which are the most exposed to intermittent wetting and drying (in the splash-ing zone). To control this corrosion a number of protective methods have been suggested and partly also applied.

PROTECTION OF REINFORCING STEEL

Cathodic protection

As long as a good electrolyte exists in the concrete, cathodic protection of the steel should always be possible. This type of protection is generally accomplished by connecting the steel to a source of electrons and then flooding the steel with a high concentration of electrons. The practical application may be effected in two ways, viz. by impressed polarization from an external generator, or by galvanic action from a bimetallic coupling (cfr. zinc on steel). Cathodic protection based on the generator method has been applied for some time on both ordinary reinforced and prestressed concrete structures (10, 11). The main problem from a practical point of view is to obtain control of potentials and current densities over the entire reinforcement. As the electrical resistivity of the concrete is highly dependent on the moisture and salt content in the concrete, the electrolytical conditions may noticeably vary from part to part within the same structure,

as well as from time to time depending on the environmental conditions. Further, the applied voltages must not be too high, since excessive alkali may then lead to softening and breakdown of the bond between the steel and concrete. In recent years some criteria have been reached for application of cathodic protection (12). However, at the time being the practical experiences are very limited.

Choking of oxygen

Since corrosion of steel in concrete is normally of the oxygen type, the simplest way to inhibit corrosion should be to choke off the access to oxygen. For methods based on this principle it is important that the choking is equally effective to all the steel which is in electrical contact. Partial choking of oxygen may only promote formation of cell action.

As already mentioned transfer of oxygen will be slowed down by water filling the pores. An experimental attempt to prevent corrosion in this way has been described by Stratfull (10), where a number of wetting units were attached to the bottom surface of a bridge deck.

Sealing of the concrete surface by a proper surface coating will also effectively reduce the access to oxygen. Furthermore, this sealing will reduce the absorption and evaporation of moisture during changes in the weather conditions and thus promote more uniform moisture content in the concrete. On the other hand a coating will also involve a certain amount of maintenance. A defective coating may only promote formation of cell action.

Inhibiting admixtures

Suitable reagents added to the fresh concrete can develop various kinds of protective surface films on the steel. Several admixtures of this type have been investigated. However, from a practical point of view attention should be paid to the different behaviour of the different types of such admixtures. Thus, filming inhibitors of the anodic type are only effective when present in sufficiently high concentrations and are otherwise dangerous since the corrosion then will be intensely localized and the attack stimulated. Even though good experiences have been obtained by the use of corrosion inhibitors in concrete, such admixtures still should be used with some caution until more fundamental research is done.

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Coating of the steel

Apart from chemical conversion coatings, where the metal is protected by its own oxide (phosphate coating), a number of non-metallic as well as metallic coatings have been suggested and partly applied as protective coatings for reinforcing steel. For the non-metallic coatings preparation of the steel surface by pickling and cleaning is necessary, and the bond to the concrete must also be secured. However, if such coatings should suffer mechanical damage, which may occur during handling of the steel, metal and hydroxyl ions will be able to pass between anodes and cathodes because no inhibitor is present, thus ending up in local corrosion.

If on the other hand the coating is of a metallic character, both a more efficient protection can be obtained as well as a rougher handling of the steel tolerated. The degree of protection will depend on the following factors:

- The polarity of the steel-metallic coating couple.
- The polarization characteristics of both the metallic coating as well as of the steel.
- Formation of macrocells on the metallic coating as a result of different environments along the surface of the metal.

Zinc has been applied for some time as a coating metal for reinforcing steel (galvanizing) (13). Since opinion has varied as to the efficiency of this coating, Bird and Strauss (14) did also investigate some other metal coatings such as high purity tin, copper, cadmium, nickel, and lead. According to these tests only zinc or cadmium could offer some protection. However, since the tests showed that the zinc itself rapidly corroded once salt had penetrated the concrete, it seems that a galvanized coating could postpone the onset of steel corrosion, but it would not delay its occurrence for a very long time. The same tests further showed that a coating of cadmium remained passive even in the presence of a high salt content in the concrete. It seems therefore that cadmium could offer a good protection, but it may be argued that both the price and the toxic properties of this metal would make such a coating less attractive.

CONCLUDING REMARKS

It should be pointed out that depending on the thickness and quality of the concrete cover it may take a long time for the salt to reach the steel. Also, the presence of salt in the concrete is only one of several factors necessary for a steel corrosion to occur. Experiences from the field indicate that a number of structures have been a long time in service without any problems due to steel corrosion (15). However, since there are so many factors involved, it may be difficult to predict a period free of corrosion for one particular structure based on experiences from other structures. As a consequence all larger structures for which the safety plays an important role, should be periodically monitored for any changes in steel potentials from the passive to the active state. By measurements of steel potentials along the concrete surface it should be possible to detect a steel corrosion at an early stage before any cracking or spalling of the concrete would occur.

The problems involved with a surface coating were previously pointed out. However, if a steel corrosion is detected at a very early stage a further steel corrosion could possibly be choked down by application of a proper coating to the concrete surface. The corrosion of the steel would then be controlled by the efficiency of the sealing and the maintenance of the surface coating.

In the long term the most direct way to reduce the problem of steel corrosion would be to develop new types of reinforcing materials which are less subjected to corrosion. On the background of the rapid development taking place in the use of reinforced concrete in ocean environments the development of such materials should be a matter of increasing importance.

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SP 49-2

SHOTCRETE COVERCOATS FOR PRESTRESSED CONCRETE TANKS

By
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Synopsis: The author provides a brief history of the original use of shotcrete to provide corrosion protection for spirally wound prestressed shotcrete and concrete tanks. In addition, various failures are described along with reasons for the failures. Details are also given of steps that must be taken to insure permanent corrosion protection for the wire.

Keywords: circular prestressing; corrosion resistance; domes (structural forms); failure; prestressed concrete; reinforcing steels; roofs; shells (structural forms); shotcrete; spiral reinforcement; tanks (containers).

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Francis X. Crowley has some twenty-five years' experience in the field of precast, prestressed concrete tank construction, the last two years as President of Natgun Corporation. A graduate of M.I.T., Mr. Crowley holds a number of patents covering construction techniques in this field.

Prestressed concrete and shotcrete tanks have been built for more than fifty years. Tanks prior to 1940 were prestressed with rods and turnbuckles. Thereafter, nearly all tanks were prestressed with high tensile wire placed spirally on the wall by "wire-winding" machines at a stress of approximately 140,000 psi. In nearly all cases, the prestressing elements were protected from corrosion by dry mix shotcrete (gunite). The reason for the selection of shotcrete for this purpose was the fact that forms were not required and relatively thin coats could be placed on the outside of the tank core wall at a cost considerably less than that of concrete encasement.

Several other factors made shotcrete the nearly universal selection for this purpose. First, the shotcrete could be bonded to the concrete core wall eliminating the danger of pockets between core wall and covercoat. These pockets can assimilate moisture and facilitate corrosion by providing free oxygen for the corrosion process. Furthermore, water pockets could make the covercoat susceptible to damage from freezing and thawing. A second factor was the high resistance of shotcrete itself to the freeze-thaw cycle. The low water cement ratio inherent in shotcrete placed against a vertical surface makes it highly resistant to spalling in cold climates. A third factor is the high cement content of the shotcrete. When placed against a vertical surface, the amount of sand aggregate which can be retained in the mix is limited. Excess sand finds its way to the ground in "rebound". Thus, the high cement content of the shotcrete on the wall helps maintain an alkali condition in any moisture which finds its way to the prestressing steel. A fourth factor is that sand will not stick to a dry vertical surface. Thus, the first layer of material retained on the surface and around the wire is a coating of neat cement. This not only is the most important element in providing the bond between the core wall and the covercoat, but it also substantially enhances the alkaline shield around the prestressing wire. Thus shotcrete seemed to be a "natural" for this purpose.

The builders of prestressed tanks in the 1930's were essentially shotcrete (gunite) companies which were building prestressed tanks to expand their product line. About thirty-five years ago, Mr. John M. Crom, Sr., then of the National Gunite Corporation, developed the first "wire-winding" machine. This machine was able to apply a high tensile wire spiral to the core wall of concrete and shotcrete tanks at controlled high stress. This opened the door to the construction of much larger tanks than was previously contemplated or even considered possible. The machine was called a "wire-winder". Since that time other "wire-winders" have been developed and thousands of wire wound, prestressed concrete tanks have been built all over the world. The shotcrete covercoat continued to be, and still is, the best, available protection against corrosion.

