Guide to Protection of Reinforcing Steel in Concrete against Corrosion

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This guide reviews the most recent developments of metal corrosion, specifically reinforcing steel, in concrete. Individual chapters are devoted to corrosion of metals in concrete, protective measures for new concrete construction, procedures for identifying corrosive environments, active corrosion in concrete, and remedial measures.

Keywords: allowable chloride; carbonation; chloride; chloride threshold; corrosion; corrosion-resistant reinforcement; durability; prestressed concrete; reinforced concrete; reinforcing steels.

CONTENTS

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CHAPTER 1—INTRODUCTION AND SCOPE

1.1—Introduction

The corrosion of metals in concrete can be a serious problem because of its widespread occurrence in certain types of structures and the high cost of repairing such structures. This holds true especially for reinforcing steel. Some of the first widely documented cases of steel reinforcement corrosion were associated with marine structures and chemical manufacturing plants (Tremper et al. 1958; Evans 1960; Biczók 1964). Later, numerous reports of its occurrence in bridge decks, parking structures, and other structures exposed to chlorides emphasized the problem (Crumpton and Pattengill 1969; Fruggiero 1972; Stratfull 1973; Litvan and Bickley 1987). Extensive research on factors contributing to steel corrosion has increased understanding of the mechanisms and causes of corrosion, especially concerning the role of chlorides. It is anticipated that application of the research findings will result in fewer instances of corrosion in new reinforced concrete structures and improved methods of repairing corrosion-induced damage in existing structures. For these improvements to occur, the research information should be disseminated to those responsible for the design, construction, and maintenance of concrete structures.

The high-alkaline environment of concrete results in the formation of a tightly adhering film over the reinforcing steel that generally protects it from extensive corrosion. Therefore, the corrosion of reinforcing steel is not a significant concern in most concrete elements or structures. Corrosion of steel, however, can become a problem if:

a) The concrete does not resist the ingress of corrosion-inducing substances

b) The structure is not properly designed for the service environment

c) The environment is not as anticipated

d) The structure exhibits changes during the service life of the structure

Corrosion of steel reinforcement is the primary subject of this guide. Although several types of metals can corrode under certain conditions when embedded in concrete, the corrosion of steel reinforcement is the most common and of greatest concern.

Exposure of reinforced concrete to chlorides is the major cause of premature corrosion of steel reinforcement, although corrosion can also occur in some circumstances in the absence of chlorides. For example, sufficient amounts of other substances such as other halides, chlorate, and hypochlorite can result in corrosion (Kerkhoff 2007; ACI 515.2R). Carbonation of concrete or other exposure conditions that reduce the concrete's alkalinity can lead to corrosion of the embedded steel reinforcement. Carbonation damage can be extensive in structures with low cover and is at times repaired without consideration of the mechanism of deterioration. As the concrete infrastructure ages, systematic carbonation is likely to become a more apparent and wider problem, particularly in locations away from salt ingress (Sagüés et al. 1997a). Widespread deterioration and consideration for holistic repair for carbonation-induced corrosion is not as common in North America as that for corrosion induced by chlorides. Chlorides are common in nature and very small amounts are generally present in the constituents of concrete. Chlorides can also be intentionally added into the concrete, most often as a constituent of accelerating admixtures. In addition, dissolved chlorides can penetrate hardened concrete in structures exposed to marine environments, salt-laden soils, or deicing or anti-icing salts.

The rate of corrosion of steel reinforcement embedded in concrete is influenced by environmental factors. Corrosion of reinforcement in concrete is an electrochemical process that generally depends on the presence of oxygen and moisture. Reinforced concrete with significant gradients of corrosive ions, such as chloride, is vulnerable to corrosion, especially when subjected to cycles of wetting and drying that is often prevalent in highway bridges and parking structures exposed to deicing or anti-icing salts, and in structures located in marine environments. Other factors that affect the rate and level of corrosion are:

(a) Heterogeneity in the concrete and reinforcing steel

(b) pH of concrete pore water

(c) Carbonation of concrete cover

(d) Cracks in the concrete

(e) Stray currents

(f) Time of wetness

(g) Galvanic effects due to contact between dissimilar metals

(h) The presence of other corrosive ions

Design features and construction practices also play an important role in the corrosion of embedded steel. Concrete mixture proportions, thickness of concrete cover over the reinforcing steel, crack-control measures, and implementation of measures designed specifically for corrosion protection are some of the factors that help control the onset and rate of corrosion.

