Analysis and Modeling of Corrosion of Steel in Prestressed Concrete

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Engineering Laboratory
Center for Building Technology
Materials Division
Washington, DC 20234

November 1981

Prepared for
Treaty of Friendship and Cooperation between Spain and the United States of America
ANALYSIS AND MODELING OF CORROSION OF STEEL IN PRESTRESSED CONCRETE

Spencer T. Wu
James R. Clifton

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ABSTRACT

Development of conceptual and mathematical models describing the corrosion of steel in prestressed concrete is outlined. The application of the principles of stress corrosion and general corrosion to understanding the mechanisms involved in corrosion of steel in prestressed concrete is discussed. The first step in estimating the failure time of a prestressed concrete structural system because of corrosion of the reinforcing steel is to estimate corrosion rates under various realistic conditions. A simplified approach based on mathematical modeling of concrete properties for estimating corrosion rates is proposed.

Before the proposed mathematical model can be applied to practical problems information is needed on the specific mechanisms of corrosion cell processes of steel in prestressed concrete. In addition, well designed corrosion tests need to be performed in which the important factors affecting the corrosion rates are considered.

Key words: concrete; corrosion; general corrosion; mathematical modeling; prestressed concrete; prestressing steel; stress corrosion.
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1. INTRODUCTION

Corrosion is the deterioration of a metal or its properties by chemical or electrochemical reactions with its environment. Development of a physical model describing the corrosion of steel in prestressed concrete (PC) is extremely difficult because the local environmental parameters are complex, and the mechanisms of the corrosion processes are not adequately understood, especially microcell processes. In this report, the basic knowledge of corrosion of prestressing steel in concrete is reviewed, the development of a mathematical model for the corrosion processes is described, and research needs are identified. The following is a description of the problem, the specific purpose, and the scope of our investigation.

1.1 PROBLEM IDENTIFICATION

The concrete of PC systems generally is of a better quality than that in reinforced concrete: the concrete of PC is designed to be less permeable and to have a higher reserve of alkalinity than normal concrete. Further, fewer macro-cracks should develop in PC because of the imposed tensile forces. Thus, the steel in prestressed concrete is generally less susceptible to general corrosion than steel reinforcing bars embedded in concrete. In addition to general corrosion, the present investigation addresses the associated problems of to stress corrosion cracking (SCC) and hydrogen embrittlement (HE) processes as well as corrosion rates. Certain engineering features such as the utilization of metal ducts in the construction of post-tensioned beams can influence the corrosion process, but the methodology to consider such effects is straightforward if the corrosion mechanism is known. Therefore it is not addressed in this report.

1.2 PURPOSE OF THE INVESTIGATION

The purpose of the investigation is to identify the significant factors and processes responsible for the corrosion of steel in prestressed concrete and then develop a model that can be used for describing the processes and for evaluating the effects of important factors. The first step in developing the model is to examine the basic mechanisms of the corrosion phenomena. SCC and HE processes have both been considered to be responsible for the degradation of high tensile strength steel. Therefore, both SCC and HE processes as well as the general theory of corrosion become important considerations in the study.

1.3 SCOPE OF THE REPORT

The processes by which steel in PC corrodes are described in section 2, and experimental data from the field and laboratory tests are discussed. In addition, a standard stress corrosion test proposed by RILEM-FIP-CEB group is mentioned. In section 3, the generally accepted theory and mechanisms of corrosion of steel in concrete are discussed. Polarization processes and the criteria that may govern the initiation of the corrosion process are also discussed. Quantitative analysis for steel corrosion in concrete is given in section 4. The existing theory for a computation model is briefly described and a simplified approach for evaluating the corrosion rates is proposed.
Design concerns for structural performance are also mentioned. Then in section 4, specific research needs are outlined.
2. STRESS CORROSION CRACKING

For the present purposes, we consider SCC as a generic term to describe the various forms of environmentally induced fraction of engineering alloys. In steels, it is accepted that HE is responsible for the failures of high strength (quenched and tempered) alloys. The mechanism of HE is itself uncertain, but is thought to involve the reduction in cohesive strength of the iron. The low strength (ferritic) alloys are considered to fail by anodic dissolution, specifically by the film-rupture model [2]. The prestressing steels are generally pearlitic and fall somewhat between the above extremes, so that either mechanism of the environmentally-induced failure may occur (depending upon the specific environment and microstructure). Experimental studies and failure analyses are the major means for determining which process occurs. The tests from laboratory and field are presented separately in the following. A general discussion is given afterwards.