With the advantages of shotcrete cited above, the shotcrete covercoat should have done the job without serious difficulties. Unfortunately this was not the case. Gross carelessness and poor engineering judgment have resulted in difficulties ranging from "minor" to "very serious" and include at least two tank failures. Regrettably, as is frequently the case, it was the failures which forced the prestressed tank industry to realize that shotcrete covercoat requires reasonable care and quality control to insure reliable performance.

Shotcrete covercoat now protects enough prestressing wire, placed over the past thirty years, to encircle several times the planet called "Earth". It should not surprise us that some problems have occurred. It is, in fact, the problems which point the way to a number of simple steps which will insure permanent protection of the wire.

The first step is to be sure that the shotcrete covercoat is bonded to the core wall. Naturally, this requires the surface of the core wall to be "bondable". Considerable difficulty was encountered with cast in place concrete core walls which were formed with plywood or steel. Oil from the forms and the "slick" surface combined to cause a covercoat separation problem. This was resolved by sandblasting the surface to enhance the bond. Rough shotcrete or broomed precast concrete surfaces are ideal for bonding. Another problem which should be noted - although it seemed to be limited to certain areas on the California coast - was the use of aggregate which caused high shrinkage and temperature coefficients in the concrete and shotcrete. Since most of the shrinkage in the concrete of the core wall has already taken place at the time the covercoat is applied, high shrinkage caused by the aggregate used in the shotcrete probably resulted in the covercoat pulling away from the core wall. In addition, during the summer, higher temperatures combined with high temperature coefficients in the covercoat (which is at the outer surface of the tank wall) also tended to pull

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the covercoat from the core wall. Such aggregate sources should be avoided.

Also, the shotcrete covercoat should be checked periodically after placement to make sure it is bonded. This can be done by sounding with a hammer. Separated areas should be removed and replaced or the void filled by epoxy injection. Checking for covercoat separation from time to time is prudent since some covercoat separation can occur on a delayed basis.

The second step is placing the prestressing wire in such a way that they can be encased in the shotcrete without excessive sand pockets (voids). This would seem to be elementary, but bunching of prestressing wires was the primary cause of an industrial tank failure in California. The wires were "bunched" at pipe sleeve openings in the tank wall (See Figure 1). In order to maintain the aperture, half the wires which were placed at the elevation of the wall opening were "snapped" above the pipe sleeve and the other half were "snapped" below the pipe sleeve. This created "bunches" of wire at the pipe sleeves which were impossible to encase with shotcrete. The disastrous solution used was to cover the "bunches" of wire with shotcrete so that the voids could not be seen. Leakage of highly corrosive slurry at the pipe sleeves corroded the wires and the tank failed.

The correct solution to the problem is to displace prestressing wires normally placed at the elevation of the wall openings to elevations above and below the openings. These wires are then placed in multiple layers horizontally around the full circumference of the tank so that each wire can be encased in protective shotcrete (See Figure 2).

Also, investigation of wire corrosion problems has shown that little care was given to wire spacing in the construction of early (prior to 1960) wire wound tanks. Removal of the covercoat on these tanks revealed that proper attention had not been given to spacing the wires so that the shotcrete could have encased each individual wire. It should not be inferred that, if one wire occasionally touches another (resulting in a sandpocket), a serious problem will result. This has not proved to be the case. On the other hand, wire spacing should be detailed so that each wire can be encased in shotcrete and sandpockets substantially eliminated.

Wire spacing is more important for shotcrete covercoats than it is for prestressing tendons which are encased in concrete or grout. The reason for this is that the shotcrete has limited opportunity to flow after it is "in place". Tanks prestressed with post-tensioned

cables where wires are deliberately grouped and subsequently encased in pressure grout do not require wire spacing. Also, there has been a recent development which utilizes a wire-winding machine to place wires grouped in a pattern similar to the strands utilized in pre-tensioned concrete. These strands are spaced away from the core wall and are subsequently encased within vibrated concrete or mortar. This technique also eliminates the necessity for the wire spacing required for shotcrete encased wire.

The third step is to use demonstrated and acceptable practices for the application of the shotcrete. Since these procedures are thoroughly covered in ACI Standard 506-66 "Recommended Practice for Shotcreting" and in the report of ACI Committee 344 published in the September 1970 issue of the ACI Journal, they will not be repeated here except for the following:

As suggested above, it is desirable to have the protective shotcrete flow around the prestressing wire. This is keyed to two factors, the velocity and the consistency of the mix as it impinges on the wall. The velocity should be high enough and the mix wet enough so that transverse flow can be seen as the wire is covered.

The fourth step is to make sure that the wire is covered with shotcrete at least 1" thick. Again, it might seem obvious that positive means should be used to insure minimum covercoat thickness. Nevertheless, the fact of the matter is that builders of the early tanks utilized the eyes of "experienced" nozzlemen to determine the thickness. Many, if not most, of the experienced nozzlemen of that era would take it as a personal affront if someone suggested that their judgment in this matter was not reliable. Unfortunately, too many engineers and tank builders acceded to their position. In later years, during the investigation of wire corrosion problems, covercoat was removed to expose the wire. The "nozzlemen's eyes" were found to be unreliable in the extreme and covercoat thicknesses were found to vary from 1/8" to 2-1/2". In general, the average thickness of covercoat was well over 1" but this is one application where averages don't count.

There is the case of the sludge digestion tank in New York. Above ground, the tank had a brick veneer which was tied to the prestressed concrete wall by dovetail anchors which fitted into dovetail anchor slots imbedded in the shotcrete. These vertical slots, formed with sheet steel, were tied to the prestressing wire approximately two feet on center and the shotcrete covercoat was placed between them. Thus, the prestressing

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wire was alternately covered for two feet and uncovered for one inch for most of the upper part of the tank.

Add to this the fact that the detail at the top of the wall allowed water to be shed from the concrete dome into the space between the brick veneer and the wall. Thus, even when the weather was sunny and dry outside, the atmosphere adjacent to the wire, which was substantially "exposed" every two feet on center, was corrosively damp.

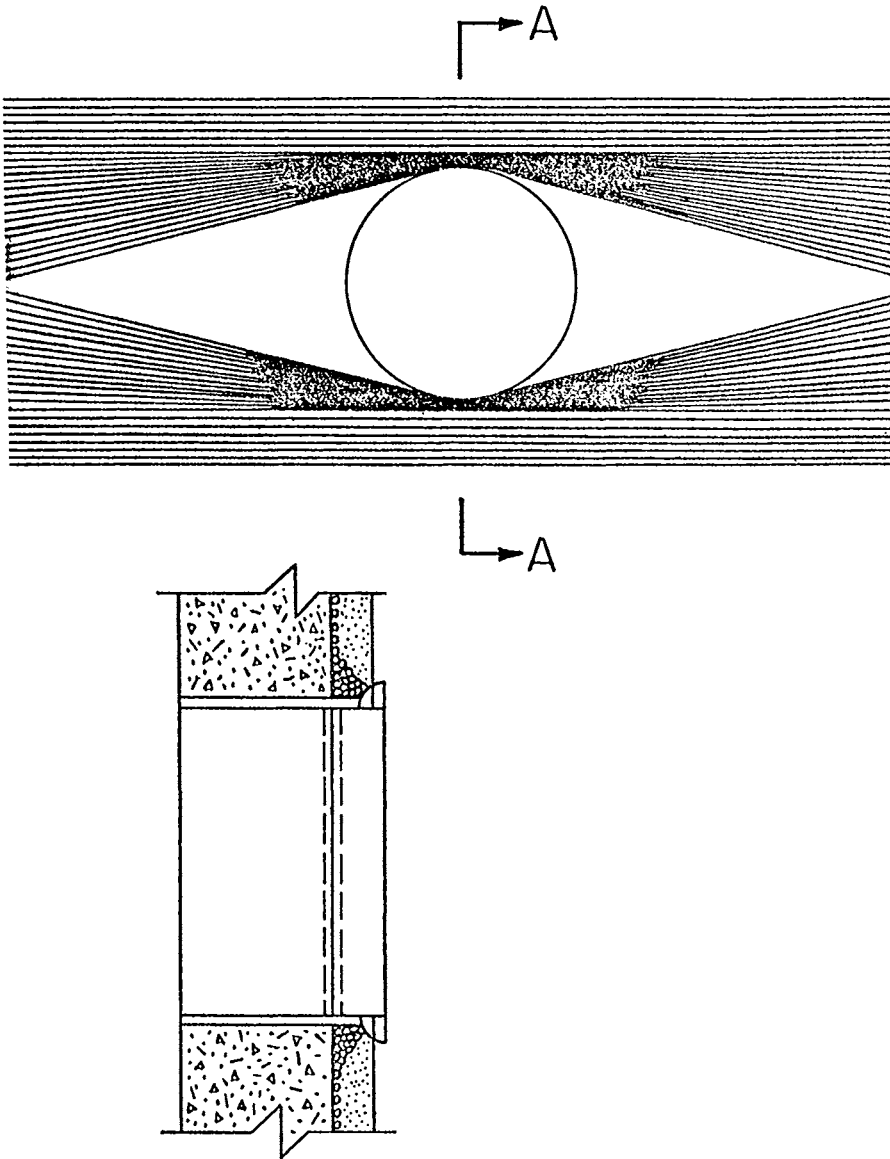
After approximately ten years, the tank failed and the question arose, "Why did the tank fail?" That question is easy to answer. A more difficult question is, "Why did it last for ten years?"