Deterioration of concrete due to corrosion of the reinforcing steel results because the solid products of corrosion (rust) occupy a greater volume than the original steel and exert expansive stresses on the surrounding concrete. The outward manifestations of the rusting include staining, cracking, and spalling of the concrete (Torres-Acosta and Sagüés 2004). Concurrently, the cross-sectional area of the reinforcing steel is reduced. With time, structural distress may occur either because of loss of bond between the reinforcing steel and concrete due to cracking, delamination, and spalling, or because of the reduced steel cross-sectional area. This latter effect can be of special concern in structures containing high-strength prestressing steel because a small amount of metal loss could trigger a failure (Pillai et al. 2010a,b).

The National Research Council (2011) reported that one challenge facing the United States is the development of a cost-effective, environmentally friendly, corrosion-resistant material. Structures are now being constructed with alternative forms of reinforcement such as stainless steels (McDonald et al. 1995; Bower et al. 2000; Wenzlick 2007) and fiber-reinforced polymer reinforcing bars (Thippeswamy et al. 1998; Trejo et al. 2006; Benmokrane et al. 2007; ACI 440R). In addition, practice and research indicate the need for quality concrete, careful design, good construction practices, and reasonable limits on the amount of chlorides in the concrete mixture constituents. Measures that are being taken and further investigated include the use of corrosion inhibitors, protective coatings on reinforcing steel, concrete coatings, cathodic protection, chloride extraction, and realkalization. Although these measures have been successful in general, problems resulting from corrosion of embedded reinforcing steel and other metals have not been eliminated. Thus, research into new measures to mitigate corrosion of reinforcing steel in concrete are vital.

1.2—Scope

This guide discusses the factors that influence corrosion of reinforcing steel in concrete, measures for protecting embedded reinforcing steel in new construction, techniques for detecting corrosion in in-service structures, and remedial procedures. Consideration of these factors and application of the discussed measures, techniques, and procedures should assist in reducing the occurrence of corrosion and result, in most instances, in the satisfactory performance of reinforced and prestressed concrete structural members.

CHAPTER 2—NOTATION AND DEFINITIONS

2.1—Notation

A = area of reinforcing steel polarized, in.^{2} (cm^2)
A_w = atomic mass, lb/mol (kg/mol)
a = constant
B = proportionality constant, mV/mA
b = Tafel slope, V/decade
c = mass of cement, lb (kg)
cm = mass of cementitious materials, lb (kg)
d_c = depth of carbonation, in. (mm)
$D_{a,28}$ = apparent chloride diffusion coefficient at 28 days, ft^2/s (m^2/s)
D_{OPC} = apparent chloride diffusion coefficient of ordinary portland cement concrete, ft^2/s (m^2/s)
D_{SF} = apparent chloride diffusion coefficient of concrete containing silica fume, ft^2/s (m^2/s)
E = applied potential, V
E_{corr} = corrosion potential, V
F = Faraday's constant, 96,500 coulombs/mol
i = current density, mA/ft^2 (μA/cm^2)
i_{corr} = corrosion current density, mA/ft^2 (μA/cm^2)
k = carbonation rate constant, in./yr$^{0.5}$ (mm/yr$^{0.5}$)
M = mass of dissolved metal, lb (kg)
n = number of equivalents
R_P = polarization resistance, ohm-ft^2 (ohm-cm^2)
R_s = concrete resistance, ohm
t = time, seconds
t_y = time, years
w = mass of water, lb (kg)
β_a = anodic Tafel constant, V/decade
β_c = cathodic Tafel constant, V/decade
η = polarization or overpotential, mV
ΔE = voltage change resulting from the applied current, mV
ΔI = applied current required to obtain ΔE, mA

2.2—Definitions

Please refer to the latest version of "ACI Concrete Terminology" for a comprehensive list of definitions.

CHAPTER 3—MECHANISM OF CORROSION OF STEEL IN CONCRETE

3.1—Introduction

This chapter describes the thermodynamics and kinetics of the corrosion of steel reinforcement embedded in concrete. Subsequent sections explain the initiation of active corrosion by chlorides, carbonation of the concrete cover, and the rate-controlling factors for corrosion after it has been initiated. Finally, the influence of reinforcement types and of the concrete environments on corrosion of steel in concrete are discussed.