2.1 LABORATORY CORROSION TESTS FOR PRESTRESSING STEEL

In the United States, published data on the corrosion testing of prestressing steel is limited. A brief summary of the available information is given in table 1. Test media, test parameters, and important results are outlined in the table. The development of research in the United States on corrosion of steel in PC is traced in the reports. In the early research, tests were developed for identifying the important metallurgical and environmental factors. Only in tests recently developed were the effects of the individual factors measured. For example, the main purpose of the test conducted at the Oak Ridge National Laboratory in 1975 [7] was to consider the effects of test media and stresses (see table 2). Later, another series of tests were conducted at the Oak Ridge Laboratory [8] in which the effectiveness of coatings were studied, and detailed information on failure modes were obtained. The test results were mostly as expected, e.g., the time to failure increases as the stress level decreases. However, the quantitative data presented in the report is valuable for developing a general theory of the corrosion of steel in prestressed concrete.

Treadaway [9] reported the results of a series of tests in which the variables selected were water to cement ratio, cement type, and the amount of added calcium chloride. Various types of corrosion were observed. These were surface corrosion, general corrosion, and pitting. However, the data for the breaking loads from the strength test were highly variable in terms of the exposure period. It has been known that reproducibility is one of the major difficulties in corrosion testing of prestressing steel.

A RILEM-FIP-CEB working group recently summarized all the studies carried out between 1970-1978 and presented a report [10] at the 7th FIP Congress. Ammonium thiocyanate was recommended as the standard test medium for prestressing steel. The recommendation was based on a series of tests for stress corrosion by utilizing various test media including boiling nitrates solutions, hydrogen sulfide solutions, and water. As was pointed out in the FIP report, tests with ammonium thiocyanate were found to be the most reproducible.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Test Specimen &amp; Media</th>
<th>Other Experimental Conditions &amp; Variables</th>
<th>Significant Data &amp; Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monroe &amp; Verbeck [4] (1960)</td>
<td>a. Prestressing steel wires were exposed to solutions of calcium chloride, calcium hydroxide, sodium chloride, sodium hydroxide.</td>
<td>o Applied stress was 1.0 gPa.</td>
<td>o Corrosion of prestressing steel was found to be an erratic process. Quantitative evaluation was difficult.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o Most beams were in moist storage for about six months.</td>
<td>o Prestressing wires were in mortar or concrete beams containing between 0 to 4 percent of calcium chloride by weight.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o For beams, test variables were cement type, temperature, amount of calcium chloride, and presence of voids.</td>
<td>o Corrosion of prestressing steel occurred whether the wire was hard drawn or stress relieved.</td>
</tr>
<tr>
<td>Godfrey [5] (1961)</td>
<td>Pretensioned concrete beams with calcium chloride contents from 0 to 2 percent, by weight.</td>
<td>o Wire strands were 9.7 mm in diameter.</td>
<td>o Oil tempered wires failed through stress corrosion.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o Applied stress was 11.8 gPa.</td>
<td>o Hard-drawn stress relieved wires failed through pitting or general corrosion.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o Beams were placed in an industrial atmosphere for three years.</td>
<td>o Stress cracking of the prestressing steel did not occur in chloride ion environment.</td>
</tr>
<tr>
<td>Moore, Klodt &amp; Hensen [6] (1970)</td>
<td>a. Prestressing steel wires were exposed to solutions of calcium hydroxide, sodium chloride, sodium hydroxide, and hydrogen sulfide.</td>
<td>o Applied stresses varied from 1.0 gPa to 1.6 gPa.</td>
<td>o Cracking of prestressing steel occurred after short exposure times in distilled water into which hydrogen sulfide was bubbled. When calcium hydroxide was also added, the cracking was accelerated.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o Wire strands were 9.7 mm in diameter.</td>
<td>o No direct correlation was found between applied load and the amount of corrosion.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o Some applied stresses and wire strands as above.</td>
<td>o Serious corrosion was observed even when the crack width in the surface of the concrete was only .10 mm. Pitting of the steel occurred.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o Concrete cover over the prestressing strands varied from 13 to 51 mm.</td>
<td></td>
</tr>
<tr>
<td>GRIESS [7] (1978)</td>
<td></td>
<td>o AISI 1080 steel wires were tested at constant strain rates.</td>
<td>o Time to break was recorded</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o Strain rate was usually $4.17 \times 10^{-6}$%/min.</td>
<td>o pH values were measured (see table 2).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o Temperature was varied.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b. Wires exposed to solutions of sodium chloride, sodium sulfate, as well as pure water.</td>
<td>o Corrosion rates were measured at 1000 and 2000 hours.</td>
<td>o Corrosion rates varied from 5.1 to 23.1 $\mu$m/yr.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o Hydrogen contents of tested wires were measured in some cases.</td>
<td></td>
</tr>
<tr>
<td>Naus [8] (1979)</td>
<td>Prestressing steel wires exposed to solution of hydrogen sulfide, sodium chloride, and ammonium nitrate.</td>
<td>o Both stressed and unstressed tendons tested.</td>
<td>o Useful data such as the failure loads, failure times, and reduction in cross-section areas of failed tendons were reported.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o Some tendons were coated with organic coatings or portland cement grout.</td>
<td></td>
</tr>
</tbody>
</table>