These two situations illustrate the fact that what is obvious in retrospect is not always obvious at the time decisions are made. The solution to the problem is to install vertical "screed wires" (See Figure 3) approximately three feet on center spaced a minimum of 1" from the prestressed wire, place the shotcrete and screed it to these wires. In this way, the minimum covercoat thickness can be checked by an inspector with a simple "carpenter's rule" prior to the placement of the shotcrete.

Thus the four simple rules to follow for reliable shotcrete corrosion protection for wire wound prestressed tanks are:

1. Provide a bondable surface and make sure the shotcrete covercoat is bonded to the core wall.
2. Space the prestressing wire in such a way that each wire is encased in shotcrete.
3. Use proven shotcrete techniques as described in ACI 506 and ACI 344.
4. Use positive methods to insure that all the wire has a minimum coat of 1" of shotcrete.

More than thirty years' experience and literally millions of square feet of shotcrete covercoat for wire wound prestressed concrete tanks (See Figure 4) have shown that adherence to these rules will assure corrosion protection for the wire. Failures and difficulties have occurred but they only point up the fact that the inadequacy was not with the process, but rather with those who applied it.



SECTION A-A

Fig. 1--Improper placement of prestressing wire at a wall casting

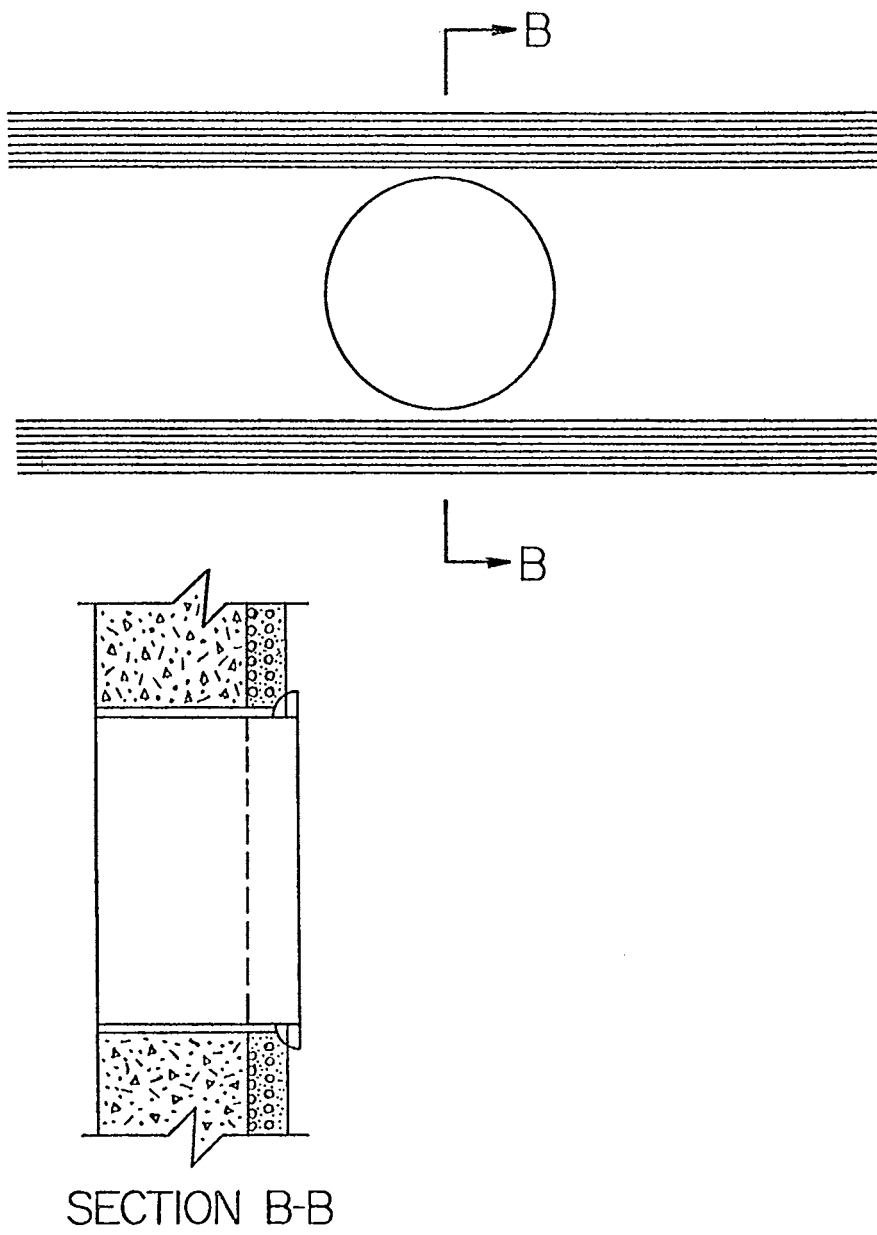


Fig. 2--Improper placement of prestressing wire at a wall casting



Fig. 3--Screed wires

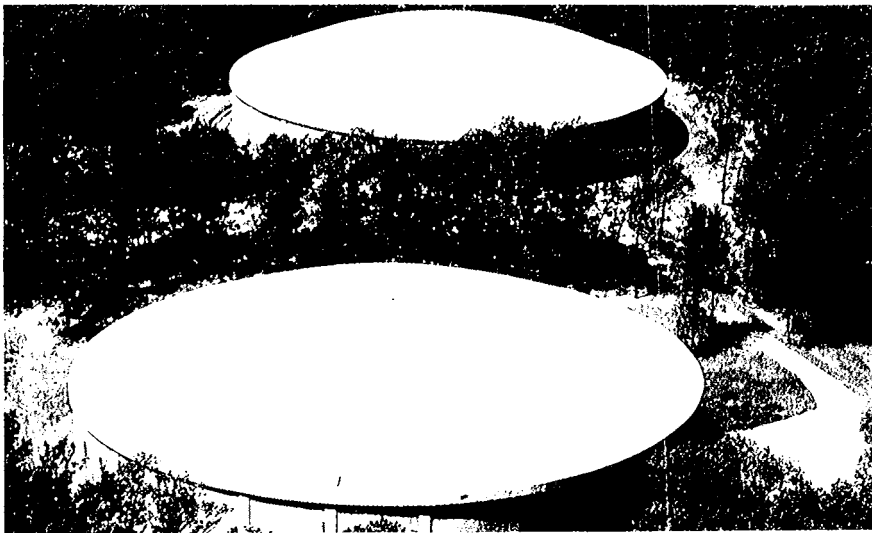


Fig. 4a--6.5 MG and 5.5 MG tanks, Warwick, R. I.

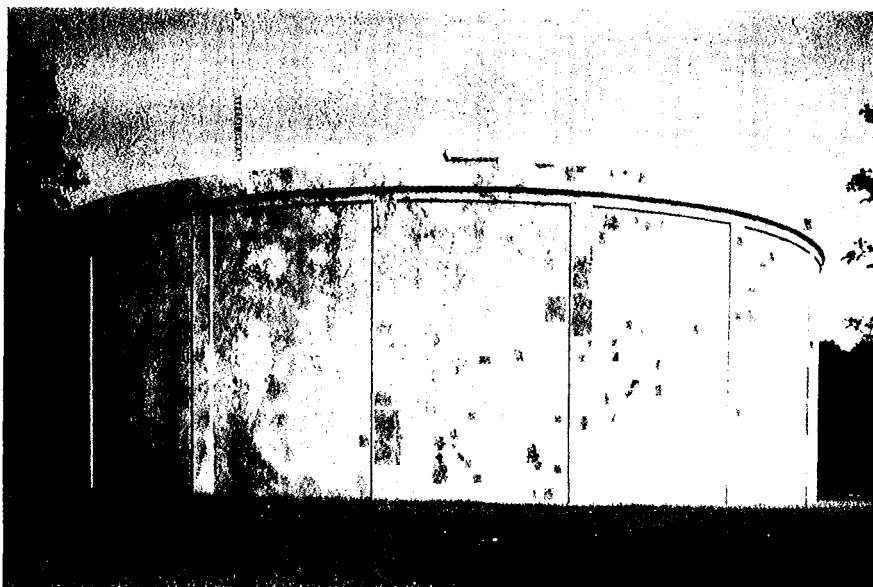


Fig. 4b--0.5 MG tank, Georgetown, Mass.