3.2—Principles of corrosion

3.2.1 *The corrosion process*—The corrosion of steel reinforcement in concrete is an electrochemical process that involves electron transfer between different species at the steel-concrete interface. In the absence of an external electrical source, the electron transfer takes place between two half-cell reactions—one capable of producing electrons and one capable of consuming electrons. The anodic half-cell reaction involves the oxidation or dissolution of iron, namely

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{++} + 2\mathrm{e}^{-} \quad (3.2.1a)$$

Under normal atmospheric exposure conditions, the Fe^{++} ions then react further with oxygen and water to form oxides or hydroxides, and the most likely cathodic half-cell reaction is oxygen reduction

$$2\mathrm{H_2O} + \mathrm{O_2} + 4\mathrm{e}^{-} \rightarrow 4(\mathrm{OH})^{-} \quad (3.2.1b)$$

When oxygen is not available, the cathodic half-cell reaction can take place in the form of hydrogen evolution via

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{H_2} \quad (3.2.1c)$$

When the two reactions occur at widely separated locations, they are termed a macrocell (Fig. 3.2.1a). When they occur close together or essentially at the same location, they are termed a microcell (Fig. 3.2.1b).

The cathodic reaction that occurs in any specific case depends on the availability of oxygen and on the pH of the cement paste pore solution near the steel reinforcement. This is shown by the Pourbaix (E-pH) diagram (Pourbaix 1974), illustrated in Fig. 3.2.1c, which delineates the thermodynamic areas of stability for each of the iron oxide types as a function of electrochemical potential and pH of the environment. The electrochemical potential is a measure of the ease of electron charge transfer between a metal and its environment; in this case, between the steel reinforcement and the cement paste pore solution. It is a property of the steel rein-

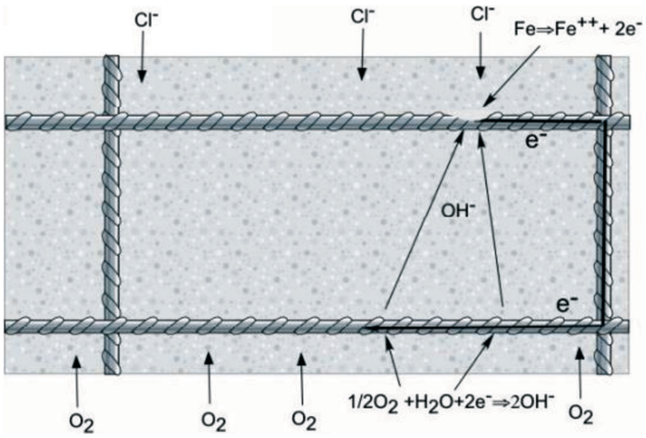

Fig. 3.2.1a—Macrocell corrosion (Hansson et al. 2006).

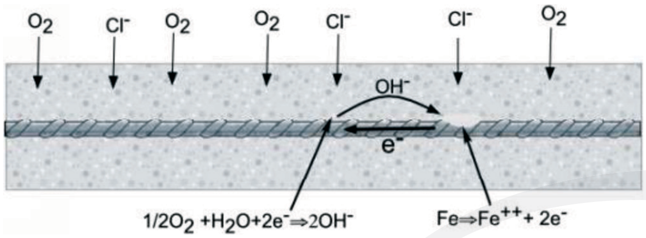

Fig. 3.2.1b—Microcell corrosion (Hansson et al. 2006).

forcement-concrete interface and not of the steel reinforcement itself. It is not possible to determine the absolute value of the potential and, therefore, it is necessary to measure the potential difference between the steel reinforcement surface and a reference electrode. This might be a standard hydrogen electrode (SHE), a saturated calomel electrode (SCE), a Cu/$CuSO_4$ electrode (CSE), or an Ag/AgCl electrode (SSCE). The value of the potential in a freely corroding system is commonly known as the corrosion potential, the open circuit potential, the free potential, or the half-cell potential. For the reaction shown in Eq. (3.2.1b) to occur, the potential should be more negative than that indicated by the upper dashed line, whereas the reaction shown in Eq. (3.2.1c) can only proceed at potentials more negative than the lower dashed line. In general, if all other factors are kept constant, when more oxygen is available, the electrochemical potential will be more positive (anodic).

For sound concrete, the pH of the pore solution is equal or greater than 13.0 and the half-cell potential more positive than –200 mV (CSE). Within this range, in the absence of any other factors, the iron oxides—Fe_3O_4 and Fe_2O_3 or hydroxides of these compounds—will form as solid phases and may develop as a protective (passive) layer on the steel reinforcement. If the pH of the pore solution is reduced, for example, by carbonation or by pozzolanic reactions, the system may be shifted to an area on the Pourbaix diagram in which these oxides do not form a protective layer and active dissolution is possible. Corrosion could theoretically be induced in very high pH environments at high temperature if the potential of the steel is held near –1.0 V (SHE), as per the following reaction

