

# Summary

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Charles B. Sanborn, independent consultant and chairman of ASTM Subcommittee G1.14 on Corrosion of Reinforcing Steel, presented a historical background concerning the activities of Subcommittee G1.14. He stated that the interest in the subject started with increased premature failure of highway bridge decks. This interest led to the first symposium held in Chicago in 1976. The result was 15 papers including the research and field practice controlling corrosion of steel in concrete (*Chloride Corrosion of Steel in Concrete*, STP 629).

A second symposium was held in Bal Harbor, FL, in 1978. The papers were aimed at the materials and testing aspects of corrosion of rebar in concrete (*Corrosion of Reinforcement Steel in Concrete*, STP 713). The following activity was to conduct a comprehensive evaluation of the multiaspects of rebar corrosion. Dr. John Slater was selected to make the study. The project was supported by the Metal Properties Council and the U.S. Department of Energy (Argonne National Laboratory) (*Corrosion of Metals in Association with Concrete*, STP 818).

The keynote speaker was Carl E. Locke of the University of Oklahoma. The title was "Corrosion of Steel in Portland Cement Concrete: Fundamental Studies." The information presented was a combination of those available in literature and work done in the University of Oklahoma.

The use of deicing salts on bridges in the United States is identified as the main cause of bridge deck deterioration. Salty runoff damages pier caps and pilings. Deicing salts carried by automobiles into parking garages have resulted in severe damage to those structures. Structures exposed to seawater are also subject to chloride ion damage. The problem is more severe in the splash zone because of the ample supply of oxygen. Very small amounts of corrosion may lead to catastrophic failures in prestressed steel structures. Hydrogen generated by the corrosion reaction can enter the high-strength steel used for prestressing tendons, and brittle failure results.

Under the corrosion mechanism, Dr. Locke explained: "Steel in the high pH environment is in a passive condition and, unless something intrudes to upset the passivity, the steel will not corrode." He added that: "Chloride ions will attack the passive nature of the reinforcing steel in a highly selective manner." Chloride ions will cause a shift in potential of the steel surface embedded in concrete. This potential shift leads to accelerated corrosion in bridge decks caused by a galvanic type corrosion known as macro-cell corrosion.

Several factors influencing the corrosion reaction were discussed as follows:

- The mix design of the concrete affects the corrosion tendencies of the reinforcing steel. Low water cement ratios and high cement contents will increase the density and are more protective.

- The chloride ion content at which passivity is not seen in the anodic polarization curves is about one to two orders of magnitude lower for chloride that diffuses into the hardened concrete in comparison to chloride ion mixed with the fresh concrete mix.

- The rate of corrosion in concrete mixed with calcium chloride has been found to be greater than the rate in concrete mixed with sodium chloride.

- A recent study at the University of Oklahoma indicates that more chloride ion is removed from the pore solution when calcium chloride is used versus sodium chloride as a mix additive.

- Oxygen must be available to support the corrosion reaction. Corrosion of steel in submerged concrete structures is greatly lowered with respect to the steel in the splash zones of the same structures.

- Resistivity of concrete affects the corrosion reaction. Dry concrete has a resistivity of  $10^9 \Omega \cdot \text{cm}$ , thus the electrolyte is not supportive to the ionic conduction. Water saturated concrete was found to have a  $10^4 \Omega \cdot \text{cm}$  resistivity, thus it is supportive to the ionic conduction.

- A current density of 100 to 1000 mA/ft<sup>2</sup> was found to decrease dramatically the bond strength of steel in concrete.

- Studies conducted in the University of Oklahoma indicated that a current density of 3 mA/ft<sup>2</sup> dropped the bond strength after 3.5 to 4 years. Sodium and potassium ions were found to accumulate at the steel surface.

Dr. Locke concluded by stating that the corrosion of steel in portland cement concrete is a complex process, and much is left to be learned.