SP 49-3

MECHANISMS OF CORROSION OF STEEL IN CONCRETE

By
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Synopsis: The purpose of this paper is to present in an interpretative manner and as briefly as is consistent with accuracy those factors of design, concrete quality, and environment that affect the corrosion of steel in concrete and the resulting performance of the structure.

Cement paste normally provides a highly alkaline environment that protects embedded steel against corrosion. Concrete of low water-cement ratio, well compacted, and well cured has a low permeability which minimizes penetration of corrosion inducing factors--oxygen, chloride ion, carbon dioxide, and water. The high alkalinity of the paste can be lost by leaching or by carbonation. Oxygen and water are required for corrosion to occur. Chloride ions in the paste tend to destroy the protective film formed on the steel by the alkaline environment. The higher the alkalinity at the paste-steel interface the higher the chloride ion concentration that can be tolerated before corrosion occurs. In addition to low concrete permeability, increasing the depth of concrete cover over the steel significantly reduces the movement of the corrosion inducing factors to the surface of the steel. The alkali and tricalcium aluminate content of the cement also influence susceptibility to corrosion.

The environment to which the concrete is exposed directly influences the electrochemical corrosion process as discussed above. In addition, the outside environment can cause non-uniformities in the local environments of the embedded steel such as preferential leaching or carbonation, or concentration cells resulting from differences in chloride ion, oxygen, or moisture.

Keywords: alkali-carbonate reactions; alkali content; cathodic protection; cement pastes; chlorides; concretes; corrosion resistance; cover; cracking (fracturing); permeability; quality control; reinforcing steels; staining; water-cement ratio.

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INTRODUCTION

Concrete normally provides to embedded steel a high degree of protection against corrosion. This is because concrete inherently provides a highly alkaline environment for the steel which protects, passivates, the steel against corrosion. In addition, concrete of low water-cement ratio and well cured has a low permeability which minimizes penetration of corrosion inducing factors--oxygen, chloride ion, carbon dioxide, and water. In addition, low permeability, to a moderate degree, increases the electrical resistivity of the concrete which assists in reducing the rate of corrosion by retarding the flow of electrical currents within the concrete that accompany electrochemical corrosion.

Because of these inherent protective characteristics, corrosion of steel does not occur in the preponderant majority of concrete structures or concrete elements. The fundamental factors contributing to corrosion of steel are well known. With concrete of suitable quality, corrosion of steel can be prevented, providing the structure or element is properly designed for the intended environmental exposure. In instances of very severe exposure, such as in bridge decks exposed to deicing salts or pilings in sea water, the use of other protective measures such as corrosion inhibitors, coatings on steel or concrete, or cathodic protection may be utilized. However, corrosion of steel and accompanying distress can result if the concrete is not of suitable quality, the structure was not properly designed for the anticipated environment, or the actual environment or other factors were not as anticipated or changed during the life of the structure.

Instances of distress due to corrosion can be found in most applications of reinforced or prestressed concrete; buildings, slabs, beams, bridge decks, piles, tanks, pipes, etc. Sometimes the first evidence of distress is brown staining of the concrete around the embedded steel. This brown staining, resulting from corrosion (rusting) of the steel may permeate to the concrete surface without cracking of the concrete but usually it accompanies cracking or cracking of the concrete occurs shortly thereafter. Concrete cracking occurs because the corrosion product of steel, an iron oxide or "rust," has a volume more than two-fold greater than the metallic iron from which it was formed. The forces generated by this expansive process can far exceed the tensile strength of the concrete with resulting cracking. Steel corrosion not only causes distress because of staining, cracking, and ravelling of the concrete but may also cause structural failure resulting from the reduced cross-section and hence reduced tensile capacity of the steel, this normally being more critical with thin prestressing steel tendons than with larger reinforcing bars.

There are different mechanisms by which corrosion or corrosion failure may occur. It is not the intent of this "State of Knowledge" summary to present a complete review of the voluminous amount of information that has been reported on this subject. The literature contains many hundreds of papers, many in the foreign literature, on the various aspects of corrosion. Significant portions of some of the reported information are incomplete or conflicting and therefore it has been necessary for this writer to personally interpret or select from the data available. The purpose of this introductory paper is to present, as briefly as is consistent with accuracy, those factors of design, concrete quality, and environment affecting the corrosion of steel in concrete and the resulting performance of the structure. It is not intended for the uninformed layman or for the well-informed few but rather for the practicing engineer, contractor, advanced student, or others having a general working knowledge of concrete and its properties.

Steel or iron corrosion may be produced by several mechanisms. Although "corrosion" of iron by direct oxidation (burning) or by acid attack can occur, such corrosion is of little concern in concrete. Indirect oxidation (electrochemical corrosion) can result from dissimilar or non-uniform metals or dissimilar environments. Corrosion of steel in concrete due to "stress corrosion," hydrogen embrittlement, or electrolysis due to "stray" electrical currents have rarely been reported as possible causes of distress. Therefore, particular emphasis will be placed in the following discussion on electrochemical corrosion, believed to be the cause for essentially all of the corrosion distress that occurs.

GENERAL MECHANISMS OF ELECTROCHEMICAL CORROSION

In electrochemical corrosion a flow of electrical current and one or more chemical processes are required. The flow of electrical current caused by "stray" electrical sources, within the structure or from the earth, or resulting from the movement of sea water (an electrical conductor) within or over the structure, may directly induce the corrosive chemical reactions. The incidence of electrochemical corrosion directly caused by such electric currents appears to be quite rare, but can be quite serious when it occurs.

Rather the preponderance of instances of electrochemical corrosion in concrete results because of the existence of differences in metals or non-uniformities of the steel (different steels, welds, active sites on the steel surface) or non-uniformities in the chemical or physical environment afforded by the surrounding concrete. These non-uniformities under certain specific conditions can produce significant electrical potential differences and resultant corrosion.

Even though a potentiality for electrochemical corrosion might exist because of non-uniformity of the steel in the concrete (active sites), the corrosion is normally prevented by a "passivating" iron oxide film which rapidly forms on the steel surface in the presence of moisture, oxygen, and the water-soluble alkaline products formed during the hydration of the cement. The principal soluble product is calcium hydroxide, Ca(OH)_2 , and the initial alkalinity of the concrete is at

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least that of saturated lime water (pH of about 12.4 depending upon the temperature). In addition, the seemingly relatively small amounts of sodium and potassium oxides in cement further increase the initial alkalinity of the concretes or paste extracts and pH values of 13.2 and higher have been reported (1, 2).

There are two general mechanisms by which the highly alkaline environment and accompanying passivating effect may be destroyed: (1) reduction of alkalinity by leaching of alkaline substances with water or partial neutralization by reaction with carbon dioxide or other "acidic" materials, and (2) by electrochemical action involving chloride ions in the presence of oxygen.

Reduction of alkalinity, by leaching with water, is an obvious process. Reduction by reaction with carbon dioxide, as present either in normal air or dissolved in water, involves neutralizing reactions with the sodium and potassium hydroxides and subsequently the calcium hydroxide and calcium silicates, etc., in the portland cement paste system. This process of carbonation, although progressing slowly, may in time penetrate the concrete to a depth of 1/4 to 1 or more inches (3, 4) (depending upon the quality of the concrete and other factors) and thereby neutralize the protective high alkalinity normally afforded.

FACTORS INFLUENCING ELECTROCHEMICAL CORROSION

In this section, the various chemical and physical factors affecting electrochemical corrosion will be considered in greater detail.

Chemical Environment in Concrete

Alkalinity and Chloride Concentrations. As previously mentioned the high alkalinity of the chemical environment normally present in concrete protects the embedded iron because of the formation of a protective oxide film on the iron. The integrity and protective quality of this film depend upon the alkalinity or pH of the environment. The higher the alkalinity, the greater the protective quality of this film. Iron in concrete becomes potentially more susceptible to corrosion as the alkalinity is reduced (by leaching or carbonation) or when soluble chlorides are present at the iron-paste interface. Chloride ion appears to be a specific and unique destroyer of the protective oxide film.

The relationship between rate of corrosion of iron and the alkalinity and chloride concentration in the environment has not been completely elucidated. The work of Shalon and Raphael (1) and of Hausmann (5) suggest that there is a threshold concentration of chloride ion which must be exceeded before corrosion occurs and that an increase in chloride ion concentration beyond this threshold concentration results in increased rate of corrosion up to some limit at which the availability of the oxygen necessary for corrosion to occur may be significantly reduced (6). This concept of threshold chloride ion concentration is shown schematically in Figure 1. This idealized figure is intended to show that increasing concentrations of chloride ions (destructive to the protective film), can be tolerated without

any resulting corrosion provided the alkalinity is increased, thereby promoting the formation of the protective oxide film.

