

Corrosion of Metals in Association with Concrete

John E. Slater



STP 818

CORROSION OF METALS IN ASSOCIATION WITH CONCRETE

A manual sponsored by ASTM
Subcommittee G01.14 on
Corrosion of Reinforcing Steel
and Metal Properties Council

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Foreword

This manual is the result of a request by ASTM, in particular by Subcommittee G01.14 on Corrosion of Reinforcing Steel, to the Metal Properties Council for a comprehensive appraisal of the many aspects of corrosion of metals in concrete. Acting through its Subcommittee 8 on Corrosion (William R. Martin, chairman), MPC organized a task group to plan and supervise the project. Dr. A. R. Cook served as task group chairman and obtained the participation of a broadly based and highly knowledgeable group. The membership consisted of K. C. Clear, E. Escalante, J. M. Gaidis, K. C. Hover, F. LaQue, H. M. Maxwell, W. J. McCoy, C. B. Sanborn, D. Stark, I. L. Stern, and D. E. Tonini.

The project was motivated by recognition that the possible deterioration of reinforced concrete structures is of national and international concern. For example, marine and offshore structures such as piling and drilling platforms are in widespread and growing use. In the future, fixed and floating platforms of reinforced concrete using reinforcing bar and prestressed steel, and reinforced concrete pipe structures, are likely to become important. In addition, the spalling and failure of bridge decks when exposed to road salt or ocean spray and especially, but not exclusively, in association with freeze-thaw conditions, is a problem of mammoth proportions.

The importance of the bridge deck problem is emphasized by estimates made by the U. S. Federal Highway Administration. The cost of repairing existing bridges built before 1974 on the interstate system will be over \$1.6 billion, and the installation of protective systems would cost another \$1.2 billion. Specifically, 560 bridges on the interstate system were judged in need of major restoration. Over 3400 bridges are considered to be in need of moderate restoration. (Little corrosion of rebar will be in evidence where minor restoration is involved.) Presently, annual repair costs are estimated to be in the hundreds of millions of dollars.

The purpose of this project, then, was as follows:

1. Assess the most advanced technology and theories and determine their limitations.
2. Evaluate the situation regarding industry standards.
3. Accumulate and report on practical experience concerning the deterioration of reinforced structures and its prevention.
4. Identify profitable areas for research into and development of corrosion prevention measures.
5. Resolve in an unbiased and noncommercial way conflicting views regarding test methods and equipment, monitoring techniques, protective measures, and design practices.

The task group selected Dr. John Slater, then of Packer Engineering Associates, as the principal investigator after reviewing proposals from a number of highly regarded contractors. The project was supported equally by the Metal Properties Council and the U. S. Department of Energy acting through Argonne National Laboratory and OTEC Biofouling, Corrosion Materials Branch (Dr. J. B. Darby, project manager).

Dr. Slater's report is considered to be a concise yet thorough state-of-the-art report. It was thoroughly reviewed by the task group prior to acceptance.

The Metal Properties Council is pleased to have been of service to ASTM and especially to Subcommittee G01.14 in this important project. It is hoped that this manual will provide a basis for future standards work.

Martin Prager

Associate Director, Metal Properties Council
Inc., New York, NY

Related ASTM Publications

Atmospheric Corrosion of Metals, STP 767 (1982), 04-767000-27

Underground Corrosion, STP 741 (1981), 04-741000-27

Electrochemical Corrosion Testing, STP 727 (1981), 04-727000-27

Geothermal Scaling and Corrosion, STP 717 (1980), 04-717000-27

Corrosion of Reinforcing Steel in Concrete, STP 713 (1980), 04-713000-27

Stress Corrosion Cracking — The Slow Strain-Rate Technique, STP 665 (1979),
04-665000-27

Compilation of ASTM Standards in Building Codes, 20th Edition, 1982,
03-002082-10

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Contents

I	Introduction and Background	1
II	Magnitude of the Problem	5
III	Fundamental Mechanisms	10
IV	Factors Influencing the Rate of Corrosion of Steel in Concrete	26
V	Measurement of Deterioration	34
VI	Fatigue of Reinforced Concrete and Influence of Environment	45
VII	Protection Methods	48
VIII	Standards	69
IX	Current and Needed Research	71
	References	74
	Index	81

Introduction and Background

Reinforced concrete is a widely accepted material of construction. It has functioned more or less acceptably in many environments, and while some deterioration of reinforcing steel has been noted, the problems have been far outweighed by the good experiences. This satisfactory situation began to change, however, when salt applications were used to implement a “bare pavement policy” in those states where ice and snow were a problem during the winter months. The increased use of salt applied to roads and bridges can be seen from data made available by the Salt Institute (Fig. 1). About the end of the 1960s, severe deterioration of many of the reinforced concrete bridge decks in the “snow belt” was noted (Fig. 2). The large sums of money needed to rehabilitate these structures and to finance possible measures of obviating the problem have encouraged further study of the fundamental mechanism of corrosion of reinforcing steel

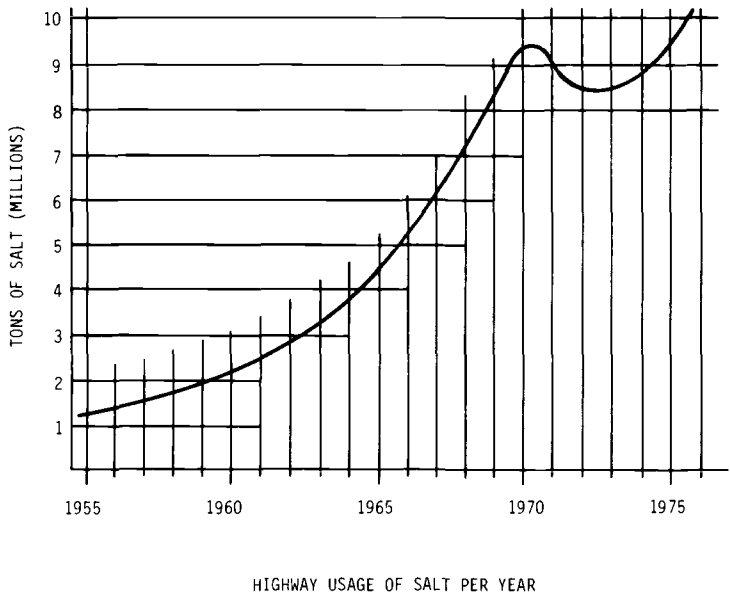


FIG. 1—De-icing salt usage in the United States as a function of year.



FIG. 2—*Ultimate deterioration of bridge deck due to chloride corrosion of reinforcing steel.*

in concrete. The number of relevant publications in America and in the rest of the world as a function of year from 1964 to 1978 is shown in Fig. 3; data are from Ref 1. One can see quite clearly that the research on this problem starts to increase about the late 1960s, especially in the United States.

Besides the problems associated with de-icing salt application, marine structures have always been subjected to deterioration where the reinforcing steel is contacted by chloride ion. This situation has grown more critical with the increasing offshore exploration for oil and gas, and with the possible utilization of thermal gradients in the ocean for power generation. The safety and longevity of such reinforced concrete structures are a prime concern, and methods of protection are important. Note that this circumstance may differ substantially from that of de-icing salt application, due to the presence of permanently saturated concrete in these structures, together with the wetting and drying situation in the splash zone (which can also be viewed as the effective environment on structures subjected to de-icing salt application). Additional problems have occurred with parking garages (due to the carry-in of de-icing salt) and in buildings where chloride was present in the concrete mix.

The increased concern in the United States with corrosion of reinforcing in concrete is also shown by the increased activity of technical societies in this area: the National Association of Corrosion Engineers (NACE), whose Committee T-3K, formed in 1968, is devoted to this subject; the American Concrete Institute (ACI), Committee 222; Committee A2G05 of the Transportation Research Board; and more recently ASTM Subcommittee G01.14 on Corrosion of Rein-

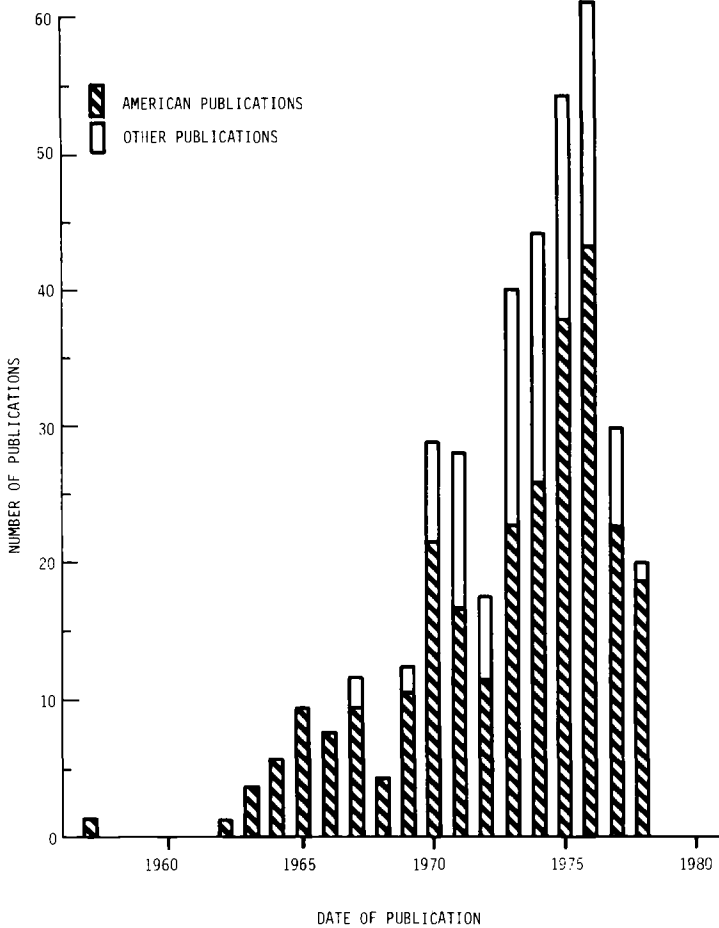


FIG. 3—Histogram showing number of published reports and papers on corrosion of steel in concrete [1].

forcing Steel. The realization by these committees of the severity of the problem has prompted the publication of several bibliographies and reviews [2,3]. The U.S. government has also published bibliographies on this subject [4–6] and foreign governments have commissioned studies [7]. Technical symposia have been held and the presented papers have been published in either pre-print or book form [8–11]. Additionally, several “overview papers” have been prepared, generally slanted either towards highway problems [12–14] or marine problems [15].

There has, however, been a lack of both a critical review of current information in all areas and an assessment as to the areas where further data are needed. Recognizing this need, the Metal Properties Council initiated Project 880–2, “A Report on the Corrosion of Metals in Association with Concrete.” This

ASTM Special Technical Publication 818 incorporates that report. Its scope was as follows:

1. To carry out a literature search and to acquire and analyze any unpublished data available relating to:
 - A. Deterioration of reinforced concrete associated with corrosion of reinforcing bar or stressed tendons.
 - B. Methods of evaluating the corrosion resistance of reinforcing material in the laboratory or in the field.
 - C. Methods of monitoring existing structures.
 - D. Identification of existing standards that might be applicable.
2. To identify and discuss technical problem areas relating to evaluation of materials, methods, and instrumentation for use in construction of reinforced concrete, and relating to the monitoring of any corrosion-induced deterioration which may occur.
3. To recommend specific areas of research relating to the aforementioned problem areas.

The following sources were used:

1. Bibliographies, governmental reports, books, periodicals, theses, unpublished papers presented at symposia, etc.
2. Funding agencies (regarding ongoing governmental and industrial research).
3. Knowledgeable individuals in the field.

This information was gathered both nationally and internationally, sifted and studied for relevancy, and incorporated as necessary.

The structure of this report is relatively straightforward. Firstly, the actual magnitude of the problem is investigated, addressing the nature of the problem, an historical perspective, some economic viewpoints, and the nature and type of structures affected. Secondly, the fundamental mechanisms regarding the corrosion of reinforcing in concrete are covered, including the properties per se of concrete and the specific aspects of corrosion of steel in concrete which are dissimilar from other types of corrosion. Some discussion is then given to factors influencing the rate of corrosion of steel in concrete (since it is considered that it is the *rate* which is of prime importance in determining subsequent deterioration of the structure [13]), methods of measuring the deterioration, and methods of protecting against the deterioration. Finally, current standards are assessed and areas of future work are suggested.

II

Magnitude of the Problem

The basic problem associated with the deterioration of conventional reinforced concrete due to corrosion of embedded reinforcement is generally not that the reinforcing itself is reduced in mechanical strength, but rather that the products of corrosion exert stresses within the concrete which cannot be supported by the limited plastic deformation of the concrete, and the concrete therefore cracks. This process is thus somewhat akin to the protectiveness or nonprotectiveness of oxide films on materials formed during high-temperature treatment, where the Pilling-Bedworth Ratio determines stresses in the oxide which are dependent on the relative volume of oxide to the volume of metal from which it came.¹ Presumably, had the corrosion product from the steel (still in some doubt at this juncture in the actual concrete environment but ultimately a hydrated ferrous fer-ric oxide) occupied less volume than the metal from which it was formed, then the problem of reinforced concrete cracking and spalling would not have occurred. As a corollary, however, should this volume change have been significant in the *reverse* direction, it is possible that bond-strength problems between the reinforcement and the concrete may have occurred during the corrosion process.

The main exception to this problem of concrete cracking resulting from corrosion is in the area of pre-stressed concrete. In these cases, most concern is directed towards the influence of corrosive environments on the mechanical strength of the pre-stressing steel. This can be both from a generalized (wastage) and localized (cracking) viewpoint. Aspects of the stress-corrosion cracking and hydrogen-induced cracking of steels used for these purposes are thus important. Finally, concern is being expressed regarding possible fatigue strength of rein-

¹The Pilling-Bedworth ratio is defined as [16]:

$$\frac{MD}{nmd}$$

where

M = molecular weight of scale,

D = density of scale,

n = number of metal atoms in formula of scale substance,

m = atomic weight of metal, and

d = density of metal.

forced concrete when in contact with a corrosive medium; this situation will be discussed to some extent later in this report. However, to reiterate, the most severe problem of deterioration of reinforced concrete is associated with corrosion of the reinforcing steel setting up tensile stresses within the concrete.

Interestingly, it is only recently that consideration has been given to experimental determination of the magnitude of these stresses. Work recently undertaken at Penn State University [17] is utilizing reinforcement within concrete surrounded by a titanium shell, with the outside of the shell being strain gaged to determine the appearance of stress as the reinforcing steel corrodes. Under the most adverse circumstances (nonuniform environment, artificially produced macrocell) strains corresponding to a stress of 490 MPa (71 ksi) have been measured. An alternative technique may be to measure the stress on the inside of hollow reinforcement, making the assumption that until the tube goes into the plastic region, the same elastic stresses are being transmitted into the concrete surrounding the tube. It is also worthwhile noting that stress induced by corrosion has been the cause of a significant derating of much of the nuclear generating capacity of the United Kingdom, namely in the "MagneX" reactors. In this case, accelerated corrosion of the magnesium alloy in carbon dioxide has resulted in severe distortion and subsequent operational problems.

The final stage of deterioration of conventional reinforced concrete from corrosion of reinforcing steel will be the cracks reaching the surface of, and causing the disintegration of, the concrete cover. This can lead to problems regarding structural soundness (on, for example, pilings), to discomfort (for example, chuck-holes in bridges), or to cosmetic problems (as in the case of facades on buildings). Since concrete that has reached this state of deterioration (spalling) is frequently extremely difficult to rehabilitate, significant effort has been expended to develop techniques capable of detecting the corrosion at an earlier stage. The development of these techniques, which have included detection of subsurface cracking, monitoring of chloride ion content in the concrete, and determination of active corrosion of reinforcing steel by its electrochemical properties, will be covered in more detail later in this report.

Bridge and Road Damage

The recent upsurge in research on the corrosion of reinforcing steel in concrete is particularly notable in the area of bridge decks and offshore structures. From an economic standpoint, it is easy to understand the attention recently given to the subject. Data from the Federal Highway Administration (FHWA) indicate that 560 bridges on the interstate system are in need of major restoration at a cost of \$227 000 000. An additional 3400 are in need of moderate restoration at a cost of \$845 000 000, and 29 000 bridges will require minor restoration at a cost of \$600 000. It is currently estimated that annual repair costs on these bridges will amount to \$200 000 000. The FHWA expects that the total cost, to the year 1996, for restoration and protection of bridges *on the interstate system only* will be 2.6

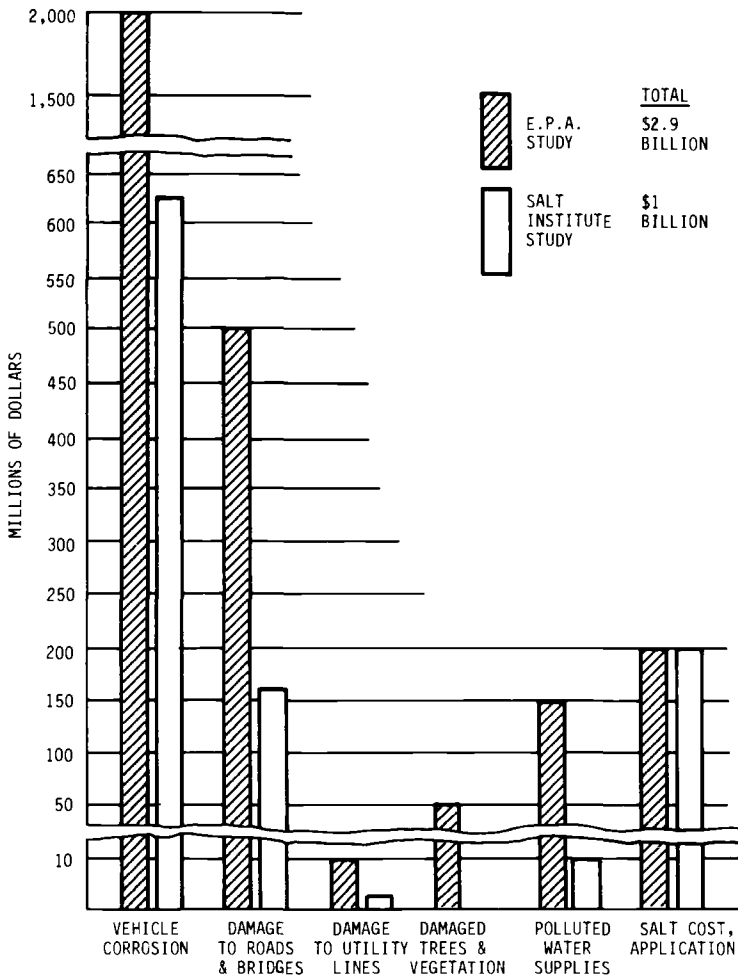
billion dollars. When it is considered that the number of bridges on the interstate system is but a small fraction of those involved in the total highway system of the United States (including state, county, and local roads), then the cost for *total* highway bridge repair will probably be at least four times that amount.

Data from the Environmental Protection Agency (EPA) [18] indicate that the cost of road and bridge damage caused by application of de-icing salt is approximately \$500 000 000 per year (Fig. 4). A Salt Institute study [19] disagrees with this figure and suggests a cost of approximately \$152 000 000 per year. It must be emphasized that the available economic data apply only to structures damaged by the application of de-icing salt; damage and repair caused by, for example, marine conditions are not included. In a recent National Bureau of Standards (NBS) study on the economic impact of corrosion to the community, there was no attempt to "pull-out" those costs directly attributable to either de-icing salt or marine-corrosion-induced deterioration of reinforced concrete structures, nor was any attempt made to consider the costs of protection of such structures against this type of deterioration. It is important to recognize the fact that corrosion-prevention techniques, whether employed during initial construction or at a later stage in the life of the structure, which attempt to prevent corrosion of the embedded reinforcing steel, will increase the cost of the structure. It is, of course, necessary to evaluate these techniques insofar as their cost-effectiveness is concerned. By taking into account the necessary life of the structure, together with initial cost versus maintenance cost considerations, different techniques of corrosion prevention can be evaluated as to their likely effect on the total life of the structure and their applicability to different situations. Certainly it is to be hoped that this type of experimentation and cost-effectiveness study will at least mitigate the currently severe problems involved in complete rehabilitation of bridge decks, piers, pilings, and buildings (Fig. 5).

A recent report to the Congress by the Comptroller General of the United States, "Solving Corrosion Problems of Bridge Surfaces Could Save Millions," reviews the Federal Highway Administration's attack on this problem. Recommendations include (1) the trial use of protective techniques on salt-contaminated but structurally-sound bridges and (2) additional emphasis on the monitoring of long-term effectiveness of rehabilitation procedures applied to such decks.

Damage to Other Structures

Some mention has been given previously to the kinds of structures which have suffered the effects of corrosion of reinforcing steel, either from deterioration of the concrete *per se* by spalling or cracking, or by loss of strength due to mechanical deterioration of pre-stressing steel. Literature review shows that for the past 15 years the major activity in this country has been associated with bridge decks. Damage to structures such as reinforced concrete pipe and buildings (particularly those seeing marine environment spray etc.) and parking structures (particularly those seeing large amounts of road salt) is much less intensively covered. The



ANNUAL COST OF ROAD SALTING
 FIG. 4—Comparative data showing costs associated with use of de-icing salt [18,19].