Dr. Th. Skoulikidis et al of the National Technical University of Athens, Greece, reported on an interesting application using the atmospheric charges to protect the rebars from corrosion. The paper explained that lightning rods exchange electrons with the atmosphere. The direction of exchange depends on local conditions. The authors reported success in harnessing this phenomenon to suppress emission and to use the absorption of electrons for the cathodic protection of the rebar in concrete. The degree of protection varied with the seasons because of the changes in atmospheric electricity. Diodes were attached to the lightning rods to control the current flow in the electron absorption direction, named, "Protective Connection." The most efficient number of lightning rods and diodes was found to be limited to only two, remaining constant between 2 and 5. This indicated the control by other unknown factors. The study indicated that winter in Greece is the ideal season for this method to work effectively since the electron emission is directed from the earth to the atmosphere. During spring time in Greece, the flow is reversed and the efficiency of protection by this method is

reduced. The method is improved when fast diodes are used, the types sensitive to the atmospheric field fluctuations. It was also found, that this system is more effective when the metal surface is in the passive range and not in the pitting range. This method is an automatic cathodic protection system for the steel rebars using the atmospheric electricity. Further research can improve this promising method.

Kenneth J. Drachnik of Raychem Corporation reported the results of a new anode (anodemesh) to be used for impressed current cathodic protection for the reinforced steel in concrete. The anodemesh consists of a polymeric anode wire woven into a mat. The anode has a No. 16 AWG copper wire core and an electrically conductive polymer outer jacket. This product configuration provides for uniform distribution and keeps the anode current density less than 10 mA/ft<sup>2</sup>. The mesh is held together at intervals with plastic cleats that also serve as anchor points to a structure. Two different types of reference electrodes were used to monitor the potential of the protected rebars; they were molybdenum/molybdenum trioxide and zinc/zinc sulfate. Three separate tests were performed: a potential survey to determine the magnitude of the corrosion problem, a polarization test to determine the current required for cathodic protection, and a potential decay test as an alternative method for evaluating cathodic protection current requirements. The test results showed that the molybdenum electrodes are more accurate than the zinc, and both types showed potential drifts with time.

The anodemesh appears to provide protective current for up to 0.6 m (2 ft) away from the end of the mats. Drachnik concluded that the anode system provided large panels easy to install and adequate current to protect the reinforcing steel directly beneath it. The system also polarizes the reinforced steel to a level consistent with the protection criteria determined by both polarization and depolarization tests.

C. Andrade et al of the Institute of Construction and Cement, "Eduardo Torroja," Madrid, Spain, discussed the determination of the corrosion rate of steel embedded in concrete by the polarization resistance  $R_p$  and AC impedance methods.

The paper discusses ways to obtain accurate data by the  $R_p$  method. A comparison between the  $R_p$  method and the weight loss method was presented. Also, the results of an AC impedance obtained by a spectrum analyzer were reported.

Polarization curves were widely used to compare the effect of concrete admixtures. However, one of the disadvantages was the ohmic drop because the concrete resistivity was not taken into account. Furthermore, the ohmic drop may change the amount of current measured and the shape of the polarization curve. And still more, the use of the "intersection method" for determining the instantaneous corrosion rate is laborious and often not accurate because a Tafel behavior is necessary in order to extrapolate the partial anodic and cathodic curves.

The polarization resistance  $R_p$  technique was developed by Stern et al

$$R_p = \left( \frac{\Delta E}{\Delta I} \right) \Delta E \rightarrow 0$$

where  $\Delta E$  is a small step potential applied at the corrosion potential and  $I$  is the electrode response.

$$I_{\text{Corr}} = \frac{B_a \times B_c}{2.3(B_a + B_c)} \times \frac{\Delta I}{\Delta E} = \frac{B}{R_p}$$

where  $B$  varies between 13 and 52 mV for the majority of metal/electrolyte. A value of 26 mV for  $B$  was used when steel is in an active state and 52 mV when the steel is in a passive state, thus, leading to a close agreement of results for the gravimetric and the electrochemical weight loss.