* Survey of U.S. Literature.
<table>
<thead>
<tr>
<th>Test</th>
<th>Test Medium</th>
<th>Temperature (°C)</th>
<th>pH Start/Finish</th>
<th>Time to Break (hr)</th>
<th>Load (kg)</th>
<th>Cracks</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Air</td>
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<td>0.2</td>
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</tr>
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<td>2</td>
<td>Air</td>
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</tr>
<tr>
<td>3</td>
<td>0.2 M NH₄NO₃</td>
<td>21</td>
<td>5.0/7.0</td>
<td>57.5</td>
<td>4100</td>
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<tr>
<td>4</td>
<td>0.2 M NH₄NO₃</td>
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<td>5.3/7.0</td>
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<td>5</td>
<td>0.2 M NH₄NO₃</td>
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<td>5.3/7.7</td>
<td>47.0</td>
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<td>No</td>
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<tr>
<td>6</td>
<td>0.2 M NH₄NO₃</td>
<td>52</td>
<td>5.3/7.3</td>
<td>49.5</td>
<td>3970</td>
<td>No</td>
</tr>
<tr>
<td>7</td>
<td>0.2 M NH₄NO₃</td>
<td>66</td>
<td>5.0/7.4</td>
<td>50.5</td>
<td>3970</td>
<td>Yes</td>
</tr>
<tr>
<td>8</td>
<td>0.2 M NH₄NO₃</td>
<td>66</td>
<td>5.0/7.0</td>
<td>5.2</td>
<td>3950</td>
<td>Yes</td>
</tr>
<tr>
<td>9</td>
<td>0.01 M KCl + CaO</td>
<td>21</td>
<td>11.9/11.5</td>
<td>55.3</td>
<td>3990</td>
<td>No</td>
</tr>
<tr>
<td>10</td>
<td>0.01 M KCl</td>
<td>66</td>
<td>5.3/6.3</td>
<td>60.8</td>
<td>3970</td>
<td>No</td>
</tr>
<tr>
<td>11</td>
<td>0.03 M KCl</td>
<td>21</td>
<td>5.5/6.4</td>
<td>58.1</td>
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<td>No</td>
</tr>
<tr>
<td>12</td>
<td>0.03 M KCl + HCl</td>
<td>21</td>
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<td>60.8</td>
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<td>0.1 M NaHSO₃</td>
<td>21</td>
<td>4.5/6.5</td>
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</tr>
<tr>
<td>14</td>
<td>0.1 M H₂S + HCl</td>
<td>21</td>
<td>3.0/3.0</td>
<td>6.6</td>
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<tr>
<td>15</td>
<td>0.1 M H₂S</td>
<td>~4</td>
<td></td>
<td>4.7</td>
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<tr>
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<td>0.001 M Na₂S</td>
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<td>57.8</td>
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<tr>
<td>17</td>
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<td>21</td>
<td>4.3/6.0</td>
<td>19.3</td>
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<tr>
<td>18</td>
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<td>17.0</td>
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</tr>
<tr>
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<td>0.003 M Na₂S + HCl</td>
<td>21</td>
<td>4.3/7</td>
<td>54.8</td>
<td>4010</td>
<td>No</td>
</tr>
<tr>
<td>21</td>
<td>0.003 M Na₂S + HCl</td>
<td>21</td>
<td>4.3/7</td>
<td>54.8</td>
<td>4010</td>
<td>No</td>
</tr>
<tr>
<td>22</td>
<td>Deionized H₂O</td>
<td>21</td>
<td>7</td>
<td>57.5</td>
<td>3980</td>
<td>No</td>
</tr>
<tr>
<td>23</td>
<td>Deionized H₂O + CO₂</td>
<td>21</td>
<td>4.0/4.0</td>
<td>55.8</td>
<td>4010</td>
<td>No</td>
</tr>
<tr>
<td>24</td>
<td>H₂O + CO₂ + 750 ppm H₃AsO₃</td>
<td>21</td>
<td>5.1/5.1</td>
<td>57.6</td>
<td>3980</td>
<td>No</td>
</tr>
<tr>
<td>25b</td>
<td>Zn plate, H₂O</td>
<td>21</td>
<td>5.8/6.3</td>
<td>60.6</td>
<td>4030</td>
<td>No</td>
</tr>
<tr>
<td>26b</td>
<td>Zn plate, 0.2 M Na₂SO₄</td>
<td>21</td>
<td>6.7/6.0</td>
<td>54.9</td>
<td>4030</td>
<td>No</td>
</tr>
<tr>
<td>27c</td>
<td>Corroded in H₂O, three days</td>
<td>21</td>
<td>5.9/6.5</td>
<td>50.9</td>
<td>4010</td>
<td>No</td>
</tr>
</tbody>
</table>