European community, particularly in Scandinavia and the United Kingdom, has been concerned in recent years with deterioration of reinforced concrete offshore structures by intrusion of marine salt. Pilings continue to be of interest. Another area of concern has been the use of pre-stressed concrete in nuclear reactor containment buildings. All these structures are susceptible to corrosion-induced damage in varying degrees.

Types of Steel and Concrete

The type of reinforcing steel important here is the “conventional” (neither pre-tensioned nor post-tensioned). Also important are two types of concrete:



FIG. 5—Spalling on building columns due to chloride admixture and inadequate depth of cover.

“pre-tensioned” (that containing reinforcing which is stressed in tension prior to concrete pouring, and where the steel is allowed to relax after concrete curing) and “post-tensioned” (that in which the steel is put in tension following concrete curing). The steels commonly used in “conventional” reinforced concrete are generally low-to-medium carbon, relatively low strength, and non-heat-treated. These steels are typically not susceptible to stress corrosion cracking in concrete environment even in the presence of corrosive agents. The higher strength steels used in pre-stressed and post-tensioned concrete, however, are much more susceptible to stress corrosion cracking in certain environments which concrete can provide, and must be protected carefully against it. In these instances, even small amounts of corrosion can be extremely detrimental to the lifetime of the structure.

Although a complete and exhaustive search has not been made, a review of literature has unearthed only one instance—an auditorium in West Berlin—where corrosion of reinforcing steel has been definitely linked to the sudden and catastrophic failure of a structure.

III

Fundamental Mechanisms

Concrete Environment

One of the purposes of this section is to discuss the properties of concrete as they affect the reinforcing steel environment. Obviously, in this type of report, it is neither possible nor necessary to cover in great detail all aspects of concrete technology. For a fuller discussion of this subject, the reader is referred to the standard textbooks or to a paper by Lankard [20] which defines and describes the necessary properties in adequate detail.

Nature of Concrete

The nature of concrete is in general a mix of water, sand, aggregate, and cement. Normal portland cement (a commercial product) is composed of approximately 80% carbonated lime and 20% clay which has been intimately mixed, ground, and calcined, followed by a further grinding operation. Several different types of portland cement are available; these are classified in ASTM Specification C 150. Normal portland cement (Type I) is used as a general purpose cement. Modified portland cement (Type II) generates less heat from hydration and is more resistant to sulfate attack. Accordingly, it is used more commonly in larger structures where heat of hydration may cause cracking. Type III cement, high early strength, is used where high strengths are required in a few days. Low-heat portland cement (Type IV) is a modification of Type II insofar as it has an even greater reduction in heat of hydration. Type V is a sulfate-resisting cement, and has not been generally used for structures susceptible to chloride infiltration. Other additives are frequently used in concrete, including air-entraining agents which, as their name implies, put small bubbles of air into the concrete, and thereby help avoid problems due to repeated freezing and thawing and the action of de-icing salts on the cementitious material.

A major influence that the composition of concrete exerts on the environment of any reinforcing steel which is placed within it is a relatively high pH. The pH appears to be governed more or less by the free calcium hydroxide within the concrete, which gives a pH somewhat above 12. It is to be noted, however, that the pH of a saturated calcium hydroxide solution (12.6) is lower than that ob-

served from concrete porewater which has been “squeezed out” of hardened concrete [21]. It has been suggested that the ultimate agent governing pH is in fact alkali content of the concrete, but this remains to be substantiated.

Permeability of Concrete

Concrete is a hard, dense material. Because of its constitution, however, it does contain pores which are interconnected throughout it, and this extensive network leads to permeability of the concrete, to both liquids and gases.

This is of critical importance in the corrosion process, because both the initiators (generally chloride ion) and supporters (for example, oxygen) of reinforcing steel corrosion must diffuse through the overlying concrete to the steel. The degree of permeability of concrete to water is generally associated with the water-to-cement ratio. Neglecting aggregate effects, the influence of water/cement ratio on permeability of cement paste is shown in Fig. 6 [22]. Thus a higher water/cement ratio apparently leads to either a greater number of pores or to larger pores, both of which can lead to increased permeability. There is obviously a close relationship between gas permeability and water permeability, although the exact mechanism of this has not been determined. For example, a relatively dry concrete might be expected to have a larger volume fraction of the pores unfilled with water, and therefore these pores should be available for gas transport. On the other hand, saturated concrete would be expected to have a

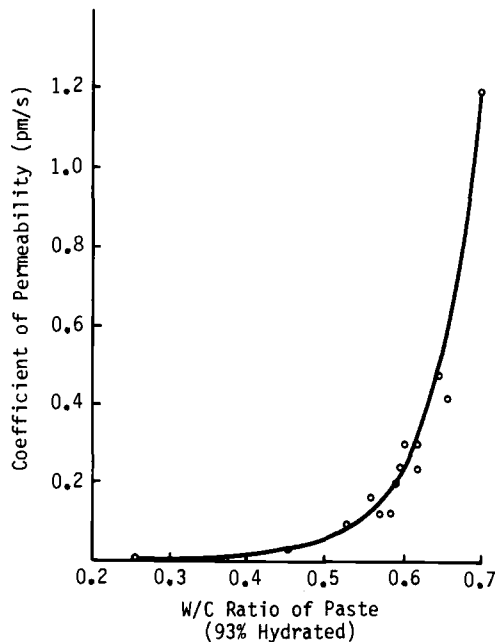


FIG. 6—Effect of water/cement ratio on permeability of cement mortar specimens [22].

much lower permeability for oxygen because of the need for diffusion to occur solely in the liquid phase.

Interestingly, little information is apparently available regarding the diffusion of gases through concrete, and on the influence of concrete properties and specifically water content on this effect. Using electrochemical techniques, Gjorv and co-workers [23] found some interesting results regarding the oxygen diffusion through concrete. Firstly, for a given quality (water/cement ratio) of concrete, the thickness of concrete has only a small effect on the flux of oxygen. As a corollary, for a given thickness of concrete, the quality of concrete has only a small effect on the flux of oxygen. For the same water/cement ratio, the rate of oxygen diffusion is lower through mortar than through concrete (probably the result of increased surface area around aggregate), and there is also an influence of entry surface on diffusion; in other words, a cast surface apparently has a greater barrier effect for diffusion than does cut surface. These results are surprising in many respects. All work in this study was undertaken on water-saturated concrete, which pertains certainly in completely water-immersed conditions but does not adequately simulate the situation in buildings, bridge decks, or indeed the splash zone of structures in marine environments. Further, Fick's law would suggest that, other facts being equal, there should certainly be a fairly large effect of thickness on flux, whereas the effect of water/cement ratio is to some extent understandable given the saturated conditions of concrete in which the work was undertaken. There are some possible problems with the technique used in this research, notably the involuntary production of oxygen close to the test electrode which was in fact trying to electrochemically reduce the same species diffusing through the concrete. The concept, however, is interesting, and further work needs to be undertaken in this area. Tuutti [24] has replotted data from Ref 22 and has included information on expected data for diffusion of oxygen in water and data for oxygen diffusion in nonsaturated concrete (Fig. 7). The effect of water saturation in inhibiting oxygen diffusion is quite clear.

Seawater Service

The possible appropriateness of seawater service—in particular, the effect of fouling organisms on reducing oxygen availability at the concrete surface—has not received significant attention.

Additives

As will be discussed later, the high pH of concrete is generally the major factor in determining the behavior of the steel embedded therein. While most pH's measured for portland cement concrete (PCC) are in the region of 12 or above, it is also possible for different types of additive to the concrete, or indeed for different types of concrete themselves, to give different values of pH. This is particularly true in the role of, for example, gypsum-type cements and additions of phosphate, both of which are used as rapid-set materials for concrete used in repairs.

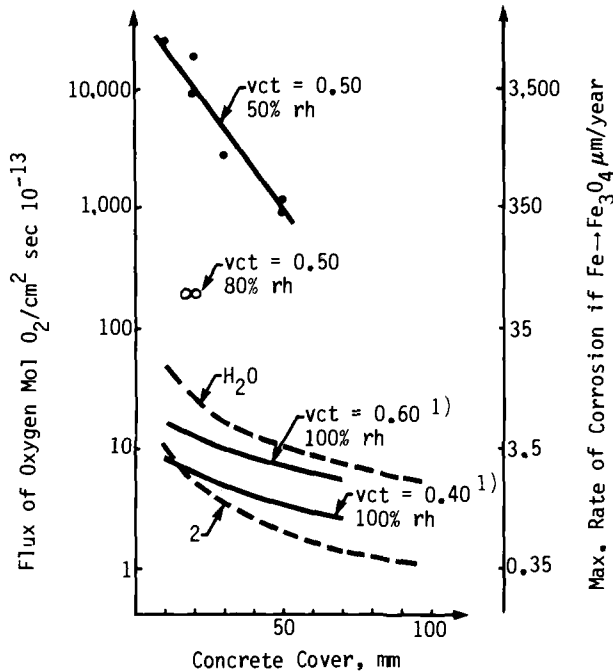


FIG. 7—Effect of degree of saturation and water/cement ratio on flux of oxygen through concrete [24].

The many types of “concrete” and patching materials available are discussed in Refs 25 and 26. It is not believed that any information exists in the open literature regarding the effect of pH values in these types of concrete and the ultimate effect which such pH values may have on the corrosion of reinforcing steels. However, because of the ways these types of concrete are used (that is, in relatively small areas of structures), it is feasible that pH cells could be set up with a small anode to large cathode area, which is extremely detrimental from the point of view of “driving” the corrosion on the rebar in the repaired areas. This subject will be discussed later.

Other types of additive have also been employed in attempts to improve the performance of reinforced concrete. Latex-modified concrete essentially uses a polymer emulsion in the mix-water which apparently impedes, at least at interfaces, the penetration of surface chlorides into the concrete (and possibly oxygen diffusion also through the concrete); this concrete has been used extensively. Several types of modifiers have been utilized. Latexes containing vinyl/vinylidene chloride are possibly unstable due to alkaline hydrolysis, which may allow the release of free chloride ion which has the potential of causing corrosion of the reinforcing steel. The solely styrene/butadiene type of latex is free from these problems, however, and has found wide acceptance as both a repair material and as a “top coat” on conventional concrete [27]. Data on the

effectiveness of latex-modified concrete in retarding chloride penetration are shown in Table 1. A similar approach has been taken in the incorporation of wax compounds in the concrete mix. This procedure, known as internally sealed concrete, uses a heating cycle following curing to cause a hydrophobic layer of wax to form on pore walls. As such, it does not change the environment seen by the rebar per se, but again acts to prevent ingress of surface chemicals [28]. Additives to PCC are used to accelerate the "set" of concrete. The earliest of these was calcium chloride (CaCl_2). Whiting [29] and Cook and McCoy [30] discuss this subject. There are definite differences as to the role of chloride in causing corrosion of reinforcing steel, depending on whether it is present in the mix or is added following curing. Other factors, such as concrete quality and depth of cover, also accentuate the differences.

The role of chloride in causing corrosion, and limitations on the use of admixtures containing chloride, will be considered in future pages.

Other Types of Concrete

Other types of "concrete" bear little resemblance to PCC and do not provide the same environment to the reinforcing steel. For example, "epoxy-type" concrete is simply an epoxy-based compound containing aggregate. Embedded reinforcing steel in such concretes should be relatively immune from corrosion, at least due to the environment which the concrete provides, because of the inert and impervious nature of the concrete.

Workmanship

Many of the properties ultimately developed by PCC are a result of workmanship during mixing, placing, and curing [29]. Thus consolidation techniques during placement of concrete are extremely important in assuring homogeneity of the concrete. In this way, the presence of different types of environment along a given piece of reinforcing steel, or from place to place in the structure, can be avoided.

TABLE 1—Comparative chloride penetrations for latex-modified and other bridge deck concretes [28].

Depth of Section in Core, mm (in.)	Percent Chlorides by Weight of Mortar		
	Latex Concrete Overlays	Sound Concrete Unspalled Decks	Sound Concrete Spalled Decks
6.4 (¼)	0.02 to 0.10	0.07 to 0.18	0.16 to 0.29
12.7 (½)	0.003 to 0.02	0.05 to 0.17	0.16 to 0.26
25.4 (1)	0.002 to 0.03	0.03 to 0.08	0.08 to 0.14
50.8 (2)	0.002 to 0.03	0.01 to 0.04	0.02 to 0.05

Corrosion of Steel in Aqueous Solutions

While recognizing the fact that the circumstances in a bulk aqueous solution and in the concrete environment may be significantly different (for example, in diffusion properties), it is appropriate here to consider briefly the corrosion behavior of steel in aqueous solutions as affected by pH, chloride, and oxygen. The rationale for this is the baseline which can thus be drawn when the concrete environment is considered. Over the pH range from approximately 4 to 10, the corrosion rate of steel or iron in an aerated soft water is constant at roughly 10 mils per year (Fig. 8) [31]. As the pH increases from 10 to 13, there is a gradual decrease in corrosion rate of approximately an order of magnitude over this pH range. This is caused by the onset of passivity of the iron or steel surface over this pH range in the presence of adequate supply of oxygen. The high pH and availability of oxygen produce a film of gamma- Fe_2O_3 (ferric oxide) on the surface, which effectively acts as a barrier against corrosion. At higher pH (>14) and temperature, this film may be disrupted due to high concentrations of alkali and the formation of HFeO_2^- , but this is not germane to the present discussion because of the inability of such pH values to occur in concrete.

It is interesting to speculate on the role of remaining millscale (Fe_3O_4) in the passivation process. Since Fe_3O_4 is an electronic conductor and a good cathode, it may facilitate initial passivation of bare steel.

It is precisely this action of passivity which generally leads to the excellent corrosion resistance of steel in normal concrete. However, passivating films are disrupted once formed, or prevented from forming, by many agents, particularly by halides. While the precise mechanism of action is still unclear [32], the presence of chloride ion reduces or destroys the protective nature of the passive film, and can lead not only to accelerated corrosion rates, but to the formation of macroscopic cells due to differences in chloride concentration. Indeed, where passivity is first broken down, the concentration of chloride tends to increase

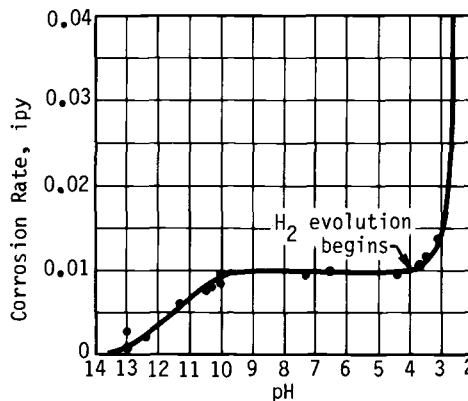


FIG. 8—Effect of pH on corrosion rate of iron in aerated soft water at room temperature [30].

autocatalytically, and this can essentially give an accelerated attack, or what is commonly known as pitting attack, at the location of initial breakdown. Cathodic millscale may also play a role in enhancing this breakdown.

In the pH range present in concrete, where hydrogen ion reduction is generally not possible (at least under initial conditions), oxygen is crucial for the corrosion reaction to continue. The effect of oxygen concentration on the corrosion rate of steel in water (either distilled or containing 165 ppm CaCl_2) shown in Fig. 9 [33] indicates that the corrosion process is controlled by such oxygen diffusion.

The role of oxygen in determining the rate of corrosion of steel in waters typical of that found in concrete is important, because it does at least theoretically allow one method of approaching control of corrosion of steel in concrete (reducing oxygen availability) and also offers explanation for some hitherto unexpected behavior.

Corrosion of Steel in Concrete

Factors Affecting Initiation Time

Because of the apparent role of calcium hydroxide in determining the pH of the concrete and hence of the environment which the reinforcing steels sees, coupled with the physical difficulty of conducting experiments in concrete itself, much of the work in the area of mechanistic determinations for corrosion of steel in concrete has been undertaken in alkaline solutions, generally of calcium hydroxide. The properties of these solutions, and the influence of chloride additions on their pH, have been studied by workers at Federal Highway Administration [34]. They and others have shown that the addition of 2.4M chloride to a saturated

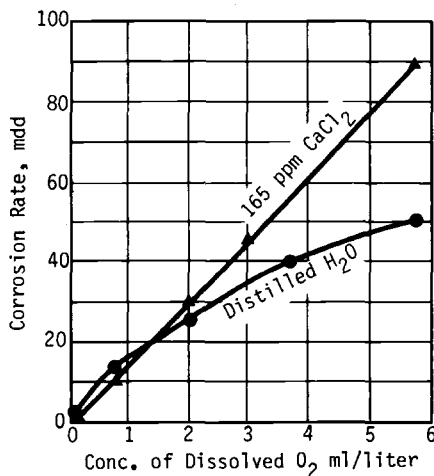


FIG. 9—Effect of oxygen concentration on corrosion of steel in water of two purities [31].

calcium hydroxide solution will decrease the pH per se from 12.6 to 12.2 after an initial rise to 12.8, presumably as a result of activity coefficient interaction effects.

Typical work undertaken in this area is that by Berman [34] and by Hausmann [35]. Both workers showed that, for corrosion of steel rebar to occur in a saturated, aerated $\text{Ca}(\text{OH})_2$ solution, the threshold concentration of Cl^- was 0.02 to 0.03M or 700 to 1000 ppm. Berman showed that, if the solutions were saturated with nitrogen instead of oxygen, the threshold level increased to above 1M. Hausmann's results indicate that in sodium hydroxide (NaOH) solutions of pH 11.6, the threshold concentrations of chloride corrosion was 0.003M (100 ppm) whereas for pH 13 no corrosion was noted at sodium chloride (NaCl) concentrations to 0.25M. Their results show (1) the critical nature of oxygen in supporting corrosion and (2) the interdependency of pH and Cl^- in differing threshold chloride levels for initiating corrosion. Essentially similar data were obtained by Shalon and Raphael [36].

Other workers have been wary of the extrapolation of results based on simulated laboratory tests in aqueous solutions to the concrete environment. The reasons for this are relatively clear:

- The physical differences between $\text{Ca}(\text{OH})_2$ solutions and concrete, and possible heterogeneity at the steel/concrete interface.
- The need for both initiators and accelerants of corrosion to diffuse through the concrete before reaching the reinforcing steel.

Instead, a preferred approach has been to undertake testing on small slabs or prisms of concrete, each containing a reinforcing bar, or on larger slabs which simulate at least a portion of a real structure. The latter approach has been prompted more or less by the ability of a concrete structure to show different regions of corrosion activity of reinforcing steel, based on a "map" of potentials observed on the surface of the concrete. The existence of these potential differences indicates that all reinforcing steel is not behaving equally, that certain regions were active whereas others were passive, and that such an effect could lead to large and widely separated "macrocells". This is distinctly unlike the action of microcells, which form the basis of the mixed potential theory of electrodis.

In these experiments it is useful to think of the total time for corrosion to cause severe deterioration of the concrete as composed of two separate intervals [37]:

$$t_{\text{total}} = t_{\text{initiation}} + t_{\text{propagation}}$$

The *initiation time* is that necessary for conditions at the reinforcing steel/concrete interface to become conducive to corrosion. The *propagation time* is that necessary for corrosion to proceed until either the corrosion is noted or the structure becomes in need of repair, depending on one's definition.

Much of the early work on the mechanism of steel corrosion in concrete concentrated on determining $t_{\text{initiation}}$ and on the factors which controlled it. The early recognition that the onset of active corrosion on reinforcing steel could be monitored by a change in the corrosion potential of the steel [38] led to the use of this technique in mechanistic studies. Spellman and Stratfull [39] used "lollipop" specimens of single reinforcing bars. These were encased in concrete and partially submerged in a saturated solution of NaCl in tap water in a laboratory environment. Clear and co-workers at FHWA [40] have employed large slabs simulating bridge decks, including reinforcing bar (although frequently only an upper mat); these slabs measure 1.52 m by 1.22 m by 152 mm (5 ft by 4 ft by 6 in.). These experiments have been useful in determining the apparent threshold level of chloride at the rebar surface in concrete that will cause breakdown of the passive film and hence corrosion of the steel. Stratfull suggests that the threshold value is about 0.025% of chloride by weight of concrete, while Clear proposes a figure of roughly 0.035% chloride by weight of concrete, for a concrete with a cement factor of 700 lb/yd.

Stratfull shows that the time to active potential is a strong function of the water/cement ratio of the concrete. Clear goes one step further and shows that the chloride penetration rate is a clear function of water/cement ratio, thus confirming Ost and Monfore's earlier work [41] using CaCl_2 solutions on concrete prisms (Fig. 10). Thus there appears to be considerable evidence that a threshold chloride level is necessary for corrosion, and that diffusion of the chloride through the concrete is a critical step. In this regard, two points should be made:

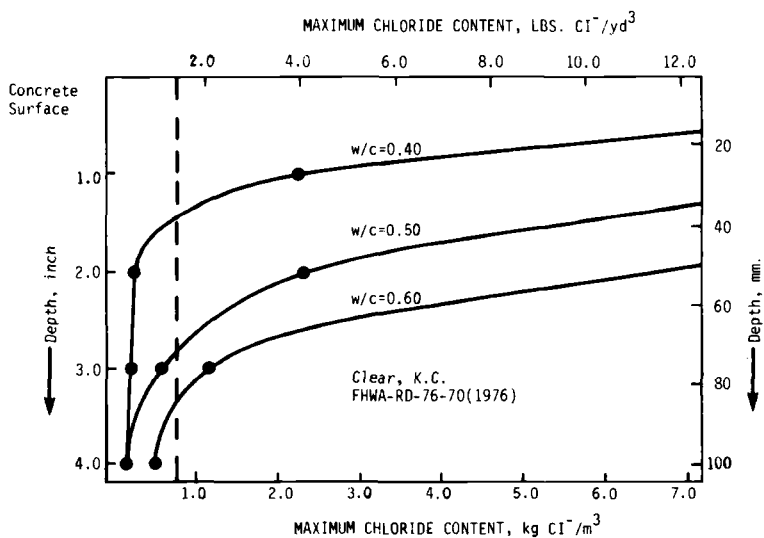


FIG. 10—Maximum salt content as function of depth for intermittently salted concrete slabs of different water/cement ratios [40].