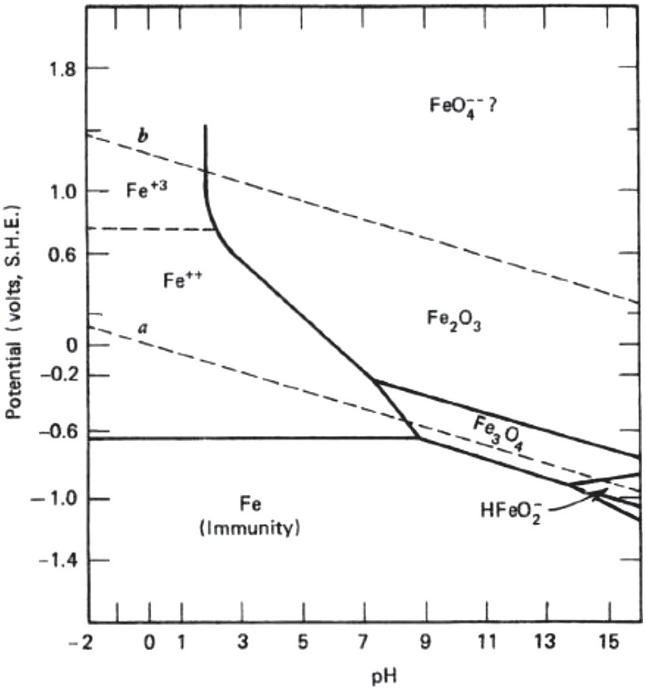

Fig. 3.2.1c—E-pH Pourbaix diagram 77°F (25°C) showing the potential pH ranges of stability of the different phases of iron in aqueous solutions (Revie and Uhlig 2008). The lines a and b represent the equilibrium potentials for the hydrogen evolution and oxygen reduction reactions, respectively.

$$Fe + OH^- + H_2O \rightarrow HFeO^{2-} + H_2 \qquad (3.2.1d)$$

where iron dissolves as $HFeO^{2-}$ (refer to Pourbaix diagram in Fig. 3.2.1d) (Townsend 1970). This condition is highly unlikely to exist in a reinforced concrete structure.

Corrosion of reinforcing steel in concrete can be caused by stray current corrosion or other environmental factors in addition to chemicals (Gummow and Meyers 1986; Bertolini at al. 2007). Stray current is received by the reinforcing steel in concrete or any metal electrically connected to the embedded steel and discharged elsewhere on its way to the source. Reinforcing steel corrodes at the point of current discharge. The most common sources of stray currents for reinforced concrete structures include DC-powered electric railways and electroplating plants. This type of corrosion most commonly occurs in structural elements in contact with the earth.

3.2.2 *Nature of the passive film*—A passive film can be relatively thick and inhibit active corrosion by providing a diffusion barrier to the reaction product of the reacting elements (Fe and O_2). Alternatively, and more commonly, it may be thin, often a few monolayers thick. In this case, the oxides simply occupy the reactive atom sites on the metal surface and prevent the metal atoms at these locations from dissolving. A passive film does not stop corrosion, but it does reduce the corrosion rate to an insignificant level. For steel reinforcement in concrete, the passive corrosion rate is typically ~4×10^{-5} in./year (~1 μm/year) or less; without the passive film, the steel reinforcement can corrode at rates at least three orders of magnitude higher than this (Hansson

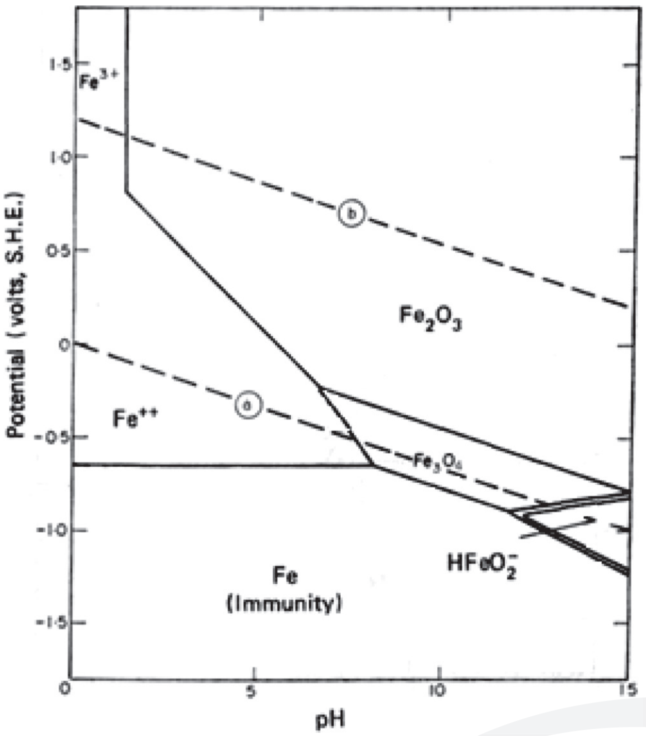

Fig. 3.2.1d—E-pH Pourbaix diagram 140°F (60°C) showing the potential pH ranges of stability of the different phases of iron in aqueous solutions (adapted from Townsend [1970]). The lines a and b represent the potentials for the hydrogen evolution and oxygen reduction reactions, respectively.