a The strain rate was 4.17 x 10⁻⁷/s, except in test No. 1 where it was 1.08 x 10⁻⁴/s; and in test 8 where it was 4.17 x 10⁻⁶/s.

b Specimen except center 12.5 mm was zinc-plated before test.

c Specimen was placed in 8 mm glass tubing and surrounded by tap water for three days before straining.
2.2 FIELD TEST EXPERIENCES

The performance of prestressing steel in concrete under natural environments may be different from that predicted by simulated laboratory tests. For this reason, two types of structural systems subjected to special environments are selected for consideration which are oceanic structures and prestressed concrete pressure vessels systems.

The U.S. Army Engineer Waterways Experiment Station conducted a series of tests on pretensioned beams as well as post-tensioned beams. The tests gave several important findings even though there was no quantitative measurements of corrosion rates. Only the results for the post-tensioned beams [11] are discussed here. It is felt that the conditions related to the post-tensioned beams may be more unpredictable from the analytic viewpoint. The test beams were placed at halftide elevation at Treat Island, Maine, and subjected to twice daily tidal inundations plus freezing in air and thawing in sea water for 12-13 years. The major results of interest were: (a) each strand of each beam was corroded to some degree; (b) the corrosion was not confined to the ends, nor concentrated at certain spots but was spread over the entire length; (c) no quantitative measurement was given, but it was stated in the report that the corrosion on the strands was usually less than .127 mm for the strand with diameter of 4.88 mm; (d) one set of strands was protected with paper conduit and filled with grease (this set of strands suffered the worst corrosion during the test); and (e) analysis showed that the chloride content within the beams was less than 0.02 percent by weight of the grout. The pH values of the grout were in the vicinity of 12.5.