● Constituents of the concrete—specifically tricalcium aluminate (C_3A)—can react with the diffusing chloride, thereby reducing “free chloride” available for depassivation. The amount of C_3A in the concrete is a function of the type of cement used.

● In seawater environments, a reaction can occur at outer surfaces of the concrete, and on down the pores, whereby $Mg(OH)_2$ is precipitated within the pores due to its decreased solubility product over $Ca(OH)_2$. This evidently leads to a decreased permeability, and thus diffusion rate, in seawater [42].

Considerable attention has been paid to the role of cracking of the concrete due to placement practice etc. Intuitively, if a crack extends down to the reinforcing steel, then a relatively easy path for chloride ingress, and hence depassivation, exists. As will be discussed later, certain codes of practice preclude the presence of cracks greater than a given width. Beeby [43], addressing this problem, concludes that there is no good evidence to support the thesis that such cracking leads to corrosion problems more severe than in uncracked concrete of similar quality. Comité Euro-International du Béton (CEB) allowable crack widths, quoted by Beeby, are shown in Table 2.

Since the initiation of corrosion depends on the diffusion of chloride through the concrete cover, any increase in cover depth would be expected to retard corrosion initiation. Thus the joint variables of water/cement ratio and cover are critical in determining the time at which threshold levels of chloride reach the reinforcing steel.

It appears that the threshold amount of chloride needed to cause corrosion in concrete is significantly in excess of that needed in, say, $Ca(OH)_2$ solutions of similar pH. Page, in a series of papers [44,45], has suggested that the reason may be the presence of a lime-rich layer on the surface of the steel, which effectively acts as a source of “reserve alkalinity” to increase the chloride ion concentration necessary for passive film breakdown.

TABLE 2—CEB permissible crack widths in structures [43].^a

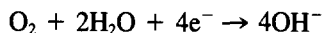
Environment	Loading	Reinforcement	
		Sensitive	Insensitive
Mild	frequent	$W \leq 0.2$	$W \leq 0.4$
	permanent	no tension or $W \leq 0.1$...
Moderate	frequent	$W \leq 0.1$	$W \leq 0.2$
	permanent	no tension	...
Severe	rare	$W \leq 0.1$	$W \leq 0.2$
	frequent	no tension	$W \leq 0.1$

^aW = crack width.

The foregoing discussion has concentrated on those mechanistic factors which may affect the initiation time for corrosion to occur. The factors governing the propagation time, or the rate of corrosion, must now be considered.

Factors Governing Propagation Time

Because of the high pH in concrete, it is believed that the controlling cathodic reaction is oxygen reduction:



Thus a major factor influencing the propagation rate of corrosion must be the oxygen diffusion to cathodic sites. However, this raises the question as to where *are* the cathodic sites? In other words, are the anodic and cathodic sites interchangeable and small? Or are they separated and large—the “macrocell” type of corrosion?

It is interesting to note that the concept of macrocell action for corrosion of steel in concrete was raised by Lewis and Copenhagen in 1959 [46]. These workers considered the action of four separate macrocells and concluded that the one “most likely to succeed” would be:

Steel (Anode)	Permeable Concrete (low pH, high Cl^-)	Less Permeable Concrete (high pH, low Cl^-)	Steel (Cathode)
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They also considered the cell:

Steel (Cathode)	High Oxygen Availability	Low Oxygen Availability	Steel (Anode)
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but concluded that it would be “weaker than the first.”

The fact that areas of different electrode potential can be determined on corroding reinforced concrete structures shows clearly that separate anodic and cathodic areas exist. It is currently believed that Lewis and Copenhagen had almost the right idea; however, in their second cell, there is a rapid depletion of oxygen at the (corroding) anode, which is then supplied with current from the surrounding oxygen-rich cathodes, even though the rate of supply of oxygen may be lower in these areas due to a lower permeability. Thus there is a change in effective level of microcell and macrocell action as corrosion proceeds.

Despite these early prognostications, and some later attempts to show the validity of macrocell action involving differential pH, differential Cl^- , and differential oxygen cells [47–50], good laboratory experimental evidence has been slow in being assembled. Boyd et al, in work at Battelle Columbus Laboratories, attempted to show the action of microcells and macrocells during a series of experiments where the effect of different repair techniques and materials on subsequent corrosion behavior of reinforcing steel was being determined [51]. Although these experiments were undertaken on large slabs, the nature of the environment was such that unrealistic conditions not expected to pertain in

field exposure of concrete were imposed. In further experiments, using coupled "lollipop" specimens, these workers did demonstrate that macrocell influences were extremely strong.

Clear [52], in work at the Federal Highway Administration, also demonstrated this effect. A steel corrosion probe placed in a highly chloride-contaminated concrete block apparently did not evidence any severe corrosion. However, when this small block was cemented to the top of a larger slab containing reinforcing steel (which was apparently at least partially passive) and the probe and slab reinforcing were connected, then rapid corrosion of the steel probe in the small block did occur, at a rate of 9 mpy. This is particularly interesting because many structures contain at least two different depths of steel reinforcing, which are commonly electrically connected. Because of the different depths, it is probable that different chloride levels pertain at the two depths; thus a macroscopic active/passive cell is available which can possess both a large driving voltage and the large-cathode/small-anode ratio known to be most detrimental under these circumstances. Similar possibilities exist where coated steel is connected to and in close proximity with black steel. Under these circumstances, it is possible that the corrosion at holidays or breaks in any organic coating could be increased, or that accelerated corrosion of galvanized steel may occur. Workers at FHWA [52] have showed that, in the first case of epoxy-coated steel, such accelerated corrosion can occur and suggest that the allowable percentage of uncoated areas in the top mat be reduced. Further work on this phenomenon appears warranted. To obviate any such effects with galvanized steel, its specifications should ensure that both top and bottom mat be galvanized. Thus the concept of macrocell action in concrete appears to be well founded. Recent Japanese marine data [53] for a segmented beam in the air, splash, and submerged zones show corrosion development and current flow to the (anodic) splash zone (Fig. 11).

Electrolytic Resistance

The presence of current flow within the concrete from anodic to cathodic areas raises the question of electrolytic resistance and its impact on macrocell action. The resistance of concrete is a function of many factors, including water content, soluble salt content, permeability, and temperature. In general, as these parameters increase, the resistance will decrease, current flow will be facilitated, and thus macrocell action will be enhanced. However, an increased water content will tend to *decrease* oxygen transport in the concrete; since oxygen transport to the cathodes will be critical in determining corrosion rate at the anodes, then some "optimum" water content will doubtless exist for maximum corrosion rates.

pH Control

The shifts in pH at anodic and cathodic sites due to hydrolysis and hydrogen ion elimination, respectively, have recently been observed in the neighborhood of reinforcing steel in concrete [52]. Some concern has been expressed that the

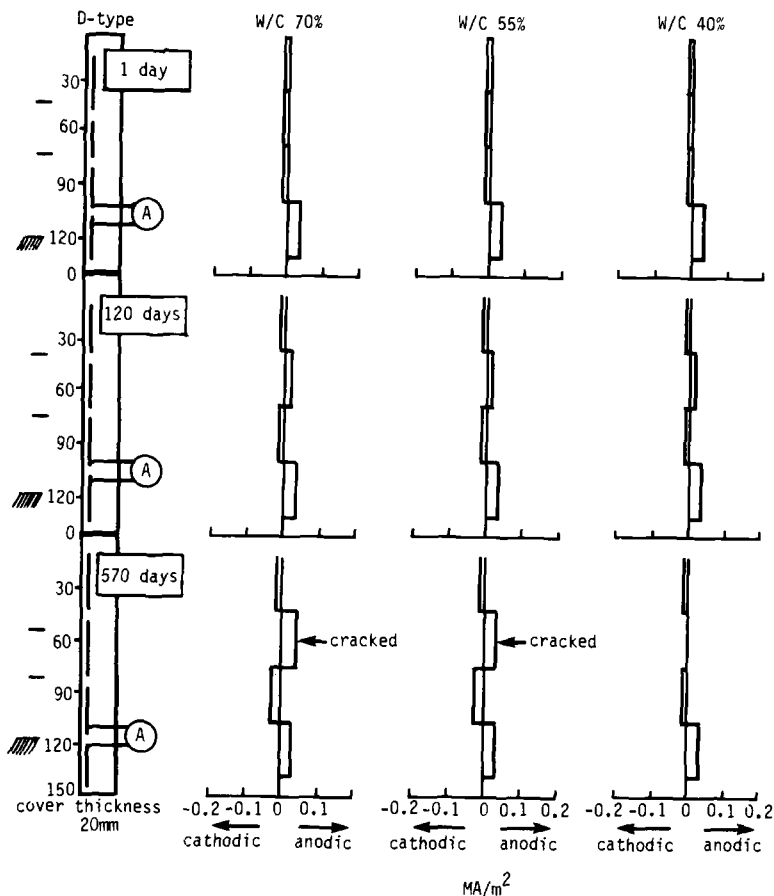


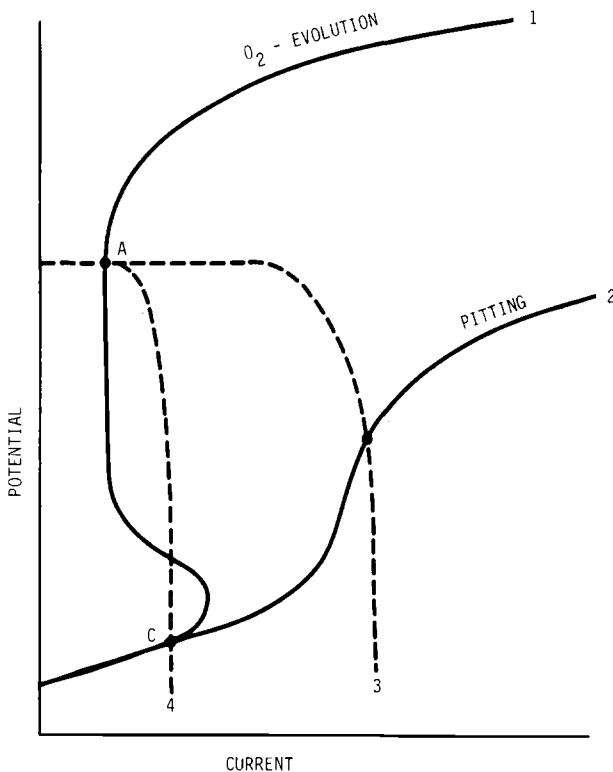
FIG. 11—Macrocircuit current flow for structures containing segmented reinforcing steel exposed to air, splash, and immersed zones in marine environment [53]. Note effect of water/cement ratio and region of cracking.

reduction in measured pH is the *cause* of corrosion, since the steel would no longer be passive. It appears to be more reasonable, however, that the restricted diffusion of oxygen and other reacting (and reacted) species in concrete aids significantly in the establishment of differential cells and thus in the separation of anodic and cathodic sites. The process can therefore be viewed as “auto-catalytic” in much the same way that restricted diffusion during pitting of stainless steels or copper alloys in chloride solutions is autocatalytic.

Escalante and co-workers [90] feel that pH control is of major importance. Once the chloride threshold level for corrosion initiation is exceeded, and provided oxygen is present, then microconcentration cells initiate the corrosion process. If the concrete then dries, the lower pH at the anodic sites is “frozen in”. Under further moisture/O₂ cycles, this lower pH makes it easier to reinitiate the corrosion of the steel. This appears to be intuitively correct, but the development of

macrocell action in later stages would seem to be the dominating damaging mechanism.

The formation of macroscopic cell action in concrete structures raises several questions regarding effective monitoring and protection against such corrosion. Firstly, it must be emphasized that, in general, it is the rate of corrosion which governs the extent of deterioration of a reinforced concrete structure. Secondly, it is the rate at specific locations which is important. In other words, an overall assessment of corrosion over a large structure by the use of individual "probes" may give an unrealistic measurement of true corrosion rate and hence rate of deterioration at specific locations. This point will be considered more carefully in later chapters of this report.



- 1: ANODIC POLARIZATION CURVE FOR STEEL IN CHLORIDE-FREE CONCRETE.
- 2: ANODIC POLARIZATION CURVE FOR STEEL IN CHLORIDE-CONTAINING CONCRETE.
- 3 & 4: CATHODIC POLARIZATION CURVES FOR O₂.

FIG. 12—Schematic polarization curves for iron oxidation (solid) and oxygen reduction (dashed) showing development of low potential active condition at low oxygen diffusion.

Low Potential Active Region

Mention must be made of the “low potential active region” for steel in concrete submerged in seawater. This has also been noted for fully immersed laboratory specimens [51]. Wilkins [54], in his summary of the proceedings of the Copenhagen symposium, has discussed this situation. It can be easily rationalized on the basis of the restricted supply of oxygen to a mixed electrode. Figure 12 shows the (probable) anodic polarization curves for steel in concrete. The restricted oxygen (diffusion-limited) line is shown to cross the curves at active but very low potentials—close to the reversible potential for Fe/Fe^{2+} at that pH.

To summarize the effects of different variables on the “propagation time” for corrosion of steel in concrete:

- Action of macrocells (separated anodes and cathodes) appears to be of prime importance.
- Rate of supply of oxygen to the cathodes is critical.
- There is a delicate balance between oxygen supply and concrete conductivity.

Future chapters will discuss how the factors involving the initiation and propagation stages are a function of the environment of a structure and how control of the process may be achieved.

Corrosion in Prestressed Structures

Up to this point, most attention has been paid to the corrosion of conventional reinforcing in concrete. Corrosion of pre-stressing materials in general is of somewhat different concern. Because of the generally high loadings in pre-stressing, particularly post-tensioning, it is not the production of corrosion product which is necessarily the most important aspect, but rather the possibilities that reduction in load-bearing cross section may lead to ultimate failure under the high loads carried by the pre-stressing (Fig. 13). As such, the comments relating to chloride-induced corrosion of conventional reinforcing steel also apply to pre-stressing steel, although the influence of macrocells may be much less important. On the other hand, an alternative potential mechanism of failure of pre-stressed concrete is unexpected brittle fracture of the pre-stressing material. This can either be due to the phenomenon of stress corrosion cracking, or of corrosion fatigue should the loading be of a cyclic nature. In general, post-tensioning is enclosed within structures in ducts which themselves are infiltrated with, for example, a wax moisture dispersant and corrosion preventative, or with cementitious grout. The ducts themselves should act to prevent possible ingress of chloride to the post-tensioning steel, although either perforation of the duct work or seepage around the ends of the duct work could lead to chloride ingress.

The stress corrosion behavior of steels used for pre-stressing or post-tensioning chloride solutions is relatively well known and documented [55]; the “normal” environment of the (chloride-free) concrete will not cause stress corrosion cracking of the steel, being too low in hydroxyl concentration and temperature to cause

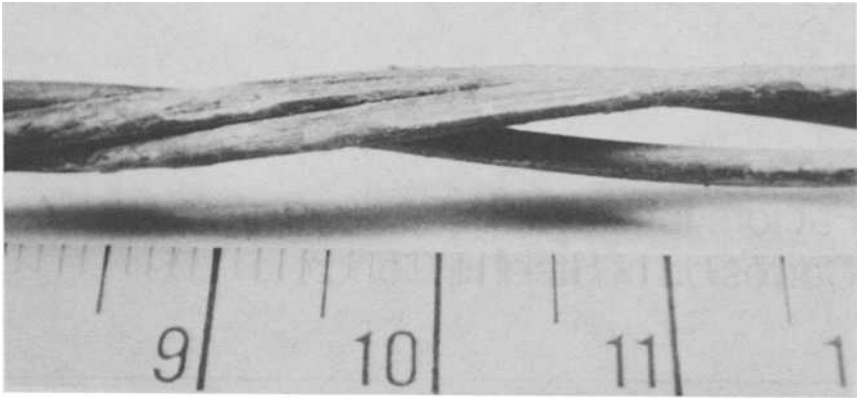


FIG. 13—Corrosion noted on unbonded post-tensioning strand following removal from building in Micronesia.

caustic cracking, and too low in chloride ion and high in pH to allow chloride stress corrosion cracking (SCC). Even in 3.5% NaCl, a pH above 11 raises the threshold stress intensity to high values. However, should the chloride content of the concrete rise sufficiently and the pH drop due to anodic activity, then problems might be anticipated.

Brachet [56] mentions but does not illustrate examples of SCC in pre-stressing steels. Monfore and Verbeck [57] and Cornet [58] describe various failure of pre-stressing steel in concrete, but all instances (except one by Cornet, apparently due to an H_2S problem) were due to corrosion reducing the load-bearing area. No failures were noted by Okada [59] in his survey. Thus problems encountered in pre-stressed concrete appear to be related to general corrosion and not to stress corrosion cracking, a supposition supported by information from Griess and Naus [60], who surveyed data from the nuclear industry where pre-stressed tendons are used in containment vessels. In several instances, pitting was noted where grease protection had failed. In the only case where hydrogen embrittlement was noted, both the humidity control in the pre-stressing ducts and the coating on the cables were found to be inadequate. While testing A416 steel pre-stressing wires, Griess found that for bare steel, cracking occurred in ammonium nitrate (NH_4NO_3) solutions above $38^\circ C$. No cracking occurred in *any* chloride solution, regardless of pH, but cracking was observed at $pH < 7$ in solutions containing H_2S . Portland cement grout coverage gave complete protection to the steel in these solutions, even when cracks 0.76 mm wide were present in the grout.

IV

Factors Influencing the Rate of Corrosion of Steel in Concrete

Previous chapters have discussed the major factors which apparently influence the initiation and propagation of corrosion of steel in concrete from a mechanistic viewpoint. These factors include pH, chloride level, oxygen level, and the presence or absence of possible macrocells. This chapter discusses how these parameters are affected in concrete structures and thus how corrosion rates are governed.

Nature of Environment

The nature of the environment which reinforcing experiences in concrete is more or less a function of the type of the structure. For example, a partially submerged reinforced concrete structure in the ocean will see a complete immersion zone, splash zone, and a salt-laden air zone. By analogy to the situation on steel structures exposed to the same type of environment, the most severe corrosion will occur in the splash zone, and it appears that the concrete-encased steel is no exception [61,62]. This is generally considered to be due to the wetting and drying environment, which allows rapid penetration of oxygen through to the steel. Additionally, it may be possible to increase the rate of penetration of salt to the steel surface by this mechanism when compared with the rate of the completely immersed zone. On this basis, Browne and Geoghegan [61] list the following factors that cause and control reinforcement corrosion in the splash zone:

1. Chloride levels exceeding 0.4% by weight of cement.
2. Quality of concrete and depth of cover above reinforcing steel [for example, a water/cement ratio of 0.7 and a cover depth of ~ 50.8 mm (~ 2 in.) give corrosion activation in six months].
3. The moisture level of the concrete, which affects both the resistivity of the concrete and its oxygen permeability, and thus the rate of corrosion once initiated [for example, a 25.4-mm (1-in.) cover, high permeability, partial drying give spalling in $2\frac{1}{2}$ years].

Under completely immersed conditions, oxygen can only be supplied under the action of diffusion through the water and then through the water-laden pores in the concrete. It is interesting to note here that, while very active potentials have been noted on continuously submerged steel, in general the rate of corrosion is quite low and no major problems have arisen [61]. As discussed earlier, this low potential with its apparently low corrosion rate is thus a direct effect of lack of supply of the cathodic reactant, oxygen, and the corrosion rate apparently is cathodically controlled. This position is also held by Sharp [62].

In bridges in marine environments on both the underside of the deck and on piers and pilings, and on the top side of a bridge deck subject to de-icing salt application, the situation is very similar to problems associated with the splash zone of the offshore marine structures. The "cycle" time of salt application to decks is much longer; corrosion can occur apparently quickly during the summer months when de-icing salt is not being applied, when rain and elevated temperature, with wetting and drying, provide the optimum environment for corrosion.

The data on bridge decks—for example, regarding the amount of chloride necessary to initiate corrosion—are in good agreement with those for marine structures. Van deVeer [63], summarizing results from 473 bridge decks, found that chloride levels of about 0.4% would initiate corrosion. From several studies of bridge decks in North America [64–69], clear correlations were obtained between:

- Depth of concrete cover and location of corrosion on deck as revealed by spalling, delamination, and active potentials.
- Onset of corrosion and depth of cover.
- Onset of corrosion and quality of concrete.

Typical results are shown in Fig. 14 [64]. The similarity between these findings, those on marine structures, and the results of laboratory experiments on large slabs is striking. It can therefore be assumed that essentially the same forces and mechanisms are operative.