Chlorides may be present in the concrete from several different sources. Soluble chlorides may be introduced in the fresh concrete by the use of aggregates containing chlorides--for instance, salt may be used in wintertime to thaw aggregate stockpiles or the aggregate may be from a saline source, such as coral. Saline water is sometimes used as the concrete mix water. Calcium chloride may be used as an accelerator or a concrete admixture containing chlorides may be used. Some cements may contain small amounts of chlorides. Chlorides may also enter the concrete from the environment, deicing salts, sea water, etc. The depth of penetration of such chlorides into the concrete towards the iron-paste interface depends upon several factors to be discussed later.

Although such chlorides in cement paste are soluble, much of the chlorides will not actually be in solution in the liquid within the paste. Chlorides react with the hydrated tricalcium sulfoaluminate phase in the paste to produce a corresponding tricalcium chloroaluminate compound perhaps in solid solution with hydrated calcium aluminate (7). The work of Monfore and Verbeck (8) and of Roberts (9) indicate that as much as 75 to 90 percent of the chloride actually present exists in the paste in the chloroaluminate compound, the amount depending upon the total amount of chloride present and the tricalcium aluminate content and degree of hydration of the cement. The effects of C_3A content and duration of curing on the equivalent concentration of calcium chloride in solution are shown in Figure 2 (8). As can also be noted in this figure the actual chemistry is more complex than as simply stated above in that the cement with 0 percent calculated tricalcium aluminate content significantly reacted with calcium chloride. Although only a fraction of the chloride is in solution, it should be noted that if the chloride in solution were removed, such as by leaching, it would be replaced in the liquid by additional chloride dissolving from the remaining chloroaluminate compound present.

As regards the relationship between alkalinity and soluble chlorides, it should be noted that from chemical considerations a distinct difference in the action of sodium chloride and calcium chloride would be expected. The addition of calcium chloride to cement paste adds chloride and would reduce alkalinity somewhat due to an increase in the total ionic strength of the resulting liquid phase. The addition of sodium chloride similarly adds chloride but would be expected to increase the alkalinity of the paste liquid above that of saturated calcium hydroxide or the liquid phase without the sodium chloride addition.

As previously mentioned, the work of Hausmann (5) suggests that there is a threshold chloride-alkalinity ratio that must be exceeded before corrosion can occur. In his tests a threshold ratio of chloride ion activity to hydroxyl ion activity of 0.6 was observed. The hydroxyl ion activity was measured using a standard pH meter and the chloride ion activity was measured using a silver chloride and a calomel electrode. For the total ionic strength of the solutions used, the chloride ion activity was depressed to approximately 0.76 of the actual chloride ion concentration in solution, a reduction which was experimentally

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observed and which can be calculated from physical chemical principles. The type of basic work undertaken by Hausmann yields considerable insight regarding details of the mechanisms involved and should be considerably extended as suggested in the subsequent paper in this symposium entitled "Needed Research."

Oxygen. As indicated previously, an essential factor required for corrosion of iron in concrete is the presence of oxygen at an iron-paste interface in addition to chloride and a reduced alkalinity. For example, sea water has been used successfully as mixing water for reinforced concrete continually and completely submerged in sea water, because of (1) maintenance of high alkalinity (sodium chloride), (2) reduced oxygen content in sea water, and (3) very slow diffusion of oxygen through the water saturated paste. Perhaps this effect is best demonstrated in the work of Griffin, et al. (6), as shown in Figure 3. It may be noted that corrosion increased as the sodium chloride concentration increased until a maximum was reached beyond which the rate of corrosion decreased despite the increased chloride concentration, because of the reduced solubility and hence availability of oxygen to sustain the corrosion process.

Cement. Although cement composition and type can effect corrosion, the role of cement is relatively small compared to major and common causes of distress from corrosion due to poor concrete quality, lack of sufficient cover over the iron, or poor consolidation. As previously discussed, the tricalcium aluminate content of the cement affects the tendency towards corrosion, but the use of a cement having a high C_3A content cannot in itself assure satisfactory performance. A cement of high alkali content would also appear to offer advantages because of the higher inherent alkalinity provided. However, other factors may mitigate such simple considerations: the actual C_3A content may be different than that calculated, the degree to which the total alkali present is readily soluble may differ among cements, the fineness and sulfate content of the cement and other factors may influence the permeability of the paste and concrete. In general it is observed (10) that cements high in C_3A afford greater corrosion protection to reinforcing steel in piles in sea water, as shown in Figure 4.

Tests by Öst and Monfore (11) of corrosion of prestressing steel in concretes did not reveal any significant differences between concretes made with portland blast-furnace slag cements and corresponding Type I portland cements.

Portland pozzolan cement might be expected to be detrimental toward corrosion in that pozzolanic action would reduce alkalinity, the amount of calcium hydroxide, remaining in the hydrated paste. However, this effect might be offset were the permeability of the resulting concrete correspondingly reduced.

Considerable difficulty was encountered, particularly in Germany, by the use of high-alumina cement in the manufacture of prestressed concrete elements. Failure of the prestressing steel by stress corrosion or hydrogen embrittlement occurred, particularly in environments involving moisture and the presence of sulfur and nitrogen compounds.

Carbonation. The passivity created by the highly alkaline environment in the cement paste can be destroyed by reduction of this alkalinity by carbonation of the alkali hydroxides, calcium hydroxide and the calcium silicates and aluminates in the cement paste matrix. Under certain conditions carbon dioxide, even the low concentration present in normal air, can permeate the concrete for some considerable distance (depending upon concrete quality, moisture content and duration of exposure) and significantly reduce the alkalinity of the paste, hence the passivity of the iron. Although carbonation can penetrate some considerable distance, in most instances carbonation which substantially reduces alkalinity is generally limited to a depth of about 1 inch or so. Considerable information is available regarding many factors influencing the depth and rate of carbonation and the resulting possibility of corrosion (3, 4). Various organic indicators have been used to reveal the depth of carbonation, phenolphthalein being used most commonly. A number of other chemical and physical procedures are also described. The references cited above contain considerable information on the influence of cement and aggregate types, concrete composition, and exposure conditions and durations on carbonation and corrosion that should at least be qualitatively applicable.

Inhibitors. Numerous chemical additives, both organic and inorganic, have been suggested as specific inhibitors of iron corrosion (12). Some of the additives may retard set of the concrete or be detrimental to later-age strength. Many would be subject to leaching and hence less effective in concrete that is aged. Among those compounds reported as inorganic inhibitors are potassium dichromate, stannous chloride, zinc and lead chromates, calcium hypophosphite and sodium nitrite. Organic inhibitors suggested have included sodium benzoate, ethyl aniline and mercaptobenzothiazole. With some inhibitors, inhibition occurs at an optimum inhibitor to chloride ratio but at lower or higher ratios the "inhibitor" may actually promote corrosion. Sodium nitrate has been used with apparent effectiveness in Europe (12).

Physical Environment in Concrete

For corrosion to occur it is not only necessary that the passivation of the iron be reduced or destroyed but that there be created within the system differences in electrochemical potential, i.e., metal areas that are anodic (positive) and cathodic (negative). Such differences may arise because of inherent differences within the concrete per se, or for inherently uniform concrete, from differences in the environmental exposure of concrete.

ELECTROCHEMICAL POTENTIAL CAUSED BY FACTORS WITHIN THE CONCRETE

Differences in electrochemical potential within the concrete may arise in various ways. Differences in metals or for any single metal the occurrence of "active sites" and less active sites will create such electrochemical potential differences. Differences in metal potential from site to site may also result from differences in chemical environment, such as differences in alkalinity from site to site due to differences in alkalinity provided by the cement localization of alkali

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at sites within the concrete due to alkali-aggregate reaction, or preferential leaching or carbonation. Similarly, differences in concentration, "concentration cells" as to chloride ion or oxygen may develop. Such differences may also result because of the presence of cracks where leaching of alkali, increased vulnerability to carbonation, and intrusion of chloride and oxygen could occur. Bleeding, segregation, or poor consolidation of the concrete would also cause differences in environment between the upper and lower sides of reinforcing steel. Temperature differences within the concrete can also create differences in electrochemical potential but the primary effect of increased temperature is that of acceleration of the electrochemical reactions and the corrosion process.