Little information is available concerning the corrosion of steel in an operating prestressed concrete pressure vessel. One power station in the United Kingdom suffered pitting corrosion, which was reported in detail [12]. The conclusion from the laboratory tests indicated that the corrosion was due to the combined action of contaminating salts from the sea and the moisture from the air. However, the effect of temperature on corrosion rates also should be considered.

2.3 NEEDED INFORMATION

While reviewed test results give useful information, several questions are posed that require further investigation. Two of the most important ones which need to be considered are:

1. Why does steel corrode when the prestressing strands are protected by the metal ducts?

2. How to establish a resistance index for the prestressing steel? For example, a NH₄CNS solution has been selected by FIP as the medium in a proposed standard test for establishing a resistance index. However, it has not been demonstrated that this test simulates the corrosive conditions encountered in the field.
There are no simple answers for either of these questions. For the first, an in-depth investigation should be made on the test conditions as well as the failure processes. It is possible that another corrosion mechanism along with the accepted corrosion phenomenon may exist. For the second question the solution could be more complex. Fracture processes of specimens tested in different media can differ, e.g., stresses steel specimens corroded in H₂S have been found to be highly cracked, but were not as highly cracked by the NH₄CNS test. The approach of measuring the tensile strength in the air (K_Ic) and in the specific environments (KISC) is reasonable for the evaluation of the failure load for a system. Creation of a set of KISC curves for various environments could be the first step in developing a resistance index for specific environments.
3. CORROSION PROCESSES

Corrosion of steel in concrete can be separated into two major mechanistic processes, diffusion and electrochemical reactions. The generally accepted theory of corrosion will be briefly described in terms of these mechanisms. Factors such as polarization that govern the corrosion rates are addressed separately. It should be pointed out that the present theory has largely evolved based on the phenomena observed. A more complete theory has not been formulated because of the complex nature of the problem.

3.1 ELECTROCHEMICAL REACTIONS

The localized reactions at or near the surface have been proposed to be:

\[
\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2 (OH)^- \text{ (cathode)} \tag{1}
\]

\[
Fe \rightarrow Fe^{++} + 2e^- \text{ (Anodic)} \tag{2}
\]

\[
Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{3}
\]

With further oxidation at the anode, Fe(OH)_3 or Fe_3O_4 may be obtained.

\[
Fe^{2+} \text{ oxidation} \rightarrow Fe^{3+} + e^- \tag{4}
\]

There would be other reactions involved in the corrosion of steel in concrete, e.g., from the chloride ions, the role of chloride ion may preserve the charge neutrality and promote pitting. It can also contribute to the breakdown of the protection oxide layers, and in retarding the reformation of these films. A recent study by the Federal Highway Administration [13], however, indicated that high rates of corrosion of steel could occur in oxygen depleted limewater solutions. The corrosion products in the tests were yellowish-green or green-blue in color. These products were found at anodic sites and were believed to be ferrous chloride and hydrated ferrous chloride. Therefore, a new hypothesis was proposed for the reactions near anodic sites based on the equations:

\[
Fe + 2 Cl^- \rightarrow [Fe^{2+} + 2Cl^-] + 2e^- \tag{5}
\]

followed by

\[
[Fe^{++} + 2 Cl^-] + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2Cl^- \tag{6}
\]

In contrast, recent tests conducted in NBS indicated that the chloride affected the initiation of the corrosion process as described in the previous paragraph [14].
3.2 DIFFUSION PROCESSES

Based on thermodynamic principles, diffusion is caused by a difference in chemical potential. However, Fick's laws are usually used to express mathematically the kinetics of the diffusion behavior of materials. For the problem under consideration, the components which need to be considered are: chloride ions, ferrous (and/or ferric) ions, oxygen, and water. Each of these species should diffuse in accordance with Fick's laws. Certain modifications may need to be introduced based on perturbing effects. Electric fields, for instance, may influence the state of the ionic flow. The conditions near electrodes are extremely complex. Various theories have been developed for the diffusive layers, e.g., quantum theory was proposed to explain the bonding orbitals of diffused layers [15]. However, a rigid theory has not been established sufficiently well to explain the entire phenomenon. Current theory has been developed largely based on classical microscopic electrostatics and involved continuum concepts. Application of correlation functions to express the diffusion layers in the concentration solutions is an example of this type of treatment. A similar approach will be described in section 4 in the development of a computational model for evaluating corrosion rates.