Building Problems

While major attention has been given to marine structures and bridge decks in the literature, buildings have not been immune to the problem of chloride-induced corrosion. Peterson [70] presents an excellent review of such problems in parking structures, where the chloride originates from de-icing salt "tracked in" by tires and chloride-contaminated drip-water from vehicles (which form well-defined "drip lanes"). Figure 15 shows the distribution of chloride in a core taken from a floor slab in a 12-year-old parking garage. Peterson also states that not only is "conventional" reinforcement attacked but that several cases of severe post-tensioned steel corrosion have been observed. In some cases, Peterson continues,

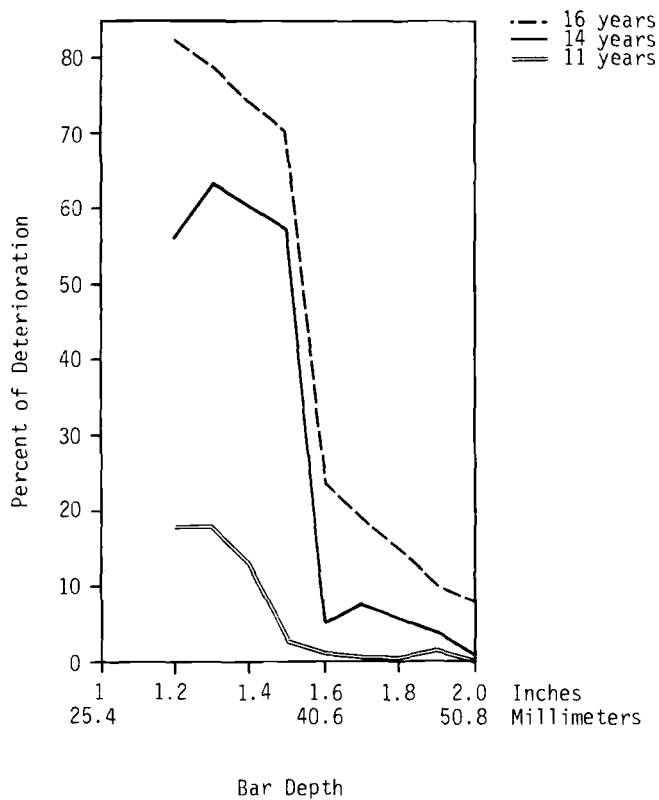


FIG. 14—Reinforcing bar depth in a bridge deck and its relation to the percentage of deterioration on the deck as a function of age [64].

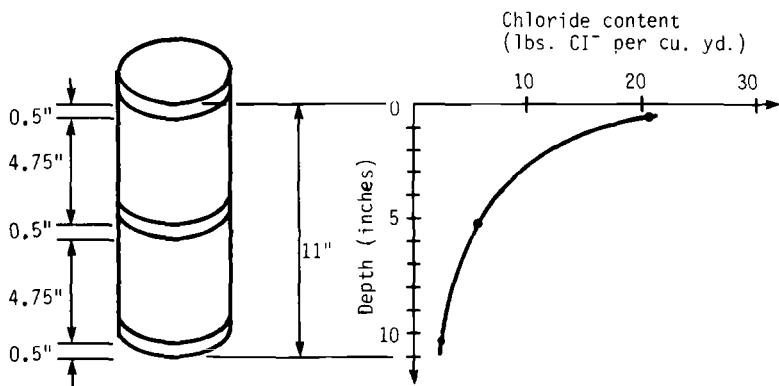


FIG. 15—Chloride ion distribution in core taken from 12-year-old flat slab in parking garage [70]. Note that Cl^- content is greater than threshold ($\sim 1 \text{ lb/yd}^3$) throughout.

only 25.4 mm (1 in.) of concrete overlays the tendon anchorages, and, since the tendon sheathing is discontinuous at these locations, severe corrosion is not to be unanticipated. Typical cracking resulting from tendon corrosion is shown in Fig. 16.

It is believed that problems in parking garages are compounded by two situations:

1. The "shielding" of the concrete from dry-out, which may place it in an almost optimum situation for both conductivity and oxygen transport.
2. Construction practice may be poorer in parking garages than in, say, bridge decks. Thus the water/cement ratio may be higher and the depth of cover lower [71].

In some locations, the use of chloride-containing water or aggregate in the original mix has ultimately led to severe reinforcement corrosion. Crooks [72]

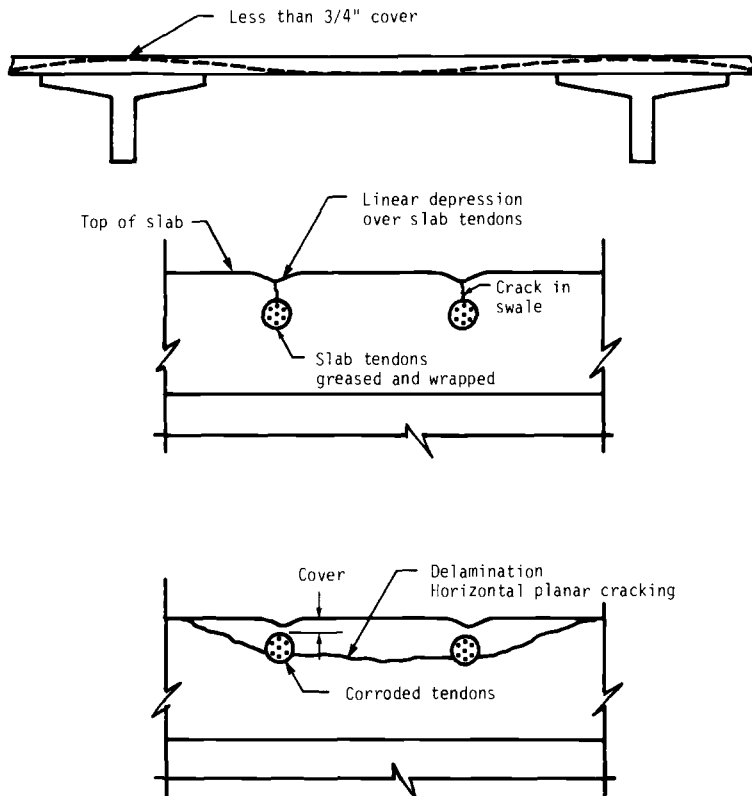


FIG. 16—Cracking pattern resulting from corrosion of post-tensioning strands in slab from parking garage [70].

describes problems with buildings constructed from concrete which incorporated mix chlorides from these sources. Severe cracking was observed in columns containing a mean of 0.57% of Cl^- three years after completion, whereas no such cracking was found on columns containing a mean of 0.21%. Concrete cover varied from 38.1 to roughly 76.2 mm (1.5 to 3 in.). The higher concentration is roughly 21 lb/yd³ of Cl^- , a very high concentration; connection between areas of different chloride levels could set up macrocell action to drive corrosion at the higher chloride locations.

Source of Chloride

This situation also brings into focus differences regarding the influence of chloride originally present in the mix of the concrete versus that which is applied to the surface of the concrete and which diffuses down to the rebar level after curing. This subject has been considered in some detail by Mehta [73]. Studies have been undertaken to determine the effect of salt-containing mix water, salt-containing sand or aggregate, or the influence of chloride-containing set accelerators (such as calcium chloride) on the corrosion of rebar. The basic conclusion appears to be that, up to a certain level, the concrete can tolerate and essentially "absorb" levels of chloride present during the curing process by incorporating this chloride into essentially insoluble compounds with the tricalcium aluminate present in the concrete. The amount of absorption is a function of the amount of C_3A in the concrete [74]; see Fig. 17. Note, however, the very high water/cement ratio used. Above a certain level, however, the chloride still apparently either prevents passivation of the reinforcing steel or can lead to breakdown of the reinforcement of passivity soon after pouring and curing. Shalon and Raphael [36] attribute this to a function of alkalinity; that is, the influence of the chloride is twofold, both breaking down the passive film and preventing its durability by reducing the alkalinity of the concrete. Possible leaching of chloride from chloride-containing constituents initially insoluble in the concrete has been mentioned previously. Presumably this can happen both with the $\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ complex and with any chloride-containing admixtures utilized for strength and plasticity.

Effects of Embedded Steel

Some concern has been expressed regarding a possible effect of embedded steel in accelerating the corrosion of "external" steel electrically connected to it by means of a "galvanic" couple, the embedded steel acting as a more noble (and large) cathode. This problem has been discussed by Miller and co-workers [75], who found high corrosion rates for the small anode and the large cathode combination. A comprehensive study has been undertaken by Arup [76]. He cites several instances of problems where this type of connection has been observed to cause problems. In all cases the apparent result is that the cathodic reaction of

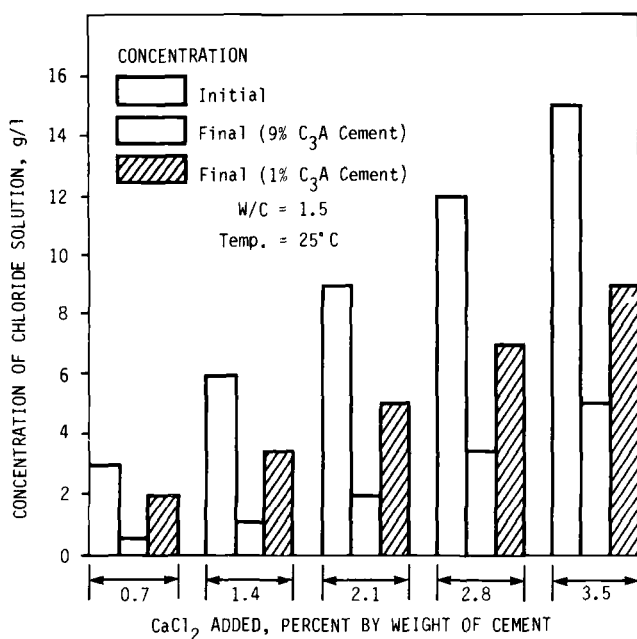


FIG. 17—Effect of C_3A content of cement on chloride level in aqueous phase of concrete [74].

oxygen reduction on the steel in the reinforced concrete drives the anodic reaction on the nonembedded steel, causing either accelerated corrosion or failure in a relatively short time. To obviate the problem, Arup suggests several procedures:

- Breaking the metallic contact (sometimes not feasible).
- Breaking the electrolytic contact (again, sometimes not feasible).
- Applying cathodic protection to the combined structure (in other words, all cathodic protection calculations must take into account the connection system).
 - Preventing oxygen from entering the concrete (possibly by sealing the surface using polymers, paints, etc.).
 - Decreasing the cathode-to-anode area ratio (sometimes only feasible in initial design).
 - Galvanizing the reinforcement. (This procedure will be discussed subsequently.)

The embedded/external steel problem is of particular concern in offshore structures, where care will certainly have to be taken should cathodic protection be implemented. In this regard, it is important to note that in hollow structures where oxygen can penetrate not only from the water side but also from the air (internal) side, a barrier coating can be applied to prevent oxygen ingress from this side. Experiments of this type have also been described by Arup.

Stray Current

The problems of stray current insofar as it affects corrosion of reinforcing steel has not been covered widely. Miller and co-workers [75] have discussed both the practical and theoretical approaches to this problem. It appears that care must be taken whenever a cathodically protected system is joined to rebar which is not directly attached to a ground bed. In this case, should there be significant quantities of chloride in the concrete, severe corrosion of the reinforcing steel could occur. In the absence of the chloride, however, it is not envisaged that any such action would be found. So far as cathodic protection of reinforcing steel in concrete is concerned, this is now a relatively common occurrence on certain types of structures and is being evaluated for others. It is clearly a very helpful technique in preventing further chloride-induced corrosion and has been the subject of significant research, which will be considered later.

Fouling

Fouling is an important consideration in any marine structure. To this end, some attempts have been made to incorporate copper compounds in concrete mixes used in marine environments [77]. While no evidence to date has been noted regarding possible problems associated with the use of this type of material, the presence of cupric ion close to steel must always be considered to be problematical because of the large difference in potential and hence the action of galvanic cells which can be induced. In the absence of chloride, however, this is not expected to be particularly detrimental, because of the pH in the region of the reinforcing steel. No problems have reportedly been encountered; however, the antifouling activity of all the additions tried was only marginal.

Noble Metal Coupling

The effect of noble metal coupling has also been raised regarding the use of copper grounding rods connected to tendons in reactor pressure vessels; again, in chloride-free concrete, this should not create any problems. On the other hand, chloride effects on corrosion of reinforcement can lead to conditions where the pH drops significantly. Under these circumstances, cupric ion and copper attachments could be a severe accelerant to the corrosion process on the reinforcing steel. It is possible that this subject is worthy of further attention.

Bacterial Action

Some effects of bacterial action on corrosion of the cementitious material of concrete — in other words, degradation of the concrete per se — have been noted. These will have an influence on corrosion of the reinforcing steel only insofar as they effectively decrease the amount of the cover present. Anaerobic bacteria may also aid in the formation of differential aeration cells; however, it is not believed that significant information exists in this area.

Stress Effects

In the area of stress effects on corrosion of steel in concrete, it is worth noting that there is apparently little influence of stress on the actual corrosion rate of steel—a factor that has been determined by many workers. The effect of stress causing “new” methods of attack (for example, stress corrosion cracking or corrosion fatigue) has been considered previously, and work on the situation as regards coated rebar will be covered later. If the reinforced concrete is subjected to cyclic stress, it is quite feasible there will be a significant increase in cracking of the concrete. Under these circumstances, accelerated corrosion of the reinforcing steel could be anticipated at the bottom of the widened cracks due to the decrease in pH from carbonation and also from ingress of salt and other contaminants down the crack.

V

Measurement of Deterioration

It is obviously important to be able to quantify the status of deterioration of a reinforced concrete structure during its lifetime, to assess the need for repair, to assess the performance of protection mechanisms in existence, and to assess the need for application of protection methods. The study of mechanistic phenomena, or of proposed ameliorative measures, in the laboratory likewise requires measurement techniques. An array of methods are available, ranging from the very mundane to the highly sophisticated; several of these are of practical use only in the laboratory at this particular stage, but do offer promise for field use in later stages. Further, most of the currently available techniques have been developed for highway structures, and only some of them have been transferred over into other areas.

Visual and Sonic Techniques

The first visible sign of reinforcing steel distress in a conventional reinforced concrete structure is frequently the appearance of rust-staining on the surface. Obviously, this only occurs where the surface can be visually examined. A later "visual" stage occurs where cracks which may have developed subsurface reach the surface and spalling of the concrete ultimately ensues. At an earlier stage it is possible to assess damage due to internal cracking by using a "sounding" technique involving chain drag or striking of the surface with a hammer, or alternatively by using an ultrasonic reflective method to determine the presence of subsurface delaminations [78]. This technique is obviously useful on the upper surfaces of bridge decks, but it also has utility on vertical surfaces, and the ultrasonic technique may be modified so as to be of value even on submerged surfaces.

Chloride Ion Monitoring

A less direct technique involves the use of chloride ion concentration measurements on the concrete. Because of the clear role of chloride in initiating corrosion of the steel, this technique has been in common use both in the laboratory (see, for example, Ref 40) and the field (see, for example, Ref 66).

The technique has some disadvantages. It is a "spot" technique which has difficulty in monitoring the range over an entire structure. Additionally, since other factors influence corrosion besides the quantity of the chloride ion in the concrete (such as oxygen availability), it can only be used essentially as an "early-warning system" and not as a definite locator of corrosion.

Most of the techniques evolved entail sampling of the concrete above and around the reinforcing steel: generally by coring, slicing the core as necessary, grinding, dissolving in either nitric acid or in water (depending on whether a water soluble or a total chloride determination is required), and then conducting either an electrometric or a conventional titration against silver nitrate solution to determine the chloride level. Research on the optimum method of determining chloride by these techniques has been ongoing at FHWA and other laboratories, and several publications are available which discuss the advantages and disadvantages of different methods [79,80].

Some research has recently been undertaken on using portable neutron activation analysis techniques to conduct scans of the structure for chloride content [81]. The equipment is bulky, however, and difficult to use, and is only appropriate at this stage for horizontal surfaces.

Electrochemical Methods

The use of electrochemical methods for assessing the state of corrosion of reinforcing steel has derived directly from, for example, the use of potential measurements to assess corrosion of buried pipelines and the use of electrochemical measurements in other corrosion situations where visual inspection etc. is not readily available. It is possible to split the techniques currently used into three areas: potential techniques, electrical resistance techniques, and electrochemical techniques involving polarization resistance and impedance. Summaries of these techniques have been provided by Vassie [82] and by Slater [83].

Potential Measurements

The relatively low conductivity of concrete, even when it is contaminated with chloride, and the fact that macrocell action is involved in the corrosion process, have allowed the use of potential measurement on the top surface of the concrete to delineate anodic and cathodic areas of the reinforcing steel. This technique, pioneered by Stratfull and co-workers at the Caltrans Laboratories in Sacramento [84], has been widely used by others since its inception, and has been applied to structures such as buildings, piers, offshore structures, etc., besides the bridge decks for which it was originally used. The technique has become so popular that it is now the subject of ASTM Test for Half Cell Potentials of Reinforcing Steel in Concrete (C 876). The equipment used to make these measurements is shown in Fig. 18; a typical potential contour map is shown in Fig. 19.

Some difficulties associated with the potential measurement technique are as follows:

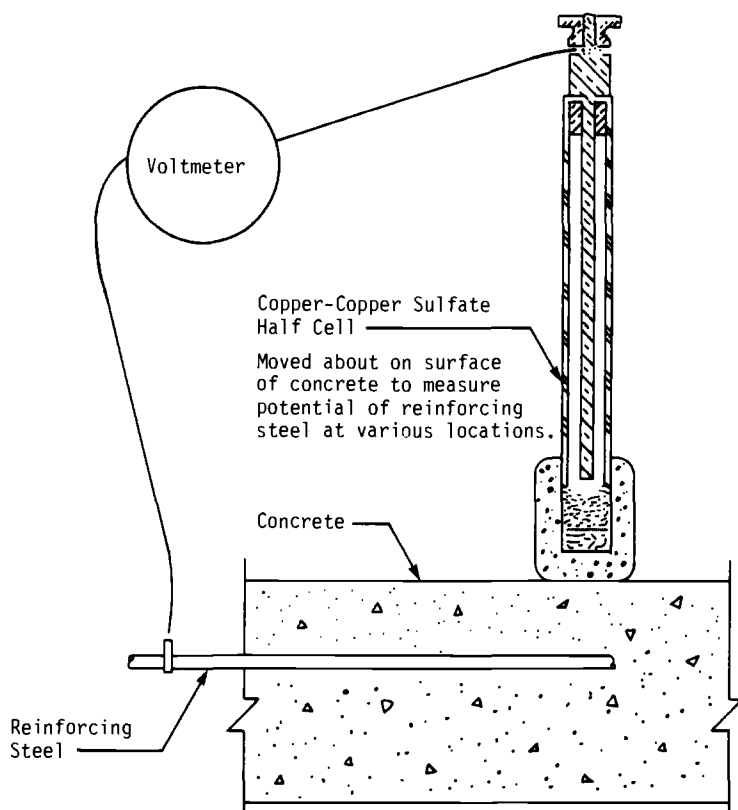


FIG. 18—Equipment used for measuring half-cell potentials of steel in concrete (in accordance with ASTM C 876).

- It is difficult to use when a dielectric layer or high-resistance layer, such as a membrane or an asphalt wearing course, is present on the concrete surface.
- It is difficult to use as a monitoring technique in cathodic protection systems because of the frequent presence of asphalt-wearing course and the (anode) coke breeze layer on the surface of the concrete in system installations.
- The interpretation of potential measurements on structures containing metal-coated or epoxy-coated steel is still uncertain.

Some fundamental problems also exist with the potential measurement technique. Firstly, just because a number is obtained from the high-impedance voltmeter used to make the readings, it should not be considered that this number represents anything regarding a rate measurement. It is exceedingly difficult, if not impossible, to assign any *rate* of corrosion to a given potential, except in a very qualitative sense. Secondly, the development of the potential is still not completely understood. By this it is meant that little critical laboratory work has been done to confirm the effects of coupling active and passive reinforcing steel

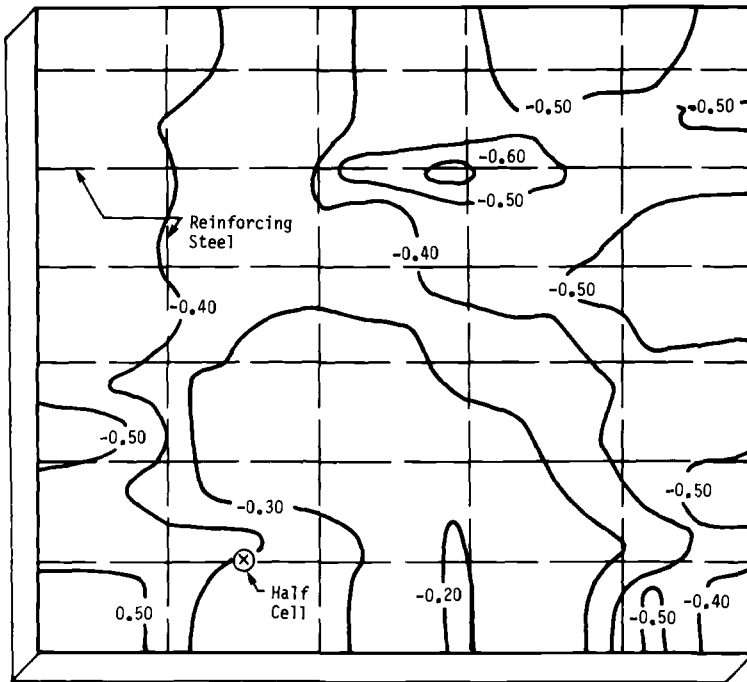


FIG. 19—Typical “potential contour map” for structure containing reinforcing steel.

in concrete under different conditions of oxygen level, chloride level, and moisture level of the concrete. In other words, while potential measurement to delineate active areas on a reinforced concrete structure depends for its usefulness on the fact that separate anodic and cathodic sites occur in a reinforced concrete structure, the laboratory correlations to quantify the effects of these actions, and in particular to separate the effects of macrocell versus microcell action, have not been performed. Such effects therefore are inadequately understood.