ELECTROCHEMICAL POTENTIALS ARISING FROM ENVIRONMENTAL FACTORS

Electrochemical potential differences may be produced by external environmental factors. For example, reinforced concrete submerged in sea water exposes the concrete to a uniform environment and any differences that arise would be due to differences inherent in the concrete. In such concrete, the salt or chloride concentration would be relatively uniform at the steel surface (assuming uniform concrete quality and depth of cover over the steel) and oxygen and carbon dioxide concentrations would be minimal. However, if a concrete is simultaneously subjected to differences in exposure various differences in active factors may result. For example, in a driven concrete pile, the concrete continuously submerged is subject to a relatively noncorrosive environment. However that part of the pile in the tidal zone is exposed to oxygen, chloride, and carbon dioxide which represents a potentially severe condition. The concentration of chloride in the concrete in the tidal zone, and particularly immediately above it, may become very high due to capillary action drawing the salt solution within the concrete where it is concentrated by evaporation of water at the surface of the pile. The top of the pile is exposed to salt spray, oxygen, and carbon dioxide. Differences in chloride concentration may occur in a bridge structure due to non-uniform application of deicing salts (to the deck), or because the upper side of the reinforcing steel in the deck being exposed to a higher concentration of chloride than the lower side, or in the structural beams due to non-uniform exposure because of salt solution leaked through joints and cracks. Prestressed concrete tanks near the ocean may have a higher concentration of chloride on one side from salt-laden ocean air.

Previously mentioned were external sources of electrical flow such as from "stray" currents within the structure or in the ground.

Influence of Concrete Quality. The most important quality of the concrete as regards corrosion is the permeability of the concrete to the diffusion of water, chlorides, oxygen and carbon dioxide. Low permeability, which retards the ingress of these corrosion promoting factors, is attained by the use of low water-cement ratio, well cured concrete. In many instances the use of air-entrainment will further reduce the ultimate permeability of the concrete although contributing to increased total porosity. The effect of initial water-cement ratio

of well cured pastes is shown in Figure 5 (13). The significant effect of water-cement ratio is noted. Adequate curing of the concrete is also very important but not always appreciated. Table 1 shows the effect of duration of curing on the water permeability of portland cement pastes. The effect of curing on the permeability of concretes should be qualitatively similar but of course the permeability of concrete is also affected by bleeding, degree of proper consolidation, permeability of the aggregate, etc. Although concrete dries out slowly after completion of moist curing, the surface region dries rapidly with resulting cessation of hydration. Thus the most critical zone, that between the concrete surface and the paste-steel interface may have a permeability many-fold that of the center-most concrete.

The importance of water-cement ratio on the diffusibility of chloride into hardened portland cement paste as derived from the work of Monfore and Ost (14) is shown in Figure 6. Increasing the duration of moist curing would also reduce the rate of subsequent chloride penetration.

Thickness of Cover Over Steel. The thickness of cover over steel is of obvious importance as this cover protects the steel from the adverse factors that promote corrosion. The effect of cover thickness is more than a simple arithmetic relationship. For normal diffusion of an electrolyte into a porous solid without chemical reaction a relationship such as is shown in Figure 7 would be anticipated. However, in the case of cement paste, the diffusion of chloride ion into the paste is accompanied by reaction of the chloride to form partially "insoluble" calcium chloroaluminate. This reaction reduces the concentration of chloride ion at any particular site and hence the tendency for inward diffusion is further reduced.

Perhaps the importance of these various factors can be summarized with a few examples. Figure 8 schematically represents a concrete of low water-cement ratio and well cured. The concrete has a low permeability and therefore the rate at which oxygen, chloride ion, and carbon dioxide can diffuse to the iron-paste interface will be very low as will the rate at which the alkalinity (hydroxyl ions) at the interface can be reduced by leaching. Also the electrical conductivity within the paste system would be somewhat reduced, thereby further impeding the galvanic action. In addition, because of the paste quality the number of capillary pores would be reduced and of smaller average diameter. Therefore, for any given, yet non-destructive stage of corrosion, the corrosion product would fill the large capillary pores for a relatively large distance from the corrosion site, which could slow diffusion of reactants and reaction products to and from the reaction site, thereby further stifling corrosion.

Figure 9 represents the opposite--concrete of high water-cement ratio and poor curing. Because of high permeability, the destructive materials, chloride, oxygen and carbon dioxide can diffuse rapidly towards the corrosion site. Since the capillary pores are large and numerous the "postulated protective zone" is significantly reduced.

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The concept of "protective zone" is further emphasized in Figure 10. All conditions are similar to those in the preceding figure except for an air pocket trapped adjacent to the steel. In this case the reaction product is released into this pocket with little opportunity for the corrosion rate to be reduced by the development of the postulated protective zone. Monfore and Verbeck (8) in studying corrosion failure of prestressed concrete pipe observed that severe corrosion was most often observed at the site of such large voids adjacent to the wire. The air voids normally present in nonair-entrained or air-entrained concrete are believed to not act in this manner because they are within the cement paste component of the concrete and not in direct contact with the reinforcing or prestressing steel.

Nature of Steel in Concrete

Reinforcing Steel. There is nothing in the literature, to date, to suggest that the newer high yield steels are either more or less subject to corrosion than the previous "standard" and lower yield steels. Although information is lacking there is every expectation that whatever differences might exist would be quite secondary to the major factors influencing corrodibility.

Type of Prestressing Steel. In connection with serious failures of prestressed concrete pipe, Monfore and Verbeck (8) compared, in concretes containing calcium chloride, the relative corrodibility of oil tempered wire, stressed relieved wire, normal cold drawn wire, and wire redrawn in the laboratory, both in the same direction and contrary to the direction of the prior drawing. No significant differences were observed among the normally drawn and treated wires. However, the wires cold redrawn in the laboratory through an unlubricated die were more susceptible to longitudinal cracking.

Degree and Type of Stressing. Evans, in a rather extensive series of tests (15), observed no obvious differences between the corrosion of prestressing wires under a load of 140,000 psi and the corrosion of wires under zero load when tested in concretes containing calcium chloride. In a series of exploratory tests undertaken at the Portland Cement Association (unpublished) a different technique was used in which various types of prestressing wires under various levels and types of stress were subjected to corrosion by exposure to solutions of calcium chloride in saturated lime water. The corrosion was "accelerated" by the application of electrical current equivalent to 0.5 milliamperes per square inch. In summary, these tests did not reveal any differences in type or rate of corrosion among the different types of wires, or any differences due to level of pretension on the rate of corrosion as shown in Figure 11, or any significant differences in corrosion tendency whether the prestressing wires were compared in direct tension, in torsion, or in bending.

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Table 1--Permeability to water rapidly reduces with cement hydration

Days of curing	Coefficient of permeability
fresh paste	1,150,000,000
1	36,300,000
2	2,050,000
3	191,000
4	23,000
5	5,900
7	1,380
12	195
24	46

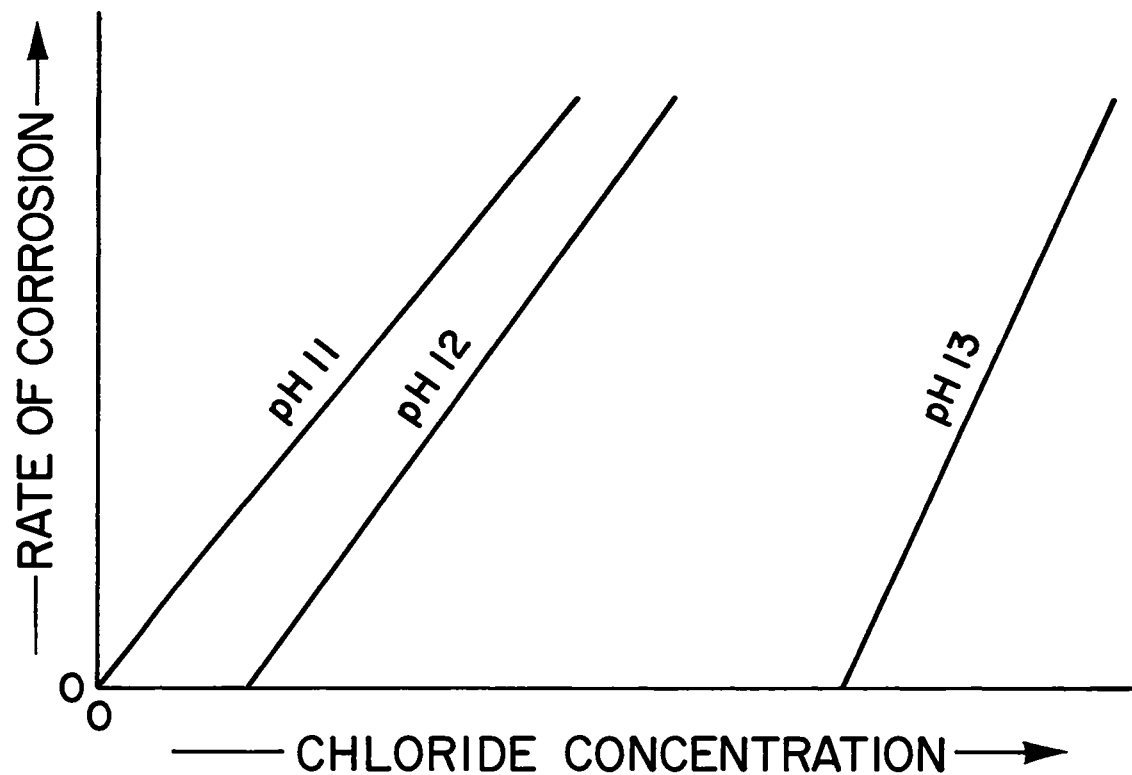


Fig. 1--Threshold chloride ion concentration required for corrosion to occur increases as the alkalinity, pH, of the cement paste liquid increases