For the DC polarization resistance measurements, the authors recommend the use of a potentiostat with electronic compensation for the ohmic drop of the electrolyte resistivity. They also recommended that after applying the  $E = 10$  mV step, the time constants must be shorter than the 30-s waiting period. Also, use a ramp with 10-MV/min sweep rate a duration of 10 to 100 times longer than the time constant. The  $R_p$  value obtained this way is free from the transient component. In the case of AC impedance technique, the following formula was used

$$Z = R_e + \frac{R_T}{i + j\omega CR_T}$$

where

$R_e$  = the electrolyte ohmic resistivity,

$C$  = the capacitance of the electrode, and

$R_T$  = the transfer resistance equivalent to polarization resistance.

The impedance  $Z$  is frequency dependent, when the frequency is changed from 0 to  $\infty$  a semicircle in a complex plot results (Nyquist diagram). From the diagram it is possible to calculate  $R_e$ ,  $R_T$ , and  $C$  values.  $R_e$  is obtained at the high-frequency range, while  $R_e + R_T$  module is obtained at the low frequency range.

The AC technique is highly dependent upon the measuring equipment. For the impedance measurement, a phase sensitive detector, a digital transfer function analyzer, or a fast fourier transformer was recommended. For more accuracy, a three electrode system can be used to overcome the difference in corrosion rate for the two electrodes system.

In conclusion, the authors stated that the  $R_p$  method (DC) is useful for calculating the instantaneous corrosion rate. The AC technique is the most promising to obtain the basic parameters of the corroding reaction. The AC technique is less accurate than the DC in measuring  $R_p$ . The AC technique is more time consuming and requires expensive equipment.

D. Whiting of the Concrete Materials Research Department, Construction Technology Laboratories, a Division of the Portland Cement Association, reported on the results of a field survey concerning the corrosion susceptibility of the metallic elements in reinforced earth systems. He defined reinforced earth as a composite structural system composed of soil fill strengthened by inclusion of

rods, bars, fibers, or nets, generally arranged isotropically within the soil mass.

The field tests included visual inspection, delamination detection, electrical potential surveys, soil and concrete resistivities, concrete cover, stray current testing, chloride analyses, chloride permeability, chemical analyses for soil, and metallographic analyses for reinforcing strips.

A copper/copper sulfate electrode (CSE) was used in the electrical potential measurements, using ASTM Test Method for Half Cell Potentials of Reinforcing Steel in Concrete (C 876). Electrical soil resistivity of the soil was measured using a standard four pin method applied to the soil placed in an acrylic soil box. As for the concrete resistivity, a miniature four pin device similar to that developed by Stratfull was used. Readings could not be obtained for very dry concrete even after pre-wetting the surface. Stray currents were observed by measuring shifts in the open circuit potential of reinforcing strips during passage of rapid transit traffic.

Chloride ions were detected by using a potentiometric titration technique, and chloride permeability of concrete was tested by application of 60-V DC across the faces of a core. The amount of charges passed (in coulombs) over a 6 h period were correlated with permeability of the concrete to chloride ions. Chemical analyses of soil samples were analyzed for chloride and sulfate ions by boiling 100-g samples in deionized water, centrifuging, filtering, and then introducing the sample in an ion chromatograph equipped with the appropriate anionic columns. Reinforcing strips were cleaned and subjected to metallographic examination.

Mr. Whiting reported that the data collected indicate the potential for corrosion. However, the design and environmental variables rendered a generalization unjustifiable. He also concluded that the environment and backfill characteristics are of prime importance. Marine environments are highly corrosive. Aluminum alloy reinforcing strips did not perform well when subjected to continuous high chloride levels in a moist soil environment.

He recommended the use of high resistivity, neutral pH, low ionic content backfills. As for the reinforcement material, he recommended compatibility with the working environment. In highly corrosive environments consideration should be given to inert materials or materials coated with corrosion resistant substance.