Notwithstanding these difficulties of use and interpretation, the potential measurement technique has proved useful and reliable as a means of delineating the corrosion activity on a reinforced concrete structure, particularly when used with other nondestructive or semidestructive techniques. These include coring for cover depth and chloride level determination, and ultrasonic delamination detection.

Electrical Resistance Methods

The changing resistance of a sensing element as corrosion reduces the cross section has been used for some time as a valuable method of determining rate of corrosion in many environments. It was first used as a practical tool by Dravnieks and Caraldi [85]. The application of this technique to corrosion of steel in concrete, and the modifications necessary for practical use, have only recently been addressed; they are described in a paper by Kelsden [86]. A schematic of

a typical installation is shown in Fig. 20. The major advantage of the electrical resistance method is that time-dependent changes in the *rate* of corrosion can be determined. From this point of view, the method has significant advantages over the potential measurement technique, but it also has some fairly significant disadvantages. For example, the electrical resistance method can only give an assessment of the corrosivity of the environment, and the rate of corrosion to be expected, at the particular location where the probe is situated. Because of the wide expanse of most reinforced concrete structures and the different conditions throughout the structure, extrapolation of this value to the rest of the steel in the structure can be difficult. Secondly, the probe introduced into the concrete is generally not in the same state as the rebar on introduction into the concrete; rebar is generally not pre-treated and has both mill-scale and rust on the surface. These surface conditions will be expected to influence at least in the early stages the corrosion behavior of the reinforcing steel. Therefore it may be difficult to interpolate directly between the corrosion rate as determined by the electrical resistance probe and that which is actually pertaining on the reinforcing steel in the vicinity of the probe. The fact that the corrosion of reinforcing steel in concrete is radically affected by galvanic action between active and passive steel means that the probe must be tied into the reinforcing steel electrically if adequate comparisons are to be made. Alternatively, the probe may be isolated electrically from the rest of the reinforcing steel; in this case, the probe assesses the self-corrosion rate at that particular location, and not the total self-corrosion plus galvanic corrosion rate.

A further problem arises when probes are to be placed in already constructed structures, because the environment of concrete is selective and always difficult to duplicate. Thus, when a probe is inserted into concrete which has been cured for some time, and which contains a certain amount of chloride, it is difficult to surround the probe with concrete adequately duplicating that which has been removed. For this reason, electrical resistance probes are difficult to use in already constructed structures. For new construction, of course, this constraint does not apply. Several probes must be placed in new construction at various locations, however, if an adequate sampling of differing conditions across the structure is to be accomplished.

The electrical resistance probe has been used successfully to monitor the effectiveness of corrosion prevention methods, even in old decks. The probe can be placed into the deck immediately before the application of a membrane or cathodic protection system [87]. If the environment around the probe is made adequately corrosive, so that corrosion will occur, and the probe is also tied electrically to the rest of the reinforcing steel, then the effectiveness of these ameliorative measures can be judged by monitoring the change in resistance of the probe.

We may summarize these particular comments by saying that the resistance probe technique has difficulties in use compared with the potential measurement

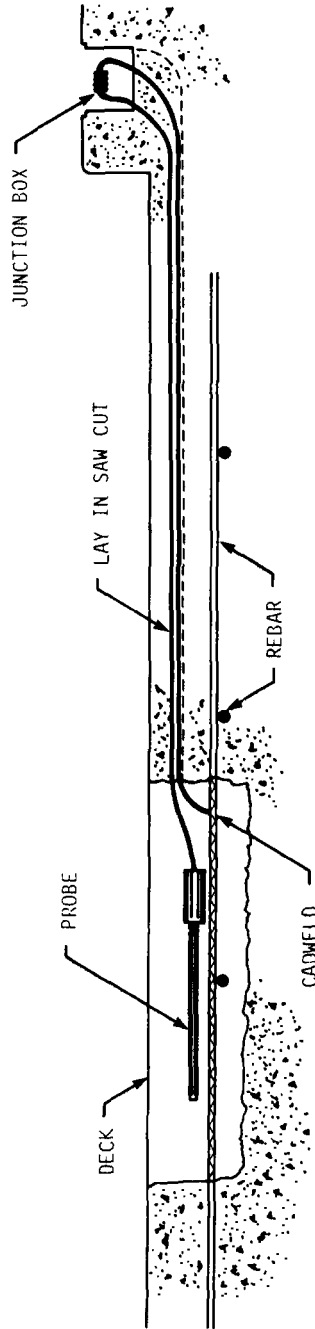


FIG. 20—Typical installation of electrical resistance probe in reinforced concrete structure.

technique. The two techniques can be viewed as complementary, however, and where one is difficult to use, the other frequently can be used with success.

Polarization Resistance Method

The polarization resistance method (or "linear polarization" method as it is frequently and unfortunately called) has been used successfully as a corrosion monitoring technique in many process industries and in many environments. So far, however, it has not enjoyed any in-field use as a measurement technique for corrosion of steel in concrete except under extremely experimental conditions.

The well-known Stern-Geary equation [88] relates the corrosion rate to the slope of the polarization curve at the free-corrosion potential as follows:

$$i_{\text{corr}} = K \frac{di}{dE} \frac{\beta_a \beta_c}{\beta_a + \beta_c}$$

where

di/dE = slope of polarization curve at $i = 0$,

β_a, β_c = anodic and cathodic Tafel coefficients, respectively, and

K = constant dependent on material, temperature, and other parameters.

Note that this equation, and thus the polarization resistance technique, *only* applies at the free-corrosion potential; that is, where $i = 0$.

Either two-electrode or three-electrode systems can be used to monitor the corrosion rate of the material/environment couple in question.

Location problems exist with a polarization resistance setup in concrete, just as for the electrical resistance probe. A small probe can be placed in the reinforced concrete structure at any desired location, but the backfill again is critical for adequate extrapolation of results to the adjacent reinforcing steel. Alternatively, linear polarization electrodes can be fabricated from the rebar in place without unduly disturbing the concrete surrounding the reinforcing steel. This has been accomplished on a trial basis with somewhat encouraging results.

Probably the major problems associated with the use of polarization resistance techniques for assessing the corrosion of steel in concrete are the high resistance of the electrolyte and the existence of macrocell action. The high resistance of the electrolyte can be overcome by using IR-drop compensation techniques; this is probably most easily accomplished using the three-electrode technique. A more serious problem is the simple fact that the polarization resistance technique only works for an unpolarized (freely corroding) system. The presence of macrocell (galvanic) action means that the corroding reinforcing steel is polarized away from its normal free-corrosion potential. Thus considerable doubt exists as to whether the technique of polarization resistance is applicable when the electrodes are tied into the standard reinforcing steel in the structure. A similar constraint exists when cathodic protection is applied to the reinforcing steel.

Where macrocell action is not a problem—that is, on short electrodes which are themselves *totally* the polarization resistance circuit—good agreement is registered for corrosion of steel, coated and uncoated, in mortar; see Fig. 21 [89]. With gravimetric measurements, Escalante et al are currently investigating the polarization resistance techniques for use as a nondestructive method for measuring corrosion rates on real structures. A summary report of this work is available [90]. Again, however, caution must be exercised in using this technique on an electrode polarized away from its free-corrosion potential (that is, where macrocells are operating).

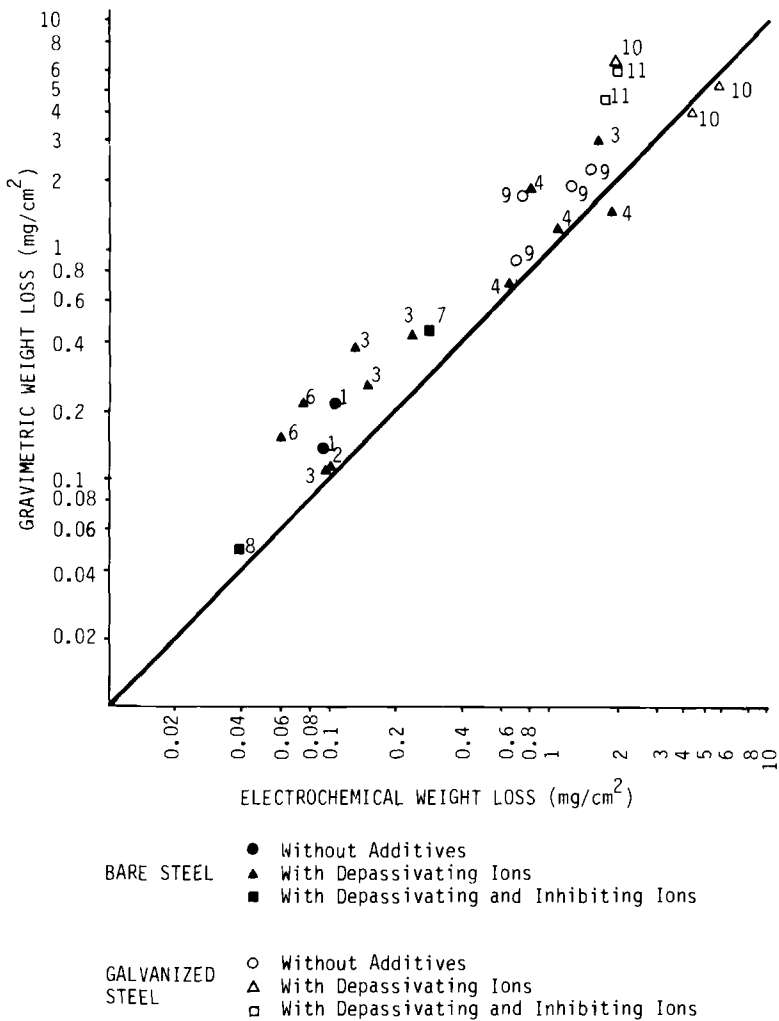


FIG. 21—Comparison between gravimetric weight loss and weight loss calculated from polarization resistance data for various steels in mortars [89].

Rosenberg and Gaidis have shown a linear relationship between corrosion current calculated from polarization resistance measurements and the free corrosion potential of the steel. This work was conducted on single-bar electrodes. Results are shown in Fig. 22 [91].

Locke and Siman [92] have used the three-electrode polarization resistance technique in a laboratory investigation of the effects of chloride content of

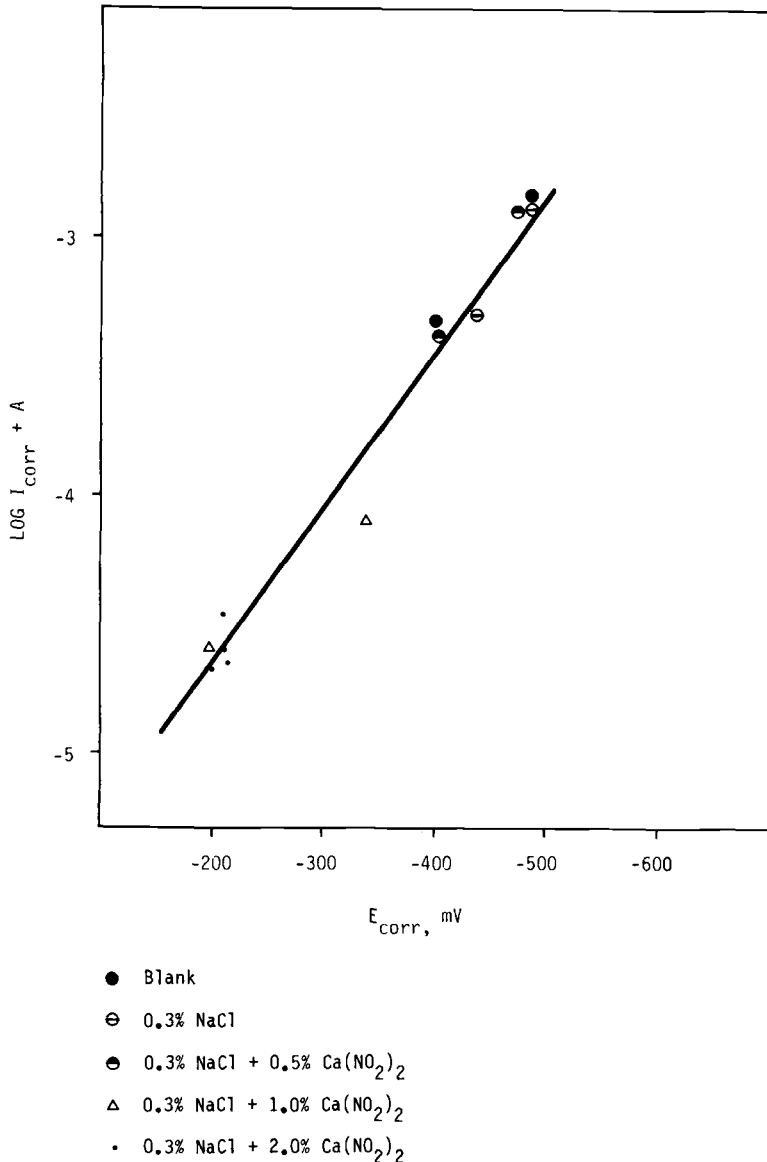


FIG. 22—Correlation between corrosion current measured by polarization resistance and free corrosion potential of steel in concrete as affected by additives to concrete [91].

concrete and surface coating of steel on corrosion. Problems arose with IR compensation at higher corrosion currents; additionally, agreement between the laboratory equipment and a commercial instrument was poor. Interestingly, data showed that the corrosion rate increased with increasing chloride content once the threshold value was exceeded. This may be a result of the combination of the increased conductivity on increased corrosion rate per se and on decreasing the IR component.

Since the polarization resistance technique is so sensitive to macrocell action, the only alternative to this particular problem is to isolate the steel of the polarization resistance cell from the reinforcing steel; in this case, the polarization resistance cell merely measures the self-corrosion rate, irrespective of any galvanic cell action. In certain circumstances this may be a most useful distinction and may allow the polarization and electrical resistance techniques to be used simultaneously to separate the microcell and macrocell action.

Macrocell Current Measurement Techniques

The measurement of current flowing externally between electrically isolated parts of simulated bridge-deck slabs containing repair areas, and between small "lollipop" specimens, has been described by Boyd et al [51] and been used by FHWA workers [52]. The technique has good applicability to laboratory situations where such internal isolation can be established in experimental protocol; in these circumstances, effects of chloride ion and oxygen concentration cells and the parameters which affect them can be readily established. For two reasons, difficulties arise when average corrosion rates are computed based on current flow:

- The actual corroding area on the total anode may be a small fraction of the available surface.
- Microcell action may be occurring on the overall anode itself.

Nevertheless, the technique holds promise for laboratory investigation, particularly since macrocell action is such a vital part of the total corrosion process of embedded steel in concrete.

Impedance Techniques

As previously mentioned, difficulties with the polarization resistance technique involve the high resistance of the concrete. One solution to this problem is to use electrical impedance measurements. The first attempt to do this was reported in 1978 by Dawson et al [93]. These workers showed that this method is in principle useful for monitoring corrosion rates of steel in concrete, although its major attraction appears to be as a research tool (for example, for studying the initial passivation or possible time to breakdown of the passive film) as distinct from practically monitoring the deterioration onset and severity with time in an actual reinforced concrete structure.

Mechanical Methods

The measurement of the stresses developed in reinforced concrete as a result of corrosion of the reinforcing steel was discussed earlier [16]. It would appear that such a measurement may be useful in assessing the stresses built up in concrete due to the corrosion of reinforcing steel in an actual structure. Again, however, in common with many systems, all stresses will basically be localized in the area where active corrosion begins, and it is not always easy to pin-point these, at least before the fact. Nevertheless, this technique could be useful and it deserves further attention.

Summary

The foregoing discussion regarding the types of measurement and monitoring techniques available shows that some are more suited to research and development activities, or at least to laboratory studies, than to actual structures. Certainly, the electrochemical techniques currently in use are only in the formative phases. A review of this topic indicates clearly that the only presently feasible means of assessing corrosion damage on an existing structure are by potential measurement and by other sonic or visual methods. Sampling of chloride levels is a useful adjunct, but is not for solitary use.

VI

Fatigue of Reinforced Concrete and Influence of Environment

The fatigue performance of reinforcing bars in concrete has lately been the subject of renewed study. The reasons for this greater interest are the use of increasingly severe loading cycles and a realization that the reinforcing steel may be affected by the environment in which the concrete is placed.

Several studies are of interest here. The general subject of fatigue of reinforced concrete, from the viewpoint of the bars themselves, has been reviewed recently by Tilly [94], who concentrates on British/European steels and construction practice. Differences in the fatigue behavior of different steels have been studied by Browne and Domone (Fig. 23) [95]. Sharp [62] also includes a summary of fatigue as it relates to concrete reinforcement used in the ocean.

Most available data indicate that the fatigue strength of unclad reinforcement is sharply reduced when the bars are tested in seawater rather than in air. Additionally, cladding the bars with approximately 25.4 mm (1 in.) of cover and testing in seawater led to approximately the same fatigue behavior as for the unclad situation (Fig. 24) [96]. Of course, these data pertain to *continuous*

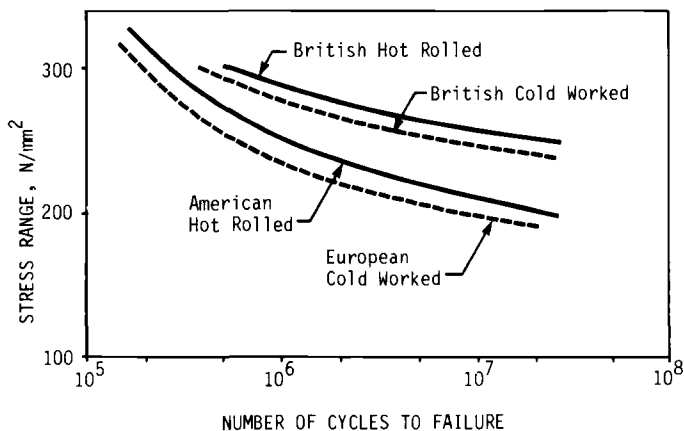


FIG. 23—Differences in fatigue behavior between reinforcing steels [95].

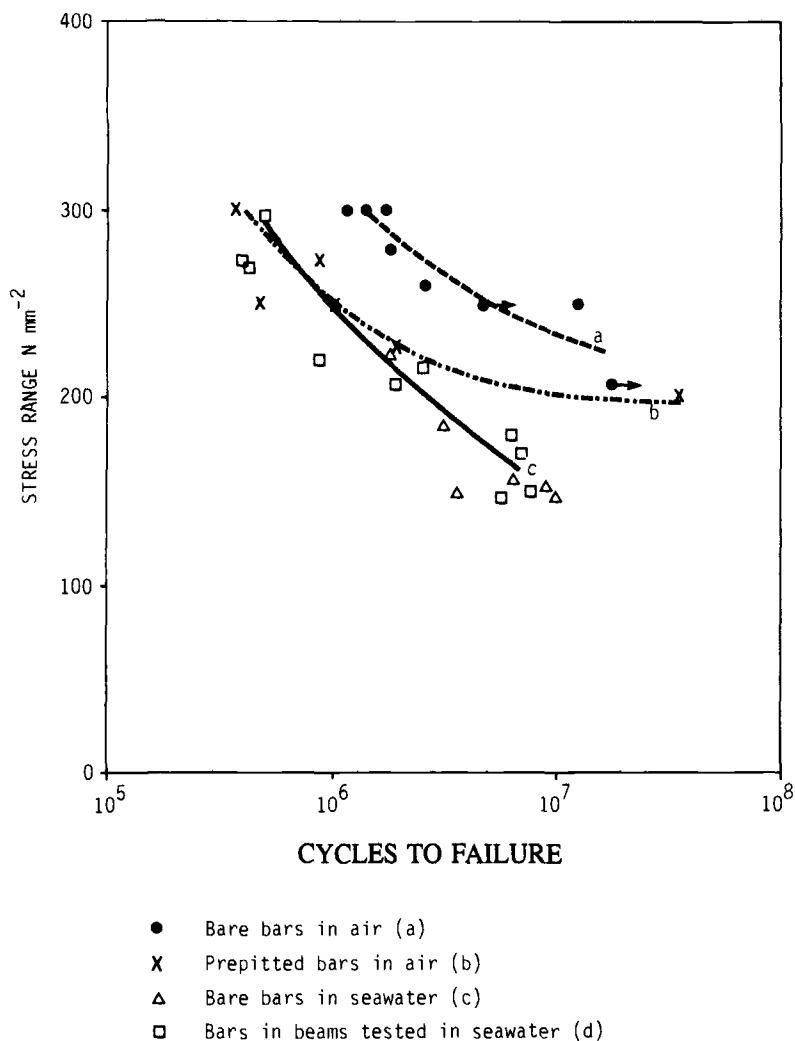


FIG. 24—S/N curves for reinforcing steel in different environments [96].

immersion in seawater, though the accelerated corrosion effects of a splash zone or bridge deck wet/dry environment may be severe.