3.3 FACTORS GOVERNING THE CORROSION RATES

3.3.1 Fundamental Concepts

When steel is immersed in an aqueous medium, it will develop an electrode potential at its surface. This potential plays an important role in determining the rate of electrochemical reactions at the surface, e.g., the corrosion reaction, eq.(2). Under certain conditions, the corrosion rate of iron, expressed as a current density, \( i_n \), is given by the Tafel equation,

\[
\eta = \beta \log \frac{i}{i_o}
\]

where \( \beta \) and \( \eta \) are constants for a given metal and environment, both being dependent on temperature and \( i_o \) is the exchange current. The over voltage, \( \eta \), is defined as the difference between the electrode potential of the steel and the reversible potential for reaction (2). This term may be expressed by Nerst equation

\[
E = E_o + \frac{RT}{nF} \ln \frac{a_{\text{oxid}}}{a_{\text{red}}}
\]

where

- \( E \) = potential difference between electrodes,
- \( E_o \) = standard electrode potential
- \( R \) = gas constant, 8.31 J/°K
- \( T \) = absolute temperature in °K
- \( F \) = Faraday (96,500 Coulombs)
- \( n \) = ionic valence of the species
- \( a_{\text{oxid}}, a_{\text{red}} \) = activities of the metal in the oxidized and reduced states
In some instances, the rate of an electrochemical reaction is determined by the transport of species to or from the surface. Such behavior is termed concentration polarization.

Concentration polarization increases as the diffusion rates of the ions decrease. Considering the corrosion of steel in concrete and the quasi-static conditions in concrete, concentration polarization probably has a significantly greater effect on the corrosion rate than IR drop and activation polarization combined. The effect of concentration polarization can be expressed as:

\[ \Delta \phi_c = \frac{RT}{nF} \ln \frac{i_L - i}{i_L} \]  \hspace{1cm} (9)

where

- \( \Delta \phi_c \) = potential difference between the electrodes due to concentration polarization
- \( i_L \) = limiting diffusion current (constant)
- \( i \) = current

The electrical potential state of a corroded metal generally follows the path shown in figure 1. The state could be active, passive or transpassive. Local environments near the electrodes usually have the largest local influence on the corrosion state.

Steel in concrete is protected from corrosion by a surface film of Fe\(_2\)O\(_3\). The passivating effect of this film has been discussed in many reports, e.g., refs. 16-17. It takes time for aggressive ions such as Cl\(^{-}\) to depassivate the film. The overall steps involved in the depassivation are as follows: a) transport of aggressive ions from bulk solution to the concrete-steel interface, b) adsorption of chloride ions on the surface of the steel, followed by c) chemical reactions causing depassivation. Details of these steps depend strongly on the local conditions and the measures used for protecting the reinforcing bars [e.g., ref. 18].

3.3.2 Effect of Chemical Variables

For many years, pH values and electric potentials (E) were taken to be the major parameters controlling the corrosion susceptibility of steel in concrete. The corrosive behavior of prestressing steels as a function of E and pH is indicated in figure 2. It was recently realized that other factors, such as the presence of chloride ion, may significantly affect the corrosion rates [1]. Bazant [20] has used an expression for pH values near the surface of steel bars in concrete in terms of the chloride concentration based on Gjorv's data [21]. Escalante, et al. [14] recently investigated the relationships and constructed interaction surfaces between O\(_2\), Cl\(^{-}\), and pH, that indicated which one of these variables controlled the initiation of corrosion under various conditions. The boundaries for corrosive and passive states have been determined for pH values between 10.5 and 12.5. The research is still being pursued and findings will be useful in developing a computational physical model for describing the corrosion process.
Figure 1. Polarization curve for iron [19].
FIELD I - Field of corrosion in the electrochemical sense of the term,
   - Field of possibility of change through general dissolution.