1984). The product FeOOH is considered to be the passive film formed at high pH. In recent years, numerous studies reported that the passive film formed on steel in alkaline solutions presents a bilayer structure (Sánchez-Moreno et al. 2009; Ghods et al. 2011a, 2012; Gunay et al. 2013) with an inner Fe^{2+} rich oxy-hydroxide (1 to 3 nm) and an outer Fe^{3+} rich film (5 to 10 nm), with the overall thickness typically in the range of 3 to 15 nm (Rossi et al. 2007; Ghods et al. 2011a, 2012; Gunay et al. 2013; Yu et al. 2015). Ghods et al. (2011a; 2012) and Gunay et al. (2013) reported that the inner film is dense and protective whereas the outer layer is relatively porous and unprotective.

3.2.3 *Kinetics of corrosion*—All metals, except very noble metals such as gold and platinum, are thermodynamically unstable in normal atmospheric conditions and will eventually revert to their oxides or other compounds, as indicated for iron in the E-pH (Pourbaix) diagram in Fig. 3.2.1c. Therefore, the information of importance to the engineer who would use a metal is not whether the metal will corrode, but how fast the corrosion will occur. The Pourbaix diagram only provides thermodynamic information on the stability of iron and its oxides, but it does not provide any information about corrosion kinetics. The corrosion rate can be determined as a corrosion current by measuring the rate at which electrons are removed from the iron in the anodic reactions described previously. The corrosion current can be converted to a rate of loss of metal from the surface of the steel using Faraday's law

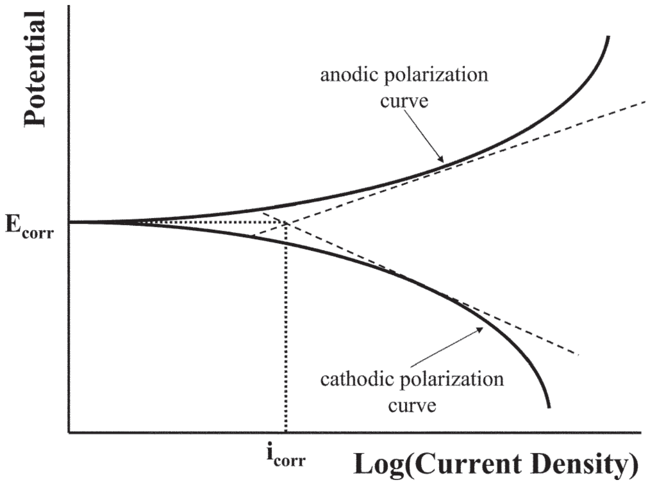

Fig. 3.2.3a—Schematic polarization curve for an actively corroding system (adapted from Jones [1996]).

$$M = \frac{itA_w}{nF} \qquad (3.2.3a)$$

By dividing the mass of metal dissolved, M, by the metal's density and the corroding area of the steel reinforcement, the mass can be converted to an average thickness of the dissolved or oxidized layer.

For iron (or steel):

$$0.09\ \text{mA/ft}^2\ (1\ \text{mA/m}^2) = 0.046\ \text{mils/year}\ (1.16\ \mu\text{m/year}) \qquad (3.2.3b)$$

The current density cannot be determined directly. This is because the requirement of a charge balance means that the rates of production and consumption of electrons by the anodic and cathodic half-cell reactions, respectively, are always equal and, therefore, no net current can be measured. Consequently, to determine the corrosion current density, the system should be displaced from equilibrium by applying an external potential and measuring the resultant net current (potentiostatic measurements). Alternatively, a known current can be applied and the resulting shift in electrochemical potential can be measured (galvanostatic measurements). The difference between the applied potential E and the original corrosion potential E_{corr} is termed the polarization and given the symbol η.

In the absence of passivity, but assuming the continued availability of oxygen and water, the net current would increase with anodic polarization, as shown by the upper curve in Fig. 3.2.3a and cathodic polarization would result in the lower curve. Note that the cathodic polarization curve current values are the absolute value of the actual current values. Tafel has shown that for values of η in the range ± 100 to 200 mV, η is directly proportional to the logarithm of the current density as follows (Burstein 2005)

$$\eta = a + b\log(i) \qquad (3.2.3c)$$