The effect of frequency is an important variable. Not only has frequency a known severe effect on crack propagation rates in corrosion fatigue but, in addition, different structures will have different frequencies of stress application. Wave action, for example, important for offshore structures, has a frequency of ~ 0.1 Hz, whereas a bridge deck will probably be subjected to higher frequency excitation. Recognizing this problem, Okamura and Hisamatsu have [97] conducted fatigue tests at 3 Hz on reinforced concrete beams in air and seawater. Results are shown in Fig. 25. The low frequency and seawater environment have

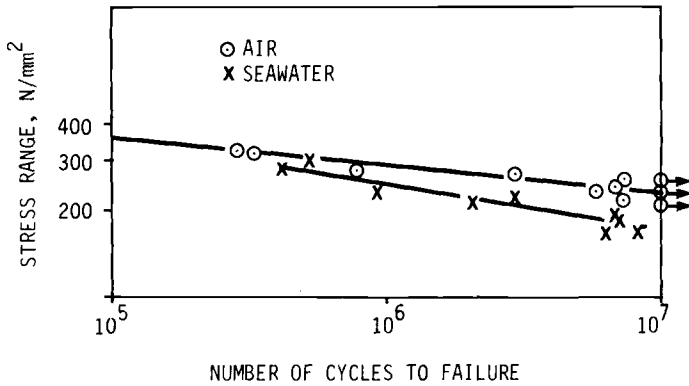


FIG. 25—Fatigue of reinforced concrete beams at 3 Hz and seawater [97].

an increasingly deleterious effect as the stress decreases and, more importantly, as the time for chloride-induced corrosion increases.

When reinforced concrete prisms tested in fatigue break, they fail at cracks in the concrete. Since most concrete, as cured, contains such cracks and more cracks may develop under load, and since the environment can reach the steel more rapidly down a crack, this can be a deleterious phenomenon. Peterson [98], however, indicates that such cracks become filled with deposit, at least during testing in seawater, which leads to “cyclic stiffening” of the specimen. Such blocking may preclude severe corrosion damage at the crack tip, but the data are scanty.

This brief review indicates that, although data on the effects of environment on fatigue of reinforced concrete are scarce, the subject continues to be of importance and interest.

VII

Protection Methods

As the nature and severity of the problem of chloride-induced deterioration of reinforcing steel in concrete have often been studied, it is not surprising that considerable research and development have been undertaken into ameliorative methods. These methods should either prevent the problem of corrosion of steel during initial design and installation, or, conversely, allow efficient repair or rehabilitation procedures which will extend the life of a structure that is deteriorating due to corrosion of reinforcing steel.

There are three basic types of protection techniques:

- Changing the environment around the reinforcing steel, either by decreasing the amount of chloride reaching the reinforcing steel to a value low enough to retard or prevent severe corrosion, or (by using admixtures to the concrete) to essentially increase the concentration of chloride necessary to initiate corrosion.
- Changing the nature of the rebar surface so as to be resistant to corrosion, either by surface treatment or by bulk alloying.
- Changing the electrochemical nature of the surface or the rebar by impressed current (cathodic protection).

Concrete Modifications

Quality, Cover, and Water/Cement Ratio

We now turn to portland cement containing conventional reinforcing steel. Significant additional life of a reinforced concrete structure subjected to salt ingress can be obtained during initial placement by:

- Ensuring the water/cement ratio is within specification and as low as possible.
- Ensuring good consolidation.
- Maintaining adequate cover, or depth of concrete, above the reinforcing steel.

The evidence for these statements and the mechanistic basis from which they come has been discussed earlier. The intimate relation between depth of cover and permeability of concrete is involved with the diffusion of chloride and oxygen to the steel. On the basis of measured diffusivities, and on the level of chloride necessary to depassivate steel, Browne and Domone [95] calculate that, to achieve a life of 50 years based on nonactivation of the reinforcement, a splash-zone concrete with a water/cement ratio of 0.40 and a concrete cover of 50.8 mm (2 in.) are needed.

The subject of concrete quality and cover where corrosion may be a problem has also been discussed by the American Concrete Institute (ACI) [99]. For concrete exposed to sea or brackish water, ACI recommends a water/cement ratio of 0.40; should workability preclude this, a ratio of 0.45 may be used, provided the thickness of cover is increased by 12.7 mm (0.5 in.). While the rationale for this is qualitatively reasonable, it is quantitatively vague. So far as cover is concerned, ACI recommends 76.2 mm (3 in.) in a splash zone area and 50.8 mm (2 in.) on bridge decks, although again the quantitative rationale is missing. Since these are minimum values, and because of the variability of the concrete cover, a specified cover of 66.0 mm (2.6 in.) should be used to ensure 90 to 95% coverage of at least 50.8 mm (2 in.). Weed [100] maintains that 79.4 mm (3½ in.) should be specified.

Walker [101], on the basis of this knowledge applied to the area of parking garages, suggests the following guidelines:

- Concrete with water/cement ratio < 0.45; six-sack mix.
- Eliminate flexure and shrinkage cracks.
- Minimum cover of 25.4 mm (1 in.); 38.1 mm (1½ in.) preferred.

Thus there are distinct discrepancies between his suggestion and that of ACI.

These data have been based on uncracked concrete which, of course, can be thought of as a laboratory curiosity; the vast majority of reinforced concrete structures contains cracks. Accordingly, attention has been paid to minimizing the size and extent of cracks in concrete. Recent requirements from the Comité Euro-International du Béton (CEB), quoted by Beeby [43], are shown in Table 2. As Beeby points out, however, there is a severe lack of information regarding influence of crack width on corrosion of reinforcing steel, and this point needs further work.

The cover needed on reinforced concrete has two functions that are of interest here: to resist penetration of chloride and to resist the expansion force of corrosion product. Corderoy et al [102] found that the time to first rust-staining of concrete varied with bar size; thus, at a cover of ~25.4 mm (~1 in.), a 20-mm bar gave staining at 15 weeks, whereas a 16-mm bar gave staining at 5 weeks. However, these covers are less than might be expected in good-quality construction. Data from Houston et al [103] indicate that large cover/rebar diameter ratios lead to

increased resistance to cracking and spalling. Therefore it still appears that adequate cover is the important parameter.

Some discussion has previously been given to the addition of set accelerants or chloride otherwise introduced into the mix to the concrete and their role in promoting corrosion of reinforcing steel. The American Concrete Institute has suggested limits for Cl in concrete (Table 3) [99] with the following caveat: "The user should exercise good judgment in applying these limits, keeping in mind that other factors (moisture and oxygen) are always necessary for corrosion." Thus, where corrosion is of major concern, no intentionally added chloride should be used. Current European convention appears to be to limit the use of chloride-containing additive agents to reinforced concrete.

Increasing Impermeability of Concrete

While control of mix design and placement approach is certainly a desirable first step, other approaches may also be taken to increase the impermeability of the concrete, either during original construction of the structure or after some service life. These approaches include (1) the use of latex-modified concretes and (2) extremely low water/cement ratio as overlays or "top coats". Both of these techniques are useful in slowing down the apparent ingress of chloride (and possibly also of oxygen). Data from Ohio State University [104], however, have recently shown that, at least for the latex-modified concrete, simply a retardation effect and not a complete barrier exists. Based on a study of 132 bridge decks, it is suggested that the use of a latex-modified overlay can increase the typical existing deck life by approximately 10 years, and if used on new deck surfaces, approximately 15 years of useful extra life can be expected. The use of very low (around 0.32) water/cement ratio concrete, with adequate air entrainment, as overlays on bridge decks had been pioneered in Iowa and Kansas [105]. Good success has been obtained with this technique, both in preventing further chloride ingress and, apparently, in stifling any existing corrosion or allowing corrosion to initiate.

Other methods have been used in the attempt to make concrete more impermeable. These have included experiments on wax bead impregnation in the

TABLE 3—Suggested maximum water-soluble chloride levels in concrete mix (prior to service) for different reinforced concrete exposures, expressed as weight percent of cement [99].

1. Prestressed concrete	0.06%
2. Conventionally reinforced concrete in a moist environment and exposed to chloride	0.10%
3. Conventionally reinforced concrete in a moist environment but not exposed to chloride (includes locations where the concrete will be occasionally wetted, such as kitchens, parking garages, waterfront structures, and areas with potential moisture condensation)	0.15%
4. Above-ground building construction where the concrete will stay dry	no limit for corrosion

original concrete mix: after placement, the structure is heated and the wax melts, thereby apparently coating the pores of the concrete with a hydrophobic wax. Several decks have been poured with this technique and implementation techniques are available [28]. The major drawback appears to be the technique of heating. Since large structures can generally only be heated in segments at a time, the differential heating and thermal expansion can cause severe cracking of the concrete; as previously discussed, the rebar can be exposed significantly and corrosion can result. Further cracking during loading can also be expected. Flick and Lloyd [106] have shown that for cracked, internally sealed concrete beams subjected to a *static* load, the rebar potential remains in the passive region, whereas for dynamically loaded cracked beams it rapidly moves into the active region. However, no work was done in their investigation to correlate potential measurements with *extent* of corrosion; thus the ability of cracked, internally sealed structures to maintain reinforcing in the uncorroded state awaits further field evaluation.

A subject of recent interest is the impregnation of the surface of concrete bridge decks with linseed oil [107], methyl methacrylate, and other polymers applied as the monomer and polymerized in place [108] and the placement of either liquid (epoxy base) or sheet-type (generally asphalt base) membranes [109] on the surface. The object of these procedures is to prevent ingress of chloride and possibly also to prevent ingress of oxygen as the cathodic reactant. Linseed oil treatments penetrated approximately 1.27 mm (0.05 in.) into the concrete, and ponded salt water took 2.5 days to penetrate 9.5 mm ($\frac{3}{8}$ in.). Thus the treatment is palliative in that it somewhat retards the penetration of chloride into the concrete (no coating gave penetration in 3 h).

Other treatments have been developed based on silane. This creates a hydrophobic layer in the surface concrete pores, apparently preventing water penetration but allowing vapor-phase diffusion. Techniques have also been developed for impregnating an existing horizontal concrete surface to a depth of 25.4 mm (1 in.) with methyl methacrylate monomers and then heating to polymerization. Problems with heating are similar to those of the wax-bead process: cracking may occur both during dry-out of the surface (to allow impregnation) and during curing. Tests show that the polymer concrete is quite impermeable to chloride intrusion; it would therefore function well as a sealant on new bridge decks. Effects of impregnating bridge decks already containing above-threshold values of chloride are, however, not known insofar as continuation or initiation of corrosion is concerned. Oxygen transfer and moisture ingress should be restricted from the top surface, but bottom surface induction may occur. Complete encapsulation of the rebar mat, such as can occur during placement of portland cement during repair, would certainly be advantageous.

The State of Vermont has conducted a significant series of experiments with membranes placed on bridge decks. Problems and performance are summarized in Table 4. Typical problems include blistering, poor curb sealing, and pinholing leading to subsequent intrusion of moisture. One of the mechanistic problems

TABLE 4—Summary of Vermont's experience with membranes on bridge decks [109].

Observations	Hot Asphalt and Glass Fabric	Mastic Asphalt and Gussasphalt	Standard Preformed Membranes (3 Products)	NCHRP Project 12-11 Preformed Membranes (5 products)	Tar Emulsion With and Without Glass Fabric	Hot-Applied PVC Polymer	Epoxies (Solvent Cut Coal-Tar-Modified 100% Solids)	Polyurethanes Modified and 100% Solids
	wash and sweep	wash and sweep	wash and sweep	wash and sweep, sand blast	wash and sweep	wash and sweep	sand blast or acid etch	sweep or acid etch or both
Surface preparation required	yes	yes	yes	yes	no	yes	sand blast or acid etch	sweep or acid etch or both
Moisture sensitive	difficult	difficult	easy to average	difficult	very easy	average	most cases average	yes
Ease of application	poor	poor	good	excellent	poor	good	poor	good
Flexibility and crack bridging properties	fair/poor	poor	fair/good	fair/good	good/poor	good	good/poor	good
Bond and seal at curb	yes	yes/no	no	no	no	yes	yes	yes
Bubbles or pinholes or both in membrane	46 000 to 71 000	infinity	infinity	14 000 to infinity (some materials conductive)	500 to 6000	infinity on protection system	1100 to 1 200 00	480 000 to 2 600 000
Resistivity reading prior to paving				fair to good	excellent	good	good	good
Bond between membrane and concrete	good	system included	fair to good	good	good	fair to good	fair to poor	poor unless roofing sheet or protection boards used
Bond between pavement and membrane	good	NA ^a	good	yes to promote adhesion between pavement and membrane	no	yes	no	yes (most cases)
Protection system required over membrane	no	NA	no/possible	yes	no	slight	no	no
Pavement subject to blistering or cracking during installation	no	NA	yes	yes	no	slight	no	no
Due to membrane								
Postconstruction problems with pavement and membrane	no	no	yes/no	yes/no	no	slight	no	no
Cost per square yard not including pavement	\$3.75	\$62.35	\$4.50	\$10.65	\$1.32, 3.50 with fabric	\$4.00	\$9.42	\$5.19
Performance based on followup evaluations	fair to good	unsatisfactory	fair to good	insufficient service life to draw conclusions	good without fabric except along curb-lines and drains	insufficient service life to draw conclusions	poor to fair	fair to good
Recommendations	await continued followup evaluations	not recommended for further use	continue use of 2 systems with liquid curb line sealant. Await followup on third system	not recommended for further use unless other systems prove to be unsatisfactory	use in combination with compatible curb line sealant; on structures not subject to severe cracking delete use of fabric	restrict use, await continued follow-up evaluations	1 of 4 systems recommended; limit other materials to use on repair projects or as curb-line sealant	

^aNA = not applicable.

with membranes—as with any system that “seals” one surface of a structure containing chloride which either contains reinforcing bar which is corroding or which has the possibility of corroding—is the effect of the seal on subsequent corrosion. Opinion and results appear divided on this issue.

Repairing Concrete Structures

It is useful here to mention problems that may arise when a concrete structure is repaired. As discussed earlier, many compounds are available for repair, and a frequent need is for a rapidly setting material which will allow use of the repaired structure as soon as possible. Any technique of repair that removes chloride-contaminated concrete, cleans the steel, and replaces the concrete with a chloride-free compound runs the risk of setting up macrocell action with steel immediately adjacent to the repair. NCHRP Project 12-16 was set up to study this problem [51]. Results were inconclusive owing to experimental problems, but the possible situation remains important and the “spall around a spall” concept is a real hazard.

Corrosion Inhibition in Concrete

It is common corrosion prevention practice to incorporate inhibitors in potentially corrosive environments. This technique has found application in the field of corrosion control of concrete likely to be chloride contaminated. A brief review of this subject is given by Griffin [110]. The approach has been the object of a considerable amount of research, with chromates, phosphates, hypophosphates, alkalis, and fluorides generally the recommended compound groups. Specific action was also noted by using sodium nitrite, sodium benzoate, and sodium metasilicate, together with other complex compounds. On the basis of a wide literature survey, Craig and Wood [111] selected sodium nitrite, potassium chromate, and sodium benzoate as “final choices”. They compared the action of these additives to portland cement mortar containing various concentrations of de-icing salt added to the mix. The technique used single rebar specimens surrounded by mortar (that is, no macrocell action) and evaluated polarization behavior and percent of surface corroded. Of the inhibitors studied, only sodium nitrite was effective in these tests, but there were deleterious effects on concrete strength. This information contradicts that found by Gouda and Monfore [112], who determined that nitrite *and* chromate were effective inhibitors.

Following the nitrite approach, Gaidis et al [113-116] have recently published several papers on the activity on calcium nitrite as an inhibitor in reinforced concrete. Calcium nitrite, the authors postulated, should avoid concrete structural problems associated with alkali-aggregate reactions. Most of their studies were undertaken on steel surrounded by concrete in simulated environments, polarization techniques being used. Partial immersion (short-term) tests were also run. These workers concluded that calcium nitrite at 2% is in accordance with ASTM Specification for Chemical Admixtures for Concrete (C 494). Polarization curves in concrete prisms show the effect of inhibitor action. Figure 26 shows that the

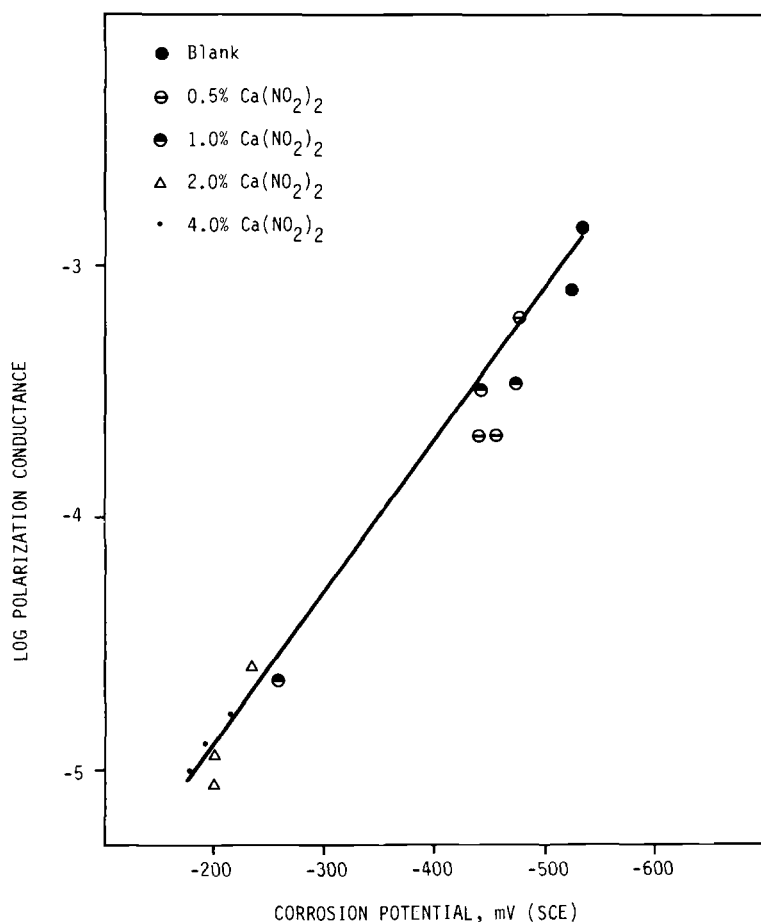


FIG. 26—Effect of calcium nitrite concentration on corrosion rate of single reinforcing bars encased in concrete; soaking time = 90 days in NaCl [115].

relative corrosion rates for samples soaked in saturated sodium chloride solution for 90 days with 2 and 4% admixed calcium nitrite are about a factor of 15 lower than those without the calcium nitrite admixture. However, these measurements used the “log polarization conductance technique”, a version of polarization resistance which was discussed in Chapter V and is open to some dispute.

Further work utilizing large simulated concrete bridge-deck slabs, of the type used in the FHWA programs, is currently in progress; initial (6 months) results of these tests are encouraging. For a high-strength concrete, the addition of 2% $\text{Ca}(\text{NO}_2)_2$ to the mix inhibited active corrosion potentials. A control deck, on the other hand, without inhibitor, showed severe corrosion. Longer term tests are needed to confirm the effectiveness of calcium nitrite under more realistic simulated environmental conditions. Perhaps the recently completed bridge decks containing calcium nitrite will determine whether the inhibitor completely negates the effect of corrosion, or, as seems possible, simply increases the amount

of chloride necessary for corrosion reaction to initiate at the reinforcing steel. Be that as it may, the outlook appears promising for the use of this inhibitor.

Finally, a technique has been developed which uses electromigration to remove chloride from contaminated concrete [117]. A large direct-current voltage is applied between the top mat of reinforcing steel and a surface anode. Approximately 10% of the ionic current in the concrete is carried by the chloride ions, which migrate out of the concrete to the anode. The conceptual approach is shown in Fig. 27. Experiments on small-scale and large-scale laboratory specimens were successful; scale-up to treat a section of actual bridge deck not only removed about 79% of the chloride from above the reinforcing steel but also led to an abrupt change in the corrosion status of the reinforcing steel from active (pre-treatment) to passive (post-treatment). Implementation and scale-up problems remain to be solved, and cost effectiveness remains to be demonstrated. A membrane or surface seal of some kind would appear necessary following treatment to eliminate future salt ingress.

Reinforcing Steel Modification

One of the easiest ways of “modifying” the surface of reinforcing steel is to remove the rust and millscale before embedment. This is rarely if ever done, however, except where previous chloride-induced corrosion has occurred (for example, before repair placement). The lack of use of this method is probably due to the following reasons:

- Bond strengths are improved with millscale etc.
- The millscale may act as a good cathode during initial curing, facilitating passivation.
- It is too expensive and time consuming.

Thus a simplistic cost-benefit analysis would mitigate against such treatment.