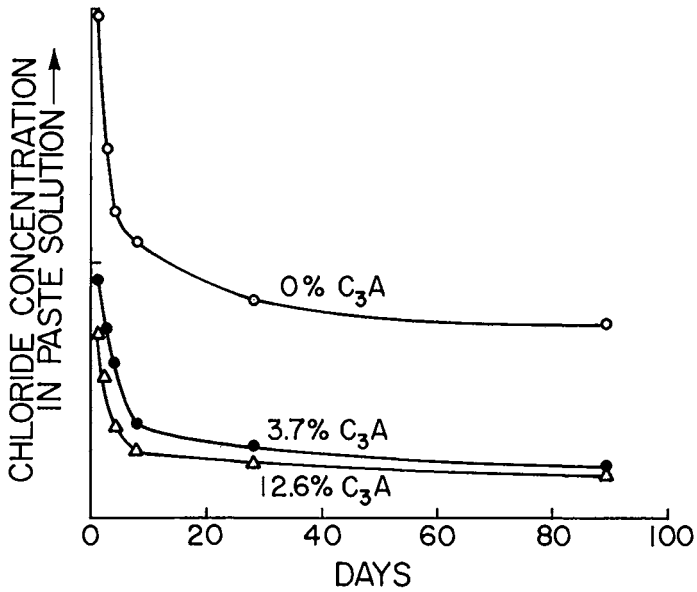


Fig. 2--Chloride concentration in paste solution decreases with hydration age and with increasing C_3A content of cement

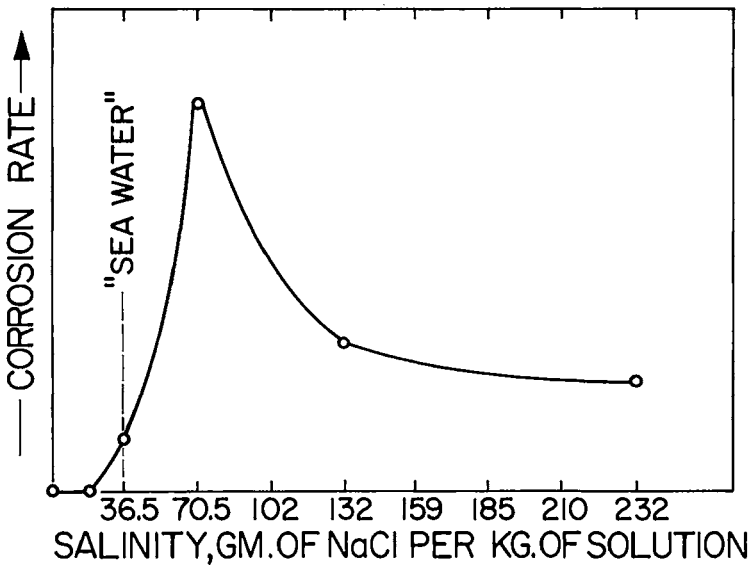


Fig. 3--Effect of concentration of sodium chloride on corrosion rate

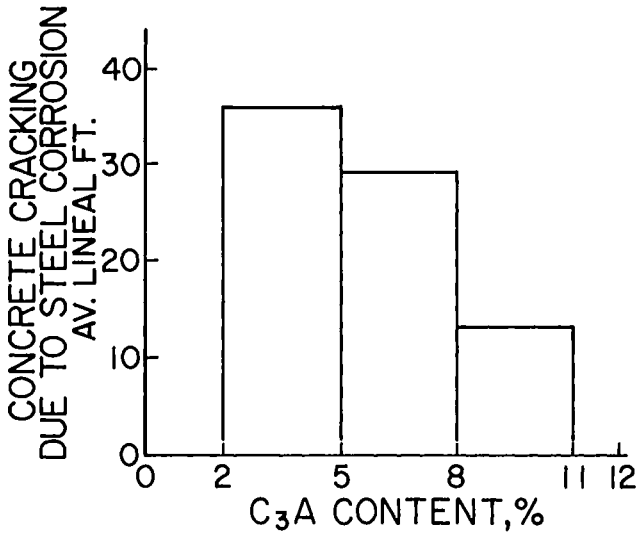


Fig. 4--Effect of C_3A content on concrete cracking due to steel corrosion

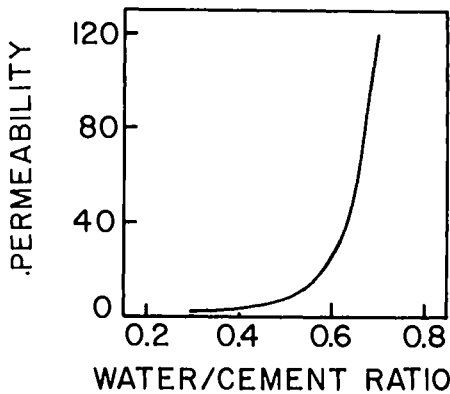


Fig. 5--Effect of water-cement ratio on permeability of hydrated paste to water 10^{-12} cm/sec

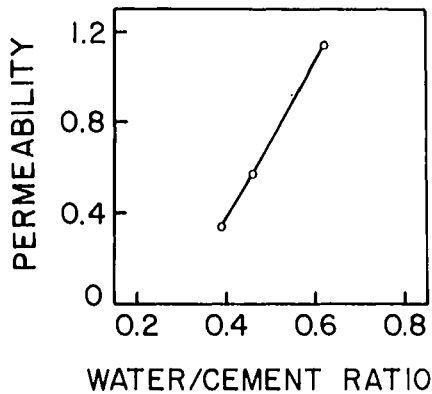


Fig. 6--Effect of water-cement ratio on permeability of hydrated pastes to chloride ions mg/(g cm day)

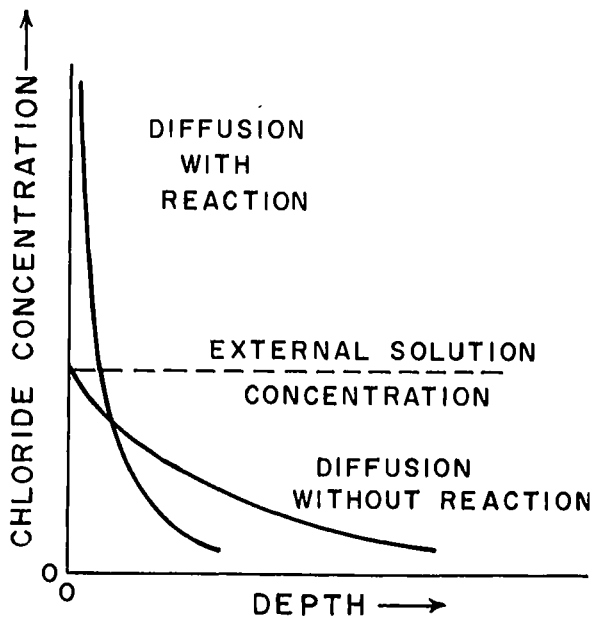


Fig. 7--The gradient of total chloride concentration depth depends upon whether chemical reaction occurs with the cement