FIELD II - Field of passivation (covering) by Fe₂O₃,
   - Field of possibility of change by local dissolution (pitting).

FIELD III - Field of immunity in the electrochemical sense of the term,
   - Field of possibility of change through hydrogen embrittlement.

FIELD IV - Field of formation of Fe₃O₄,
   - Field of the possibility of change by stress corrosion cracking.

Figure 2. Possible alternative corrosion processes in prestressing steels
under mechanical stress, as a function of the various fields
of the Pourbaix diagram [10].
4. QUANTITATIVE ANALYSIS OF CORROSION RATES

In this section, a mathematical model based on general corrosion theory is briefly described. A simplified approach is proposed for evaluating the corrosion rates. Design considerations for prestressed concrete are also discussed.

4.1 FORMULATION BASED ON GENERAL CORROSION THEORY

The description given here is largely based on Bazant's work [18]. In an electric field, Ohm's laws and the conservative laws for electric charges are the fundamental laws to be considered. These laws are assumed to be valid in the electrochemical process, i.e.,

\[ \lambda_i = \nabla \phi \]  
\[ \nabla \phi = 0 \]  

where

\( \lambda = \) resistivity of the substance  
\( i = \) current density  
\( \phi = \) electric potentials

Fick's laws with some modification are used for describing the diffusion process. They are:

\[ J_j = C_j \nabla U_j + \Delta J_j \]  
\[ \frac{\partial U_j}{\partial t} - \nabla J_j - J_w \nabla U_j + M_j = 0 \]  

where

\( J = \) mass flux  
\( C = \) diffusivity constant  
\( u = \) concentration  
\( \Delta J = \) an expression for modifying the Fick's laws, e.g., charged ions in the electric field.  
\( t = \) time  
\( J_w = \) water mass flux  
\( m = \) sink or source terms  
\( \text{Sub. } j = \) quantities of substance \( j \)  
\( N = \) total number of substances under consideration

The important substances to be considered are oxygen, chlorides, ferrous (and or ferric) ions and water. For each substance, the form of the Fick's law may be slightly different, e.g., the 3rd term in equation (12b) vanishes for some cases. The rate law for the chemical reactions needs to be included with the expression:
\[ m_j = K_{Ir} u_i u_r \]  

(13)

where

\[ K_{Ir} = \text{a constant which is a function of activation energy.} \]

The mass sink or source terms can be evaluated based on equation (13).

Equations (10) to (13) form a set of equations that govern the field processes. When the specific boundary and initial conditions are specified, the problem is completely formulated. More complete details may be found in Bazant's paper [20]. An important term is that representing the differential potential between the electrodes. This term can be expressed in the following form:

\[ \Delta \phi = \Delta \phi_0 + n^c \log U^c - n^a \log U^a \]  

(14)

where the superscripts \( c \) represents the condition at cathode and \( A \) represents the condition at anode. \( \Delta \phi_0 \), is a potential term that covers the effects discussed in section 3.3.1.

If \( N \) is to be taken to be 4, there are a total of 13 equations including equation (13). It is not a simple effort to solve such a large set of equations. Even if a solution is obtained, the results may not reflect the actual corrosion behavior because of difficulties in selecting realistic values for the coefficients. Therefore, a simplified approach for evaluating the corrosion rates is being pursued and is described in the following section.

4.2 AN SIMPLIFIED APPROACH FOR PREDICTING THE CORROSION RATES

In this section, a simplified scheme is proposed for evaluating the corrosion rates. Several material functions are introduced which need to be determined. Only conditions that are considered to be important are covered. The proposed scheme is based on the assumption that equations (1) through (4) describe the entire corrosion process.