Nonmetallic Coatings

Because of the success of coatings in preventing corrosion (for example, in buried pipeline applications), a considerable amount of testing has been per-

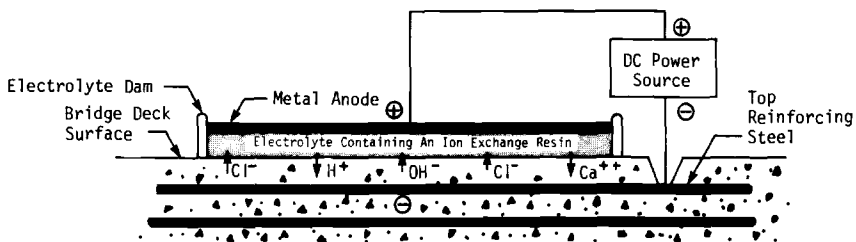


FIG. 27—Experimental technique used for electrochemical removal of chloride ions from a portland cement bridge deck [117].

formed, notably by workers at the National Bureau of Standards, on the most effective type of organic coating for reinforcing steel in concrete [118]. After testing 47 different compounds, these workers found that the application of an epoxy under careful conditions—by spraying the dry powder and subsequent heating of the reinforcing bar—is the best method. Williams [119] describes the manufacturing methods used and Kilaeski [120] describes field experiences. Bars coated in accordance with this technique have been used in bridge decks since 1973. Thus far it seems that field repair of the coating, at bar ends and holidays etc., can be undertaken using repair materials.

A concern always exists whenever a coating of this type is applied. If the material is in contact with bare steel, then the holidays in the coating can act as very small anodes, resulting in intensive attack. As previously discussed, this situation has been studied recently in some detail in FHWA laboratories [52] using simulated deck slabs. Preliminary data (after only three months' exposure) suggest no major problem, but longer term information is obviously needed.

Some questions have been raised regarding the effects of epoxy coating on bond strength. Pike et al [118] showed that, for epoxy coatings of less than 10 mils thickness, the bond strength under pull-out tests was only slightly less than for uncoated bars and within acceptable limits. High-build coatings (>25 mils) suffered severe bond-strength problems, presumably due to "wash-out" of the deformations. For the recommended coating thicknesses (7 ± 2 mils), however, the bond-strength concern appears to be a "non-problem".

It may be concluded therefore that the epoxy coating of rebar, although expensive, does appear to be a promising method of corrosion protection for reinforced concrete at this particular time.

Metallic Coatings

Because of the success enjoyed by metallic coatings on steel as corrosion amelioratives in other environments, it is not surprising that they have been investigated for use in concrete. The only two presently under serious consideration are zinc and nickel.

In reviewing the data on evaluations of these coatings, it is apparent there is a wide range of experimental techniques that has been used, from laboratory studies in simulated concrete environments to field evaluations of large structures which have seen many years of service. Data from laboratory investigations are extremely inconclusive and evidently very dependent on experimental techniques, some of which appear inappropriate for the parameters evaluated. On the other hand, "hard" large-structure data are scarce. The following review of the literature data will follow the order: large in-service structures; specimens in field environments; specimens in simulated environments; and mechanistic or screening studies, usually electrochemical in nature.

What have been the results of field studies on structures containing galvanized reinforcement? A series of evaluations conducted by the Portland Cement Association (PCA) on bridges containing galvanized reinforcement has been under-

taken [121,122]. For salt-contaminated bridges in Bermuda which had been in service for (up to) 20 years, no corrosion damage was noted. Summary data on these studies are given in Table 5 [13]. Data from Michigan, where experimental bridge decks were constructed incorporating galvanized reinforcement, indicate that after four years of service in Detroit such decks were in "excellent condition" but that adjacent black steel also did not exhibit distress [123].

Thus available field data suggest that galvanized reinforcement may provide increased corrosion resistance compared with black steel. Such studies are relatively limited in scope, however, and have not covered all environments of interest. Data are not available from heavy de-icing salt environments. As with other protective systems, questions remain to be answered relating to the magnitude of the improvement shown by galvanized reinforcement exposed under a variety of service and concrete conditions.

Difficulties associated with the development and use of test methods for evaluating the performance of galvanized steel reinforcement in concrete have been discussed by Cornet and Bresler [124]. These authors point out the lack of any standardized test procedure for evaluating reinforcement corrosion performance in concrete and cite inconsistencies, poor correlation between field performance and laboratory tests, and lack of "theoretical justification" in such testing. There can be no doubt that these concerns are valid. However, such problems arise from the very complex situation arising in chloride-contaminated reinforced concrete structures, a situation only now being understood. Thus the more simplistic tests ("lollipop" specimens and the like) that have been used in research which is claimed to both support and detract from the use of coated steel must be viewed with circumspection. The fact that the results of such testing practices are frequently inconclusive undoubtedly has been the basis for disagreement about the use of galvanized reinforcing concrete structures which may see chloride penetration.

Simulated service and laboratory test results of metallic coated reinforcing steel are voluminous. Duffaut et al [125] have presented results of a large series of tests on reinforced concrete prisms exposed at different levels in the Rance Estuary,

TABLE 5—*Summary of exposure data and corrosion status of bridge decks containing galvanized reinforcing steel [14].*

	Age, years	Concrete at Level of Steel, kg Cl ⁻ /m ³ (lbs Cl ⁻ /yd ³)	Average Corrosion Layer Thickness, mils	Percent of Coating Remaining
St. George (SG 17)	7	14.4 (5.0)	0.1	98
Bermuda Yacht Club (BYC 3)	8	17.6 (6.1)	none	100
Hamilton (H 22)	10	9.2 (3.2)	0.2	95
Hamilton (H 26)	10	17.3 (6.0)	0.3	96
St. George (SG 10)	10	22.16 (7.7)	0.2	99
St. George (SG 9)	12	30.8 (10.7)	0.5	92
Longbird (LB 20)	23	21.0 (7.3)	0.2	98

France. Variables included quality of concrete, depth of cover, galvanized versus nongalvanized reinforcement, and cathodic protection. Exposure time is unclear, but appears to be around 12 years. Based on examination of the reinforcing after removal from the specimens, galvanized reinforcing did provide corrosion protection at all depths of cover compared with black steel, although the results were not quantitative. Data from the Michigan Department of Transportation indicate that galvanizing lessens, but does not prevent, cracking and spalling, based on large slabs which were salted and weathered but not loaded [123].

A review of simulated service environments may begin with work at the Cement and Concrete Research Institute of the University of Trondheim, Norway, which has exposed prisms containing both black and galvanized steel to the effects of "tidal flows" of seawater under laboratory conditions [126]. Variables were depth of cover (1.5 and 3.0 cm) and water/cement ratio (0.5 and 0.67). Data from this report are shown in Table 6, which summarizes the time-to-cracking and severity of cracking. Note that the data are relatively consistent in that shallow cover and low water/cement ratios initiate cracking earlier. A comparison of Specimen 31 with Specimen 44, however, showed that both the black steel and galvanized steel reinforcement initiated cracking at the same time after immersion, but that following initiation more severe cracking was observed on the galvanized steel. There was a tendency for the galvanized steel to generally retard the cracking, but once the cracking occurred it tended to be more severe on the galvanized steel specimens.

Literature data from solution-based laboratory tests are available, but are often in conflict with more service-oriented data. Bird and Strauss [127] investigated the behavior of steel, zinc, cadmium, nickel, tin, and copper in both simulated and actual chloride-contaminated concrete environments. For single bars in concrete, exposed to salt-spray/dry cycles for three years, steel and zinc showed severe corrosion, while cadmium remained largely unattacked. Tripler et al [128] investigated the behavior of zinc-coated and nickel-coated steel in simulated concrete (calcium-hydroxide/sodium-chloride) environments. They found that zinc showed quite severe corrosion in these tests, whereas nickel did not. Interestingly, if the nickel coatings were damaged to expose the underlying steel, then the expected severe galvanic corrosion of the exposed steel did not develop. The conflict between these data and those from the specimen/actual environment regarding effect of coatings is obvious. Cornet and Bresler [131] indicate that, in performance of galvanized versus black steel reinforced specimens alternately exposed to 4% NaCl in the stressed state, the galvanized specimens cracked less and later than did the black steel. Caution should be exercised here, however, because of the lack of replicate specimens; there was only one specimen per "condition".

Treadaway and co-workers [129] reached a similar conclusion: galvanized steel retards, but does not prevent, the formation of cracks during laboratory tests on specimens containing reinforcing steel.

TABLE 6—Time-to-cracking and number of cracks for prisms alternately exposed to seawater beginning in 11/68 [126].

[illegible]

Pursuing the subject of cracking of specimens, and a comparison between nickel and zinc, let us examine one of the more comprehensive long-term tests of both these coatings. It was conducted by the International Nickel Company (INCO) and has been reported by Baker et al [130]. The ten-year INCO study results show that the cracking incidence for zinc-coated and nickel-coated bars in concrete exposed to seawater is approximately that observed for uncoated steel; however, this cracking did not lead to the relatively high spalling failure rate which was reported for the unprotected bar specimens. After ten years, none of the specimens with coated bars had spalled. These data raise questions as to the *cause* of cracking in these specimens. Possibly, decreased corrosion after cracking on the coated bars had prevented spalling, but imposition of "live loads" on a concrete structure may negate this advantage.

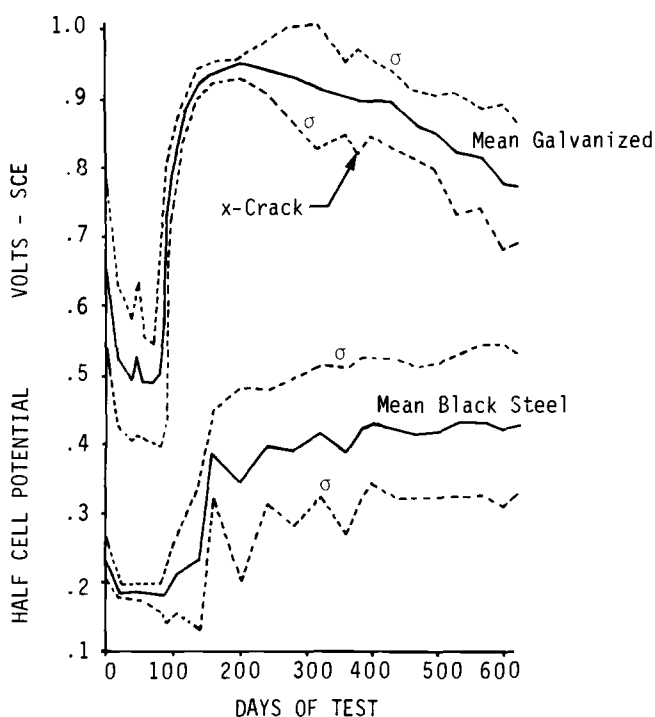
Other experimentation in the FHWA time-to-corrosion studies [39] did not incorporate sufficient slabs containing galvanizing to allow meaningful conclusions to be drawn.

The use of "lollipop" tests at the California Department of Transportation (CalTrans) to investigate basic parameters such as potential of steel versus time to cracking, and influence of concrete quality and cover depth on corrosion and cracking, has been discussed in a previous section. The same technique has been used by Hill et al [132] to investigate the behavior of galvanized versus black steel reinforcement in lollipop specimens partially immersed in saturated NaCl solution. Data from this series of tests indicated that there was no benefit from galvanizing and that corrosion began at roughly the same time for both types of steel. Further, for low water/cement ratio concrete, galvanized steel specimens cracked earlier than black steel specimens. Typical results are shown in Fig. 28.

Upon presentation of these data, concern was expressed regarding the poor statistical control of specimen preparation, distortions present in accelerated testing, and inadequate statistical techniques. Certainly, the effect of some earlier cracking for galvanized versus black steel is difficult to rationalize and is contrary to most other studies, both small and large scale. Confirming data using similar or even more realistic conditions are needed before these conclusions can be considered valid, and even then extension of these data to large structures must be considered very carefully.

Galvanized coatings have been investigated as a method of corrosion prevention for pre-stressing steel, with beneficial results [133]. Possible damage by hydrogen evolution does not appear to be a problem, particularly when a chromate dip is used after galvanizing. This is good practice for any type of galvanizing used in concrete, because of the possibility of hydrogen evolution (and hence a reduction in bond strength) during the pouring and curing process. Available data [134,135] suggest that galvanizing may be beneficial in maintaining fatigue strength of cracked, pre-stressed concrete specimens following exposure to NaCl solutions.

Much less information is available on the use of nickel-coated bars. Basing their findings on the ten-year marine exposure test discussed earlier, Baker et al



GALVANIZED

\bar{x} , Mean. = 386 days for conc. crack

σ , Std. Dev. = 134 days

BLACK STEEL

8 out of 20 conc. specimens cracked in test period of 622 days.

FIG. 28—Potentials and mean times to cracking for black and galvanized steel reinforced concrete specimens partially immersed in NaCl [132].

[130] concluded that rolled-on-nickel is more-or-less impervious to the action of chloride in the concrete. Accordingly, the use of nickel-coated rebar was recently authorized for the seawater intake ducts in a nuclear power plant, and it will be most interesting to determine the performance under these circumstances [136]. The requirement in this application was for a 40-year life.

Cathodic Protection

Cathodic protection is a well-established means of preventing corrosion in a variety of environments, particularly for pipe lines buried in soil. It has also been used successfully to ensure protection of steel pipelines buried or encased in concrete [137–139]. It was first applied to the problem of conventional reinforcement deterioration in structure due to corrosion in concrete by Stratfull in Califor-

nia [140,141], who found that, because of the low throwing power and generally high resistance of concrete, it was necessary to use a "total surface anode" over the extent of the structure to be protected—in this case, the top surface of the bridge deck. Using this technique it was found that large decks could be protected by the use of only tens of watts of power and that the process was relatively trouble free. The surface anode situation did, however, require the use of a relatively soft "overlay" composed of coke-asphalt mix, which could be subject to fairly rapid deterioration by traffic. The validity of the technique by potential shift of the steel and the rate of corrosion on a probe placed in the deck are shown in Fig. 29. Others have reported on their success with this technique [142,143] and improvements are on-going. Application to structures other than the top surface of bridge decks is an important consideration. For example, the development of conductive paints, and conductive concrete which can be applied by shotcreting techniques, makes the cathodic protection of the underside and vertical surfaces of concrete structures feasible.

Studies are also continuing on the use of galvanic systems, which are to be distinguished from the impressed current systems previously utilized [144,145]. For example, zinc wires are placed in slots above the reinforcing steel, and the sacrificial action of the zinc is then transferred to the steel directly beneath. This system has recently been installed in a deck in Ohio, but results available to date do not allow a specific statement regarding its validity or use.

Impressed current systems using platinized wires in slots in the concrete surface and surrounded by a conductive grout are now commercially available. The very limited experience with these systems has been clouded because of the degradation of the grout and surrounding concrete by the low pH developed at the anode and also by poor throwing power [52].

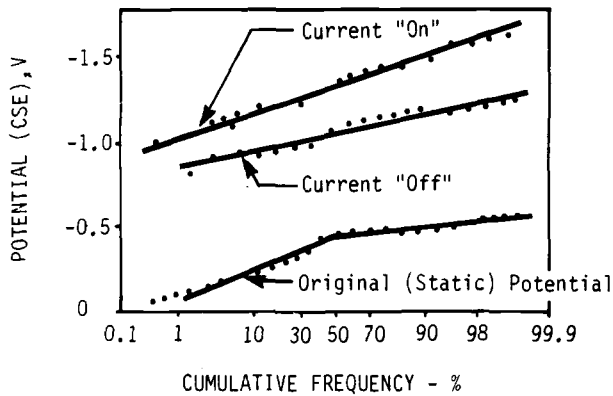
A recent survey of literature has revealed no in-place cathodic protection of a marine structure constructed from reinforced concrete [146]. Heuze [147], however, has discussed the concept for a "hypothetical" offshore platform; realistically the cathodic protection system using zinc electrodes is designed to protect bare steel first and foremost, with the rebar being protected because of its connection into the bare steel system. Concern has been expressed in the area of cathodic protection of steel in concrete, because of electrical charge transfer at the rebar/concrete interface possibly causing deterioration in bond strength. This problem is intimately related with another: the determination of the optimum cathodic protection criteria for steel in concrete.

Hoover [71] has discussed problems associated with cathodic protection of parking garage floors. The main problem is associated with weight and height restrictions resulting from overlay, which the garage (unlike bridge decks) was not designed to take.

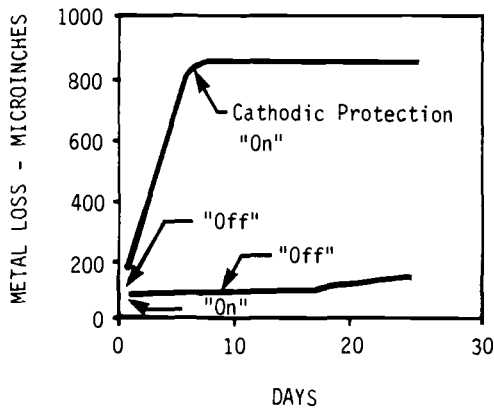
Criteria for Cathodic Protection of Steel in Concrete

Possible Approaches

Unz [148] and Deskins [149] have discussed criteria for cathodic protection of steel in concrete pipes. More generally, there are four distinct bases on which the



(a)



(b)

FIG. 29—Effect of cathodic protection on (a) potential of reinforcing steel and (b) embedded resistance probe for bridge deck system [141].

adequacy of cathodic protection can be judged. The first of these is a consideration of the thermodynamics involved and calls for the potential of the steel to be placed in the "immune" area of the potential-pH diagram. For steel in *water* at pH's below 10, the Fe/Fe^{2+} equilibrium, with an effective ferrous ion concentration of $10^{-6}M$, indicates immunity at potentials below $-0.62 V_{\text{SHE}}$ or $-0.94 V_{\text{CSE}}$. For steel in *concrete*, however, the applicable pH is roughly 12.5. Thus the potential is shifted to a value given by

$$\begin{aligned} e &= -0.09 - 0.059 \text{ pH} \\ &= -0.82 V_{\text{SHE}} (-1.13 V_{\text{CSE}}) \text{ at pH } 12.5 \end{aligned}$$

These values are, of course, not usually recognized as effective or economical protection criteria, because of the high levels of protective current necessary. Two aspects, however, are worth noting:

- At pH 12.5, the immunity limit is *below* that at pH 7; in other words, the protection criteria may be more stringent in concrete.
- Both immunity levels are below the hydrogen evolution potential for these pH's.

The second method for assessing the adequacy of cathodic protection relies on an assessment of overpotential and kinetics, rather than thermodynamics, and on mixed potential theory. In experiments with cathodic protection of base steel in aerated seawater, LaQue [150] showed that there was no change in the potential of steel subjected to cathodic currents until corrosion as measured by weight loss had been reduced to zero. This occurred when a cathodic reaction (O_2 reduction) had been created over 100% of the metal surface. With more current, the cathodic reaction involved hydrogen evolution at a more negative potential. A potential related to hydrogen evolution cannot be expected to occur in the pH range likely to be encountered in concrete. Since the suggested mechanism is the achievement of a cathodic reaction over the whole surface of the metal, whatever potential is associated with that reaction becomes the significant potential. It appears that more work is needed to study the potential associated with protection of steel in the environment of steel embedded in concrete containing chlorides if potential measurements are to be used as criteria for applying and monitoring cathodic protection.

A third approach depends on the Tafel relationship between overpotential and current density. Given that the Tafel constant for steel in concrete will be between 30 and 100 mV/decade, then a cathodic polarization of 100 mV will correspond to between a 10 and 30 times reduction in corrosion rate. The logarithmic relationship between overpotential and current density will, of course, lead to much enhanced corrosion rate reduction by further cathodic polarization. A determination of criteria adequacy under this arrangement would have to ensure a conservative value of the Tafel constant for steel in concrete (which, as discussed, will vary considerably) and an "acceptable" rate of corrosion. Difficulties also arise when this technique must be utilized in the "current-on" mode, because of the polarizability of the steel/concrete interface and because of the generally low but variable conductivity of concrete.

The final theoretical method for assessing the adequacy of cathodic protection is the use of the polarization (E -log i) curve. The object of this method is to impose a potential which is at least at the start of the Tafel slope for the cathodic reaction, as determined for the metal/environment in question. The basis for this is that, when the Tafel slope can be determined, the anodic (corrosion) reaction has effectively been eliminated from the surface of the metal, or in other words, either the anodic area or total anodic current is now insignificant. While this technique is applicable to the steel/concrete interface, it can present practical difficulties in measurement and also in reacting to possible changes in the environment after the E -log i scan has been completed and the determined potential imposed. This will be discussed later.

Laboratory and Field Results

Two pieces of laboratory work throw critical light on this subject. Hausmann [151], using a series of $\text{Ca}(\text{OH})_2/0.64M$ NaCl solutions to simulate the environment of chloride-contaminated concrete, showed that:

- For reinforcing steel immersed in the solution and *immediately* cathodically protected, corrosion is prevented at potentials more active than $-0.50 V_{\text{CSE}}$.
- For reinforcing steel exposed to the same environment without protection for one day, and then cathodically protected, a potential of $-0.71 V_{\text{CSE}}$ will protect the steel.

Hausmann used a visual examination of the reinforcing steel for absence of pitting as the arbiter for protection.