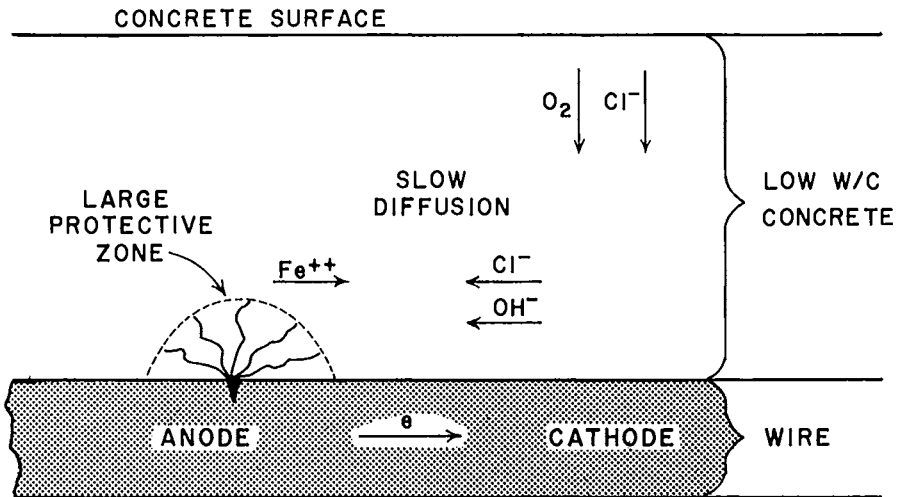


Fig. 8--Schematic representation of corrosion in concrete of low water-cement ratio and well cured

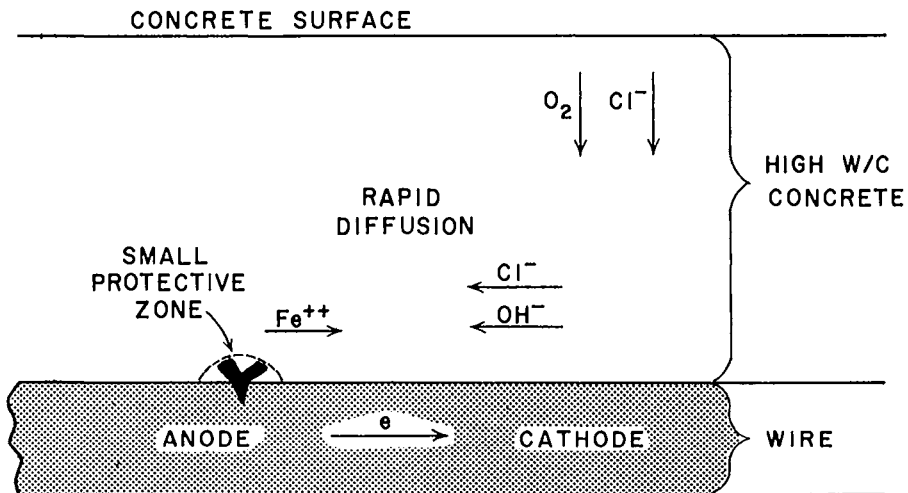


Fig. 9--Schematic representation of corrosion in concrete of high water-cement ratio and poorly cured

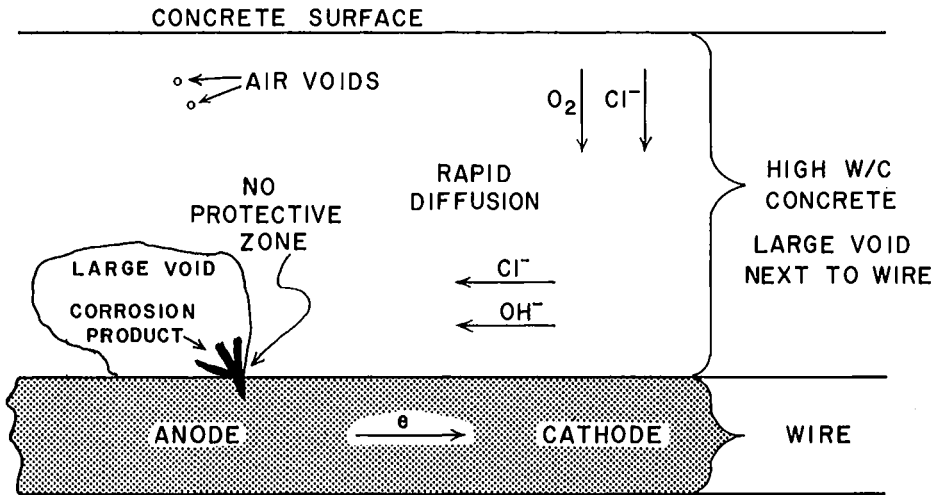


Fig. 10--Schematic representation of corrosion in concrete of high water-cement ratio and with air pocket on steel

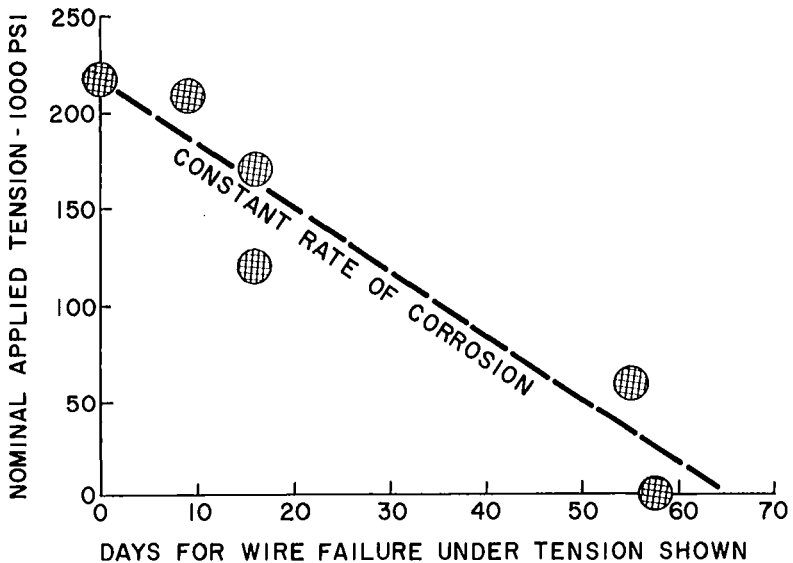


Fig. 11--Applied tension did not influence rate of corrosion of prestressing wire

SP 49-4

CORROSION OF METALS IN CONCRETE - NEEDED RESEARCH

By

Bernard Erlin and George J. Verbeck

Synopsis: The electrochemical and physical mechanisms causing the corrosion of steel in concrete are known. There is, however, a need for information that will more specifically characterize the effects of individual factors that initiate corrosion, and for methods that can be used to stop the corrosion process once it has begun.

That information is needed so that: (1) the design of new structures can incorporate methods that will automatically provide positive protection against corrosion of embedded steel, and (2) suitable methods of repair of existing structures where corrosion is occurring can be made.

The needed research involves the relationship of pH and chloride, and their combined effect on corrosion; methods for insuring that the high pH of concrete in contact with steel is maintained; physical methods for protecting steel; and chemical methods that will alter the environment of concrete so that the electrochemical requirements for corrosion are not present.

Keywords: alkalies; alkalinity; cathodic protection; chlorides; coatings; concretes; corrosion; corrosion resistance; electrolysis; pH; reinforcing steels; research.

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The previous authors have discussed the general electrochemical and physical mechanisms operative in the corrosion of steel in concrete, plus, in some detail, the role of coatings, chemical inhibitors, and cathodic protection in preventing or breaking the electrochemical corrosion cycle.

Although previously discussed, a review of the process of corrosion and the various factors involved may provide a basis for evaluating where we are in our state of the knowledge, and where some of the more promising areas for needed research appear to be. The discussion to follow pertains only to the corrosion of a single metal, iron, and not to bi-metallic cells. In the case of a single metal, the anodic and cathodic cell areas are developed by chemical or physical non-uniformities in the metal itself, or by variations in the chemical environment of different areas of the metal.

The simplest expression of the basic electrochemical cycle, shown in Figure 1, considers the reactions at the anodic and cathodic zones of corroding steel, and the electrical flow between these two zones.

As has been discussed by others, a flow of current in the steel from an anodic to a cathodic area, in the presence of oxygen and water, results in the production of hydroxyl ions at the cathode. As these migrate to the anode, they react with ferrous iron and form hydrous iron oxides (Figure 2).

The natural alkalinity of concrete ($\text{pH} > 12.5$) inhibits corrosion. For corrosion to occur either the alkalinity of the concrete in contact with the steel must be reduced (below about 11.5) or chlorides introduced. The former may occur because of leaching of the alkalis or their reaction with pozzolanic materials in the concrete, by carbonation of the paste, or possibly the presence of calcium chloride. The latter may occur through the use of some admixtures or exposure to deicing salts or saline solutions (sea water). Chloride ion has the special property of markedly breaking the passivity of the iron in the alkaline concrete system, thus causing corrosion. Although many theories have been advanced to explain the role of chloride regarding the destruction of passivity, research regarding that phenomenon is needed.

The preventative techniques that have been studied are generally limited to cathodic protection or, more recently, coatings for the steel or concrete. The advances made in those areas have not been widely applied and are still under study.