The diffusion equations, equations (12a) and (12b), for oxygen diffusing in concrete still need to be considered. The sink or source terms may be neglected. The chloride concentration near the electrode must be evaluated if the ions are diffusing to the steel surface, e.g., pretensioned beam without conduit. At the electrodes, the proposed equations are:

\[ \frac{du_o}{dt} = C_o \frac{u_o^{b} - u_o}{A_1^2} + C_1 (\Delta \phi, u_o) + C_2 (u_c^1) \]  

(15)

\[ \frac{du_f}{dt} = C_f \frac{u_f^{b} - u_f}{A_2^2} + C_3 (\Delta \phi, u_o) + C_2 (u_c^1) \]  

(16)
Where \( U_0 \), \( U_f \), and \( U_{C1} \) represent the concentrations of oxygen, ferrous and ferric ions, and chloride ions, respectively in the diffusive layers. The values of the superscript \( b \) depend on the concentrations of oxygen and ferrous and ferric ions at the boundaries of ionic and hydrous layers surrounding the prestressing steel. \( C_0 \) and \( C_f \) are the equivalent diffusivities of oxygen, and ferrous and ferric ions at corrosive site on prestressing steel. The parameters \( a_1 \) and \( a_2 \) define the thickness of effective ionic and hydrous layers around corrosive sites. The variables \( C_1, C_2, C_3, \) and \( C_4 \) are functions to be determined.

It is anticipated that the functions \( C_1 \) and \( C_3 \) will represent physical parameters. They should include the effects due to the adsorption of oxygen and other implicit reactions at corrosion sites. \( C_2 \) is dependent on depassivation processes due to chloride ions. \( C_4 \) has a function similar to \( C_2 \), except it is used to consider the effect of chloride ions as given in equations (5) and (6). All of these functions will be determined analytically based on experimental data.

Equations (14) to (16) are the basic equations to be solved. The boundary and initial conditions should be based on the real physical conditions such as the geometry of the ducts in the post-tensioned beams or the surface condition of the beams without a metal conduit.

### 4.3 DESIGN CONSIDERATIONS

Severe steel corrosion will undoubtedly affect the performance of the PC systems. Other than the reduction in sectional area, the major direct effect will probably be the reduction of the strength due to the fracture of the steel. Using \( K_{ISC} \) as an indication of the effects of corrosion is a reasonable approach, (as noted in section 2.3), but the interpretation of the magnitudes of \( K_{ISC} \) from various test environments under consideration could be difficult. There may be some secondary effects such as the reduction of the ductility of the prestressing steel or an increase in the prestressing loss.

The effect of the geometric shape of the steel cracking on \( K_{IC} \) is another problem which needs to be solved. The determination of \( K_{IC} \) as a function of the original cracking shape has been investigated for prestressing steel [21]. Further work in this area is needed to demonstrate the validity of this approach.
5. SUMMARY AND NEEDED RESEARCH

The application of the principles of stress corrosion and general corrosion to the steel in prestressing concrete has been discussed. The first step in estimating the failure time of a structural system because of corrosion of the steel is to estimate corrosion rates assuming general corrosion.

A simplified approach based on mathematical modeling concepts, is proposed for fulfilling such a goal. Further research must be performed before the model can be numerically applied to practical problems and further developed to include SCC and HE processes. The following is an outline of the needed research.

1. A more complete identification of the specific mechanisms of general corrosion cell, SCC and HE processes of steel in concrete.

2. Perform corrosion tests in which the important factors affecting the corrosion rates are taken into consideration.

3. Determine the functions in equations (15) and (16) using the data obtained in research need no. 2.

4. Validate the proposed model by comparing predicted corrosion rates with experimental data.

The subject items listed above should be performed sequentially, except 1 and 2 may be performed simultaneously.
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7. REFERENCES


Analysis and Modeling of Corrosion of Steel in Prestressed Concrete

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Development of conceptual and mathematical models describing the corrosion of steel in prestressed concrete is outlined. The application of the principles of stress corrosion and general corrosion to understanding the mechanisms involved in corrosion of steel in prestressed concrete is discussed. The first step in estimating the failure time of a prestressed concrete structural system because of corrosion of the reinforced steel is to estimate corrosion rates under various but realistic conditions. A simplified approach based on mathematical modeling of concretes properties for estimating corrosion rates is proposed.

Before the proposed mathematical model can be applied to practical problems information is needed on the specific mechanisms of corrosion cell processes of steel in prestressed concrete. In addition, well designed corrosion tests need to be performed in which all the important factors affecting the corrosion rates are considered.