N. S. Berke of W. R. Grace & Co. discussed the use of anodic polarization to determine the effectiveness of calcium nitrate as an anodic inhibitor. The chloride induced corrosion of steel in concrete initiates in the form of highly localized attack or pitting. Thus, a rapid test that provides information as to the susceptibility of steel in concrete to pitting is desirable. Anodic polarization with a reverse scan is used to determine the pitting resistance of alloys. The presence of chloride ions causes the passivity of the steel to break down at potentials below that of the transpassive region and results in rapid localized corrosion or pitting. Passive steel in concrete is generally in a potential region above  $-270$  mV SCE and usually at potentials above  $-120$  mV SCE. Thus, if the pit nucleation potential  $E_n$  is more active than  $-120$  mV SCE pit nucleation is very likely to

occur. The actual pitting corrosion rates will depend on the cathodic reaction (oxygen reduction).

Calcium nitrite in deaerated calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) solution containing 0.1 M chloride should not be detrimental even if large chloride concentrations develop, it may even improve the conditions. The mechanism of improved steel corrosion resistance when calcium nitrite ( $\text{Ca}(\text{NO}_2)_2$ ) is in the concrete is related to anodic inhibition. If oxygen is present at the pits, it should inhibit pitting and improve the protective oxide film (localized corrosion generally occurs in oxygen free zones). Care must be taken in designing cathodic protection systems to ensure that protection is not occurring in a potential range where steel is actively corroding.

He concluded that the cyclic anodic polarization tests of a  $\text{Ca}(\text{OH})_2$  concrete like pore environment has been used to show that:

- Chloride ions can cause severe corrosion of steel to occur in concentrations equivalent to 0.12 to 15.6 kg/M<sup>3</sup> (0.2 to 26 lb/yd<sup>3</sup>) total chloride can in concrete.
- Nitrite ions are very effective anodic inhibitors, which increase steel corrosion resistance to pitting when chlorides are present.
- Corrosion of steel can occur in concrete environments without chloride ions if the steel is polarized into the transpassive region (stray voltages) or into the active region by stray voltages or improperly applied cathodic protection.

P. S. Rothman et al of Harco Corporation presented a discussion on the corrosion problems associated with prestressed concrete pipes and considerations concerning the detection of corrosion. They described the construction of a prestressed concrete cylinder pipe (PCCP), which involves winding a high-strength steel wire circumferentially, under tension, around a concrete core containing a steel cylinder. They added, that corrosion of the steel wire results in pitting, embrittlement or the dissolution of the iron, with a corresponding reduction in cross-sectional area. The result is degradation of the physical strength of the high tensile wire and possible failure of the prestressed concrete cylinder pipe. The lack of electrical continuity between the metallic components can be responsible for the failure of the steel prestressing wires by stray current corrosion.

Investigation of failures indicates the breakage of prestressed wires being the main reason. Galvanic corrosion, stray current electrolysis, or loss of strength through embrittlement or all of these have been the major causes of failure linked to corrosion. The underlying causes were either poor quality or imperfections in protective mortar coating created during manufacturing, handling, or installation damage, intrusion of a depassivating agent, such as chlorides, and imposition of live currents on the pipe.

The mortar coating around the wires is designed to provide protection for the steel against corrosion. This protection is based on a highly alkaline environment, which arrests steel corrosion through passivation, low permeability limiting the penetration of oxygen and aggressive chemicals, and a uniform environment

along the entire structure, thus maintaining a relatively constant potential and reducing the galvanic corrosion. This ideal case is often hard to achieve because of cracks in the mortar, high permeability, thin mortar cover, voids in mortar, carbonation of mortar, chloride ion contamination, and delamination of mortar coating from the wire.

Rothman enumerated some of the problems concerning the detection techniques, such as lack of contact point with the metallic parts, no electrical continuity between the metallic components (prestressed wires, steel cylinder, and bell and spigot rings), and no dependable electrical continuity between adjacent joints of PCCP.

One recommended technique for the potential measurement makes use of a computerized close order surveying technique. This technique utilizes a high input impedance digital voltmeter, solid state memory, keyboard, and display.