In a more recent study, Vrabie [144] used both simulated and actual concrete environments to determine the potential range for cathodic protection of steel under a variety of conditions. Corrosion probes (utilizing the electrical resistance technique) were used to measure rates of corrosion. The results briefly were that in all cases (1) cathodic protection was achieved at a value of $-0.77 V_{\text{CSE}}$ and (2) this value will prevent pitting as well as general corrosion. Vrabie also showed that overprotection should be avoided; he suggests a limit of $-1.1 V_{\text{CSE}}$ (which is roughly that corresponding to *immunity* at pH 12.5). Vrabie states that the visible hydrogen evolution potential for steel in concrete is $-1.17 V_{\text{CSE}}$, a value $\sim 0.12 V$ more active than the hydrogen evolution reaction (HER) line at 12.5 pH. The implication here is that visible hydrogen evolution is detrimental to the bond strength between the concrete and rebar.

These studies are useful in obtaining experimental evidence for possible potential criteria. At least one, however, is somewhat far-removed from the real world of the large reinforced concrete structure, and the time of experimentation was very short. However, taken together, the studies indicate that:

- The condition of the steel/concrete interface (no corrosion, no chloride; no corrosion, chloride; or corrosion, chloride) may make different criteria relevant. However, a change from one condition to another during life-time may necessitate criteria reevaluation.
- Protection can be achieved at potentials much below the theoretical immunity values.
- Protection can be achieved at potentials somewhat more noble than those needed for steel in seawater or in soils.

Practical difficulties in ensuring good cathodic protection over the entire steel in a reinforced concrete structure have largely overridden any considerations of useful criteria for ensuring protection. This is particularly true of bridge decks, where a conductive asphalt has had to be developed to ensure the necessary throwing power. So far as the present author is aware, most examples of reinforced structures being protected have used $-0.85 V_{\text{CSE}}$ as the maintained poten-

tial, and even the location of measurement (on top of the effective anode) has been criticized. Nevertheless, adequacy of protection has frequently been monitored by noting the change in resistance of corrosion probes placed in the deck and tied to the steel. The use of the -0.85-V criterion derives from much practical experience in cathodic protection of steel, mainly in underground or submerged piping systems. This practical experience is set out in NACE Recommended Practice RP-01-69, of which there is a 1976 revision. This document also sets out other criteria (including polarization shift and $E\text{-log}i$ methods).

One of the problems in potential measurement for cathodic protection systems is the nature and location of the reference electrode. Measurements with a Cu/CuSO_4 electrode on the surface of the conductive overlay are not meaningful. Reference electrodes embedded in the concrete close to the rebar are the better approach, but difficulties regarding stability and reproducibility are encountered for zinc electrodes; alternative electrodes, including $\text{Mo}/\text{Mo}_2\text{O}_3$ and Hg/HgO , are currently the subject of research [152]. Ag/AgCl electrodes have been used, but this electrode is very sensitive to the $\text{OH}^-:\text{Cl}^-$ ratio and must therefore be used with caution or unexpected drifting in potential may occur.

One of the few workers to study possible new approaches to the cathodic protection of corroded steel in chloride-contaminated concrete is Schutt [153]. It is Schutt's contention that different areas of a reinforced concrete structure will exhibit different corrosion potentials (a fact well documented in the literature) and that an across-the-board potential criterion of, for example, -0.85 V cannot be used. He therefore measures, using "current-off" techniques, a separate $E\text{-log}i$ curve on each section of the structure, and thereby sets the protection potential for each section. It appears that this technique, while interesting, may have some drawbacks:

- The selection of reference electrode placement will be critical because of the poor conductivity of concrete; in other words, the "worst" corrosion area in a section may be inadvertently monitored.
- The continued buildup of chloride at the rebar/concrete interface may lead to a change in $E\text{-log}i$ curve *after* the original survey. In this case, an initially adequate protection level may become quite inadequate.

Other in-field studies on the adequacy of different cathodic protection criteria are lacking. More information needs to be developed in this area either on actual or simulated reinforced concrete structures, so as to enable laboratory and empirical criteria to be checked in the field.

This brief discussion has shown that the conditions seen by steel in concrete are sufficiently different from steel in seawater or in soil as to warrant critical evaluation of cathodic protection criteria for this particular circumstance. Among the factors that must be considered are:

- The high pH of concrete.
- The generally poor, but variable, conductivity of concrete.
- The extreme polarizability of the steel/concrete interface.
- The possibility of different conditions pertaining on different *areas* of the same structure.
- The possibility of different conditions pertaining at different *times*.
- The reduction in bond strength of the steel/concrete interface due to excessive cathodic current and hydrogen evolution.

The most commonly used criterion for adequate cathodic protection is $-0.85 V_{CSE}$. This potential is more active than that determined by laboratory experiment to be adequate ($-0.77 V_{CSE}$), but appreciably more noble than the recommended maximum negative potential to cause interface bond strength reduction ($-1.1 V$). Interestingly, Schutt [153] states that $-0.90 V$ was necessary (current-on) on one section of a deck to give adequate protection based on his *E-logi* technique; this corresponds to $-0.77 V$ for the current-off situation. Thus there is a discrepancy between field observations and laboratory experimentation which needs resolution. It may simply be due to different criteria being utilized and the *E-logi*-derived potential in this circumstance being conservative, but the apparent dichotomy needs investigation.

While the difference between -0.85 and $-0.77 V$ appears to be minimal, it could have profound effects on the system installation for cathodic protection. Because of the poor throwing power of most cathodic protection systems on reinforced concrete structures (due to the low conductivity of concrete), a complete surface anode has been used for most installations (except obviously for galvanic anode systems, which in this application are in their infancy). A relaxation of minimum potential requirements may allow the revaluation of discrete anodes, resulting in significant savings in system installation.

The field observations of different corrosion potentials over a reinforced concrete structure, together with the experimental observation that the necessary protection potential may vary depending on the state of corrosion of the steel, raise an interesting issue. If a cathodic protection system is installed on a new or completely rehabilitated (chloride-free concrete with old rebar) structure, will the criteria be the same as for a corroding structure? It is probably not possible to answer this question at the present time, because there are no available data on possible effects of cathodic protection per se on chloride intrusion, or of chloride levels necessary to cause corrosion at given maintained potentials. This is needed work, particularly if the *E-logi* determinations on different sections of a structure are to be long-term corrosion-prevention measures.

Little investigation has been undertaken on the feasibility of establishing polarized potential values (current on or off) versus the free-corrosion potential as a possible criterion for adequate protection. This could be investigated using elec-

trical resistance type probes; however, the implementation of such a technique could be difficult due to increases in chloride levels at specific locations because of differing concrete cover thicknesses of permeability.

Summary

The establishment of criteria for cathodic protection of reinforcing steel in concrete is in a state of flux. More critical thinking, experimentation, and evaluation are needed before criteria directly attuned to a specific circumstance may be promulgated. At this time, however, it does appear that a potential of $-0.85 V_{CSE}$ is probably conservative, although the use of electrical resistance probes to ensure absence of corrosion may be desirable.

The consensus of opinion suggests that, if criteria commonly enforced are used, there is little possibility that cathodic protection of a structure containing reinforced concrete will lead to deterioration of bond strength sufficient to cause problems. It has also been determined that the nature of the reduction in bond strength is really a function of the charge passed and not of the current; in other words, it is a total quantity and not a rate-related situation. Further work may need to be done in this area, particularly on structures that have been subjected to cathodic protection for significant periods of time, in order to evaluate any long-term problems.

VIII

Standards

American Standards

ASTM is the primary standards-writing organization in the United States. An investigation of current ASTM standards shows that specifications are available for both conventional and pre-stressed steel. Specifications also exist for zinc-coated (galvanized) bars for concrete reinforcement (A 767) and for epoxy-coated reinforcing steel bars (A 775) but no standard is available for nickel-coated bars. (Epoxy-coated bars are also under study by NACE Committee T-3K-3, which will promulgate an NACE standard.)

There are a number of ASTM specifications relating to quality of concrete. Specifications for composition of cement are also covered by ASTM standards; these have been discussed previously. It is feasible that, given the future good performance of inhibitors in concrete, an inhibitor formulation and its use in concrete may be the subject of an ASTM standard. The American Association of State Highway Transportation Organizations have put forward two recommended methods related to chloride in concrete: T 259, a method for measuring the chloride permeability of concrete, and T 260, a method for measuring the total chloride ion content of concrete.

As previously discussed, ASTM has recently developed a test for conducting half-cell potential measurements on reinforced concrete structures (C 876). So far as is known, there are no other ASTM standards developed for corrosion testing of reinforcing steel in concrete. Cathodic protection measures have never been the subject of ASTM standards, but have frequently formed the basis of NACE standards. In this respect, work is ongoing within NACE Committee T-3K to develop a recommended practice for cathodic protection criteria for steel in concrete. It is probable that this will also include monitoring techniques.

ASTM Committee D-4 on Road and Paving Materials is currently considering a practice for the use of waterproof membranes on bridge decks. Committee 201 of the American Concrete Institute publishes the "Guide to Durable Concrete," which sets limits on such important criteria as water/cement ratio, depth of cover, and chloride present in the concrete as a function of structure environment. Building code requirements for reinforced concrete are covered in ACI 318.

Other summaries may be used as design guides but not as standards. For example, NCHRP Project 57, "Durability of Concrete Bridge Decks," contains much information regarding the resistance of bridge decks to chloride-induced corrosion.

Foreign Standards

The British standard covering the general use of concrete is BS CP 110, "The Structural Use of Concrete." Other European standards are contained in the "International System of Unified Standard Code of Practice for Structures, Volume 2, Model Code for Concrete Structures," published by Comité Euro-International du Béton. These codes, as mentioned before, pay much attention to the presence of cracks within the structure and to the width of the cracks. BS CP 110 stipulates depth of cover required according to concrete type and mix and environmental exposure conditions. This is to some extent governed by carbonation of concrete and not necessarily by the influence of chloride. It is believed that Det norske Veritas also promulgates codes regarding the construction of, for example, reinforced concrete offshore platforms, but specific information is currently not available.

Future Action

It thus seems that the problem of corrosion of reinforcing steel in chloride-contaminated concrete is generally receiving appropriate attention from the various standards and code organizations. Further attention to this situation may be desired, particularly in the following areas:

- More emphasis on quality and depth of concrete necessary for retardation of corrosion, taking into account use of coated steel.
- Possible standardization of membranes for application as surface sealers.
- Inhibitor test procedures and requirements.

Since chloride corrosion of steel embedded in concrete is an international problem, however, a more unified approach towards standards and codes would seem to be appropriate. For example, cracking and its severity in concrete structures is considered important in Europe, but less so in the United States. The International Standards Organization (ISO) could profitably look at the current state of standardization in this area, and should perhaps consider adoption of the standards of individual countries on a world-wide basis where appropriate.

IX

Current and Needed Research

Ongoing Work

There is a considerable amount of as yet unpublished research currently underway in the United States and elsewhere on the corrosion of reinforcing steel in various types in concrete and the influence of such corrosion on other properties of the concrete. The National Association of Corrosion Engineers, Committee T-3K on Corrosion of Metals in Concrete, recently requested a questionnaire completion from members regarding research interests. While most members were interested mainly in the practical applications of current knowledge, there were some topics of interest so far as current research was concerned. Further studies on the fundamental mechanism of corrosion of steel in concrete, as affected by cement content and type, oxygen and moisture content, steel type and stresses, and cement type is underway at the University of Oklahoma, where additional work is continuing on the optimization of reference electrodes for embedment in reinforced concrete. The problem here is the maintenance of stability and reproducibility of potential as the environment around the electrode changes; this is crucial in cathodic protection monitoring, for example.

Hartt and co-workers at Florida Atlantic University are continuing to study the corrosion behavior of epoxy-coated bars, and also have an interesting approach to determining corrosion and concrete cracking by acoustic emission testing. The use of this technique is not novel in other corrosion circumstances and its applicability here as a nondestructive testing tool may be most useful.

The direct influence of moisture and oxygen levels on corrosion of reinforcing steel has been discussed earlier in this report. Under Federal Highway Administration sponsorship, workers at the Southwest Research Institute and the Portland Cement Association are developing nondestructive methods for determining moisture and oxygen levels in structural concrete in the hope that assessments as to likely corrosion rate for given chloride levels may be ascertained. The current approach utilizes the nuclear magnetic resonance technique.

Current work elsewhere in the world on the subject of reinforcing steel in concrete is mainly centered in Britain and Scandinavia. An ambitious government-funded and industry-funded program in the United Kingdom, "The United King-

dom Concrete-in-the-Oceans Program," is described in detail by Sharp and Pullar-Strecker [154]. This program was started in March 1976 and over 1 million pounds sterling has been allotted for its completion, scheduled apparently for 1982. As its name implies, this program directly attacks problems in marine environments. Not all the projects, of course, are related to corrosion. Studies are underway to investigate corrosion behavior in both complete immersion and splash-zone areas, the influence of cracking on corrosion, and the influence of exposure to marine environments on fatigue strength of reinforced concrete. Other ongoing work in Britain includes studies at the University of Aston in Birmingham, where attention is being paid to the nature of the steel/concrete interface and its influence of maintenance of passivity and ease of breakdown of passivity by chloride ion.

Much of the work in Scandinavia is centered at Korrosionscentralen in Denmark. Work is in progress on the influence of fly ash on protective qualities of concrete and on optimization of potential-mapping techniques for inspection of reinforced concrete structures other than bridge decks.

Needed Work

It appears that the fundamental mechanism of chloride ion corrosion of reinforcing steel in concrete is relatively well understood. Certain important features remain to be investigated, however. Further work needs to be performed to further resolve the role which macrocell action plays in the corrosion process on different types of structure. This is important because of the availability of protective techniques which may stifle corrosion should macrocell action be the major contributor to the corrosion process. The use of large simulated bridge decks and other structures, such as utilized by Clear [40], would appear to be prerequisites for this type of experimentation, because of their more reasonable simulative properties, given the concern frequently expressed regarding the use of small-scale specimens and nonrepresentative exposures.

It is obvious that the influence of concrete cover and permeability over bare reinforcing steel is of importance in retarding, but not completely preventing under all conditions, the corrosion of the reinforcing steel. Further work in this area does not appear warranted; however, the influence of cracking of concrete on corrosion is as yet incompletely understood. The use of inhibitors has been discussed, and further long-term exposures are needed to confirm the feasibility, for example, of the calcium nitrite inhibition system. So far as coated reinforcing steel is concerned, it is difficult to conceive the type of tests that would satisfy both the adequate simulation and acceleration requirements for metal-coated reinforcing steel. Epoxy-coated steel appears to be increasingly accepted, but further research on its properties when connected to passive steel (for example, small-anode/large-cathode area) is needed. Long-term field data are also required.

There still remain questions to be answered concerning the reduction of corrosion rate once the reinforcing steel has started to corrode. This appears to be

influenced by diffusion of oxygen to the steel, and the possible effects of surface curing on this must be carefully determined. It is recognized that oxygen diffusion rate experiments are difficult to perform, but the apparently pivotal role which oxygen plays in the corrosion process makes such experiments important. Additionally, it may be that the control exercised by the conductivity or resistivity of the concrete in controlling reinforcing steel corrosion has been looked at from too broad a perspective. The probable controlling factor here may be resistance of the concrete close to the rebar or other reinforcing steel; this subject does not appear to have been adequately researched and bulk measurements only are usually described. Further attention to this problem may well be warranted. Finally, there are few good data on the influence of depth of cover and strength of concrete on the ability to absorb stresses set up by the corrosion product. This would appear to be a relatively straightforward series of experiments, perhaps involving stress measurements, but none designed specifically to investigate this problem has yet been undertaken. Here again, the influence of bar diameter and its relation to necessary concrete depth is an important parameter.

So far as inspection methods are concerned, the vast majority of work undertaken on novel methods has been in laboratory studies. The only techniques currently available for structural purposes are potential measurement, chloride measurement, and visual inspection, together with delamination detection. There are significant problems with further experimentation in the area of polarization resistance techniques for measuring rate of corrosion in structures; these problems have been discussed in Chapter V. Some work has apparently used infrared thermography to determine the presence of corroding reinforcing steel or sub-surface delaminations. This would be useful on horizontal structures, but would be difficult on vertical or submerged surfaces.

Cathodic protection appears to be a promising method of preventing corrosion of reinforcing steel, but its current use is solely as a post-corrosion salvage technique. More attention needs to be paid to its possible incorporation in original design, as is common in other cathodic protection installations. This area does not seem the subject of research at this particular time and could certainly be a fruitful avenue of investigation. Additional areas for research into cathodic protection of reinforced concrete structures are in the area of protection of vertical surfaces and in buildings where conductive concretes etc. appear to be useful.

This review has previously indicated that more work is required in the area of fatigue cracking of reinforced concrete. Dynamic loading of structures and its effect on both corrosion and corrosion fatigue of reinforcing steel needs more careful work, particularly in the area of submerged versus splash-zone/wet-dry conditions. Some caution must be applied concerning the possible action of cathodic protection under these circumstances; analogous work on corrosion fatigue on bare steel in seawater under cathodic protection has indicated that there are possible deleterious effects of overprotection. This would appear to be an area where more research should be undertaken.

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Index

A

- Additives, to concrete, 12–14, 50–53
 - Calcium chloride, 13
 - Effect on corrosion, 50
 - Effect on permeability, 50
 - Inhibitors, 53–55
 - Latex, 13
 - Wax, 14

B

- Bacterial action, 32
- Bibliographies, 3

C

- Cathodic protection, 61–68
 - Galvanic systems, 62
 - Impressed current systems, 62
 - Of bridge decks, 62
 - Of parking garages, 62
 - Protection criteria, 62–68
- Cement, types, 10
- Chloride
 - Level monitoring, 34, 35
 - Removal by electromigration, 55
 - Sources of in concrete, 30
 - Threshold levels for corrosion, 19, 26
- Coatings, for reinforcement, 55–61
 - Galvanized, 57–61
 - Metallic, 56–61
 - Nickel-coated, 58, 60–61
 - Nonmetallic, 56

Corrosion

- Caused by chloride levels, 17, 18
- Rate effects, 4

Costs

- Bridge restoration, 6, 7
- Damage due to salting, 7
- Road salting, 7

Cover

- Effect on corrosion, 19, 26
- Effect on protection, 48, 49
- Versus expansive force, 49

Cracking

- Corrosion induced, 6
- Effect on corrosion in concrete, 19, 49
- Stress corrosion, 5, 9, 24, 25

D

- De-icing salt, application, 1
- Diffusion
 - Effect of water/cement ratio on, 12
 - In concrete, 12

E

- Electrical resistance
 - Effect of chloride and moisture on concrete, 34, 35
 - Technique for corrosion measurement, 37, 38
- Electromigration, 55
- Embedded/external steel interactions, 30, 31

Epoxy
 Coatings for reinforcement, 55–61
 Concrete, 14

F

Fatigue, 6, 45–47
 Effect of cracks in concrete on, 47
 Effect of frequency on, 46
 Effect of steel reinforcement types, 45
 Of unclad reinforcement, 45
 Fouling, 32

G

Galvanic effects, 32
 Garages
 Corrosion of reinforcement in, 27
 Protection against corrosion in, 49

I

Impedance, corrosion measurement method, 43
 Inhibitors, 53–55
 Inspection, visual, 34

M

Macrocells
 Action in concrete, 20, 21, 23
 Current measurement techniques, 43
 Effect on polarization resistance, 41–43
 Effect on potential, 17
 Membranes, 51–53
 Methyl methacrylate, 51
 Millscale, effect on passivation, 15

O

Overlays
 High-density concrete, 50
 Latex concrete, 50
 Oxygen
 Diffusion through concrete, 12, 21

Effect on passivation, 15
 Effect on corrosion rate, 16, 20, 21, 23, 27

P

Passivation
 Breakdown by chloride, 15
 Effect of millscale, 15
 Effect of pH, 15
 Permeability
 Effect of additives on, 50
 Of concrete, 11
 pH
 Effect on passivity, 15
 Levels in concrete, 15, 22
 Polarization, criterion for cathodic protection, 64
 Polarization resistance
 Effect of macrocells on, 40
 Technique for corrosion measurement, 40, 41
 Potential
 Corrosion mapping, 17, 37
 Criterion for cathodic protection, 64, 65
 Effect of macrocell versus microcell, 37
 Low active region, 23
 Measurement techniques, 35, 36
 Prestressing
 Corrosion fatigue, 24
 Corrosion of, 24, 29
 Stress-corrosion of, 5, 9, 24, 25
 Protection, methods of, 48–68

R

Ratio
 Pilling-Bedworth, 5
 Water/cement
 Effect on concrete permeability, 18
 Effect on protection, 48, 49
 Effect on time to corrosion, 18, 26
 Of concrete, 11

Reference electrodes
 For embedded use, 66
 For use in potential scans, 36
 Repairs, effect on subsequent corrosion, 20, 53

S

Seawater
 Corrosion of reinforcing steel in, 26
 Effect on diffusion in concrete, 19
 Silane treatment, 51
 Standards, 69–70
 American, 69
 Foreign, 70

Stray currents, 32
 Stress
 Due to corrosion product, 6
 Effects on corrosion rate, 33

T

Test specimens
 Large-scale, 18, 60
 Small-scale, 18, 57, 60

W

Workmanship, 14