Rothman discussed three case histories and concluded that PCCP can undergo corrosion when the mortar coating is damaged. Extreme care must be exercised when applying cathodic protection because of the electrical discontinuity between the different segments of the pipes, as well as the different metallic elements that need to be made continuous. The presence of active corrosion can be detected by special electrical survey techniques.

Th. Skoulikidis, et al of the University of Athens, Greece, presented a second paper describing the use of X-ray as a measure of prediction of concrete cracking, and the rate of corrosion of rebars. By using an Electron Probe Micro-Analysis (EPMA) a solid state diffusion of ferrous ions, it was proven that the corrosion products have the tendency to be formed from the rebar surface towards the corrosive environment. He also reported the possibility of following the evolution of the corrosion products by X-rays and from their permeability to predict the cracking of the concrete caused by the formation of corrosion products.

In order to find a method to predict the time of cracking of the concrete caused by corrosion of the rebars, he stated that it was necessary to separate the phenomenon of carbonation from the electrochemical corrosion. The electrochemical corrosion of rebars was accelerated by impressing +850-mV anodic potential in order to minimize the carbonation.

The time of concrete cracking was found to be 27 days when the weight loss method was used. It was also found, using the current-time measurement, that the cracking of concrete takes place at the point where a sudden increase of current density appears. This method also showed that concrete cracking occurs after 27 days of exposure. When using the X-ray permeability while focusing on the concrete surface, the cracks were detected after 28 days. The same results were found when the focusing was on the rebar surface. It was also noticed that the corrosion products became less transparent by increasing the days of exposure beyond 28 days.

Skoulikidis stated in the discussion that the evolution of corrosion of rebars in 3.5% sodium chloride (NaCl) solution under impressed anodic charge is hyperbolic instead of parabolic without the anodic charge. Twenty-seven days of

exposure corresponded to cracking of the concrete, and about  $10^3$  g/m<sup>2</sup> of steel have been transformed to corrosion products.

He concluded by applying an anodic potential of +850-mV accelerating corrosion and eliminating the carbonation resulting in electrochemical corrosion effect only. By increasing the current density, the weight loss increases and from the X-ray permeability of concrete, it was found that concrete cracking occurs after 27 days of exposure or after the formation of 1000 g/m<sup>2</sup> of corrosion products. The transparency of the corrosion products decreases with time because of the stress exerted by concrete. After the cracking, the transparency increases. This method can be used to predict the concrete cracking by correlating the absorption on the X-ray photographs to the mechanical tension.

Th. Skoulidakis et al of the University of Athens, Greece, submitted a third paper for publication, concerning the additives, "Terra Theraic and SIMAC," for the protection of rebars.

They explained that Terra Theraic is a natural colloidal material of volcanic origin. It is composed of 60% silica (SiO<sub>2</sub>), 12 to 15% alumina (Al<sub>2</sub>O<sub>3</sub>), 5% iron oxide (Fe<sub>2</sub>O<sub>3</sub>), 20 to 23% MgO + CaO + TiO<sub>2</sub>. And SIMAC (MgO) is prepared by heating MgCO<sub>3</sub> to 1200°C and suddenly cooling.

A series of tests were conducted using the additives separately and with cathodic protection, anodic potential, and lightning rods-diodes cathodic protection. The results were as follows:

- Using the weight loss test method, the two additives tested by Skoulidakis et al offered good protection.
- In the case of cathodic protection (−850 mV SCE) combined with the additives, the percent of protection increased drastically from 82 to 174 and 169%.
- In the case of lightning protection rods with diodes combined with the additives, the protection level improved from 25 to 123%.
- In the case of applied anodic potential of +850 mV, in other words under accelerated corrosion, the two additives protected the rebars.
- In the case of actual seawater testing compared to laboratory testing, the corrosion in the seawater is less than the laboratory because of the protective properties of the fouling on the surface of the specimens.

Skoulidakis concluded that the two additives he used gave good protection to the rebars under all conditions.

The authors of the papers have presented a wide range of test techniques and results in various applications. The information is the result of many years of hard work and is compiled herein as a guide for the reader for future investigation, especially in the field of stray current corrosion, which needs further work.

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