ORNL
MASTER

**Corrosion of Steel Tendons in Concrete
Pressure Vessels—Review of Recent
Literature and Experimental Investigations**

J. C. Griess

for the U.S. Nuclear Regulatory Commission
of Nuclear Regulatory Research
ements DOE 40-551-75 and 40-

NUREG/CR-0092
ORNL/NUREG-37
Dist. Category R5

Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

**CORROSION OF STEEL TENDONS IN CONCRETE PRESSURE VESSELS — REVIEW
OF RECENT LITERATURE AND EXPERIMENTAL INVESTIGATIONS**

J. C. Griess

Manuscript Completed — April 14, 1978

Date Published: June 1978

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Prepared for the
U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Under Interagency Agreements DOE 40-551-75 and 40-552-75
NRC FIN No. B0119

Prepared by the
OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

DISSEMINATION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

ABSTRACT	1
INTRODUCTION	1
LOCALIZED CORROSION	2
Pitting	3
Crevice Corrosion	4
Stress-Corrosion Cracking	5
Hydrogen Embrittlement	6
CORROSION OF CARBON STEEL	7
General Corrosion of Steel in Aqueous Environments	8
Stress-Corrosion Cracking of Steel	9
Corrosion of Steel in Concrete and in Organic Compounds	12
EXPERIMENTAL INVESTIGATION	17
Experimental Considerations	17
Experimental Procedures	18
Results	20
DISCUSSION	28
SUMMARY	34
ACKNOWLEDGMENTS	35
REFERENCES	35

CORROSION OF STEEL TENDONS ON CONCRETE PRESSURE VESSELS - REVIEW OF RECENT LITERATURE AND EXPERIMENTAL INVESTIGATIONS

J. C. Griess

ABSTRACT

The fundamentals of localized corrosion are briefly discussed, and the literature concerning corrosion of carbon steel in aqueous environments, in particular the stress-corrosion cracking of carbon steels, is reviewed. The behavior of high-strength steels in specific environments, including concrete and organic substances, is also summarized. The available information indicates that the corrosion of steels in correctly formulated concrete is minimal. Even appreciable concentrations of chloride, sulfate, sulfide, and nitrate salts can be tolerated in the concrete or grout without detrimental effects. Adherence to established standards in the preparation and application of grouts in tendon-bearing conduits should guarantee very long tendon lifetimes. Little is reported about the behavior of tendons in proprietary organic greases or waxes, but very good corrosion resistance is expected if the organic material remains intact.

Stress-corrosion cracking tests performed with AISI 1080 steel tendon wires, using the constant-strain-rate method, produced results expected from data in the literature. Cracking was observed only in neutral or acid solutions containing hydrogen sulfide, in ammonium nitrate solutions, and possibly in a dilute solution of sodium bisulfite. General corrosion tests in water and in dilute solutions of sodium nitrate, chloride, or sulfate showed that oxygen was an important factor; corrosion was substantially greater when oxygen had free access to the solution than when access to oxygen was restricted. In the tests with oxygen the heaviest attack on the steel tendons was at the waterline of the solution.

INTRODUCTION

In the construction of concrete pressure vessels, high-strength steel tendons are usually strung through vertical conduits and stressed to some predetermined level. After tensioning, the conduits with the tendons in place are pumped full of either a concrete grout or an organic

substance (petroleum-base grease or wax with additives) to provide corrosion protection to the tendons. Although steels are normally quite compatible with concrete and most organic compounds, the presence of impurities in either substance, which could be leached into pockets of water, could cause serious corrosion, eventually leading to failure of the load-carrying tendons.

In a test with a small-scale model of a concrete pressure vessel conducted at Oak Ridge National Laboratory, some of the cold-worked AISI 1080 steel (conforming to ASTM A 416, grade 270) tensioning tendons failed, and the failures appeared to be caused by stress-corrosion cracking.¹ The tendons were supposed to be protected by a proprietary wax, but there was evidence that wax did not completely fill all of the conduits. In addition, some unusual conditions existed during the test which could have been responsible for the cracking. Although it was not proven, ammonium nitrate in the environment was suggested as the cause of cracking.

As a result of the above experience and at the request of the Nuclear Regulatory Commission, we conducted a review of recent literature on the cracking of high-strength steels and, subsequently, a limited experimental program to determine the relative susceptibility of cold-worked AISI 1080 steel to cracking in several environments. This report presents the results. Before presenting the results from the literature review and test program, a few pertinent facts about localized corrosion are reviewed. Recognition of these facts is essential to an understanding of the literature.

LOCALIZED CORROSION

For the purpose of this discussion, corrosion is defined as the destructive action of an environment on a metallic substance. In the process, the metal is oxidized and some component in the environment is reduced. That part of the process involving oxidation is called the anodic reaction, and the reduction part is called the cathodic reaction. In some forms of corrosion, visual examination of a corroded surface does not allow location of specific anodic and cathodic areas, but in other

cases, anodic and cathodic areas are clearly separated. Since the overall corrosion process in aqueous environments involves the transfer of electrons and the formation of ions, corrosion is an electrochemical process and is subject to the laws of electrochemical kinetics. While it is not the purpose of this paper to dwell on the electrochemical nature of corrosion, one should not lose sight of this fact when discussing corrosion-related phenomena.

Corrosion can manifest itself in two general ways: uniform dissolution or thinning, and localized attack. Although the former mode of attack occasionally produces failures, by far the largest number of serious failures is produced by localized corrosion, which implies corrosion on only a small area of the metal exposed to the environment. Pitting, crevice corrosion, and stress-corrosion cracking (SCC) are probably the most common forms of localized attack, but others such as corrosion fatigue, grain-boundary attack, impingement and erosive attack, and selective dissolution of one element from an alloy (e.g., dezincification of brass) also are capable of producing failures. Although somewhat different in origin, hydrogen embrittlement is frequently classed as localized attack.

Most corrosion-related failures are produced by either pitting, crevice corrosion, SCC, hydrogen embrittlement, or by combinations of them. In the following paragraphs, some pertinent facts about each of these types of attack are presented.

Pitting

When random penetrations which have depths equal to or greater than the diameter occur on freely exposed surfaces, the material is said to have undergone pitting. Pits are often nearly hemispherical and distinguished from cracks primarily by their shape and depth. Pitting is most likely to occur in an environment in which the metal is nearly inert (passive) but where breakdown of passivity occurs in very small random areas. Halide ions, particularly chloride ions, are notorious for their ability to produce pitting.

When pitting occurs, the anodic current density on the walls of the pit is much greater than the current density on the surface surrounding the pit, although the total anodic and cathodic currents must be equal. As a pit deepens, mixing of the electrolyte in the pit with the bulk solution is limited, and the composition of the solution in the pit is significantly different from that of the bulk solution. In most cases the pH of the solution in the pit is lower than that of the bulk solution because of hydrolysis of the metal ions. Frequently, hydrolysis products precipitate at the mouth of the pit and further restrict mixing of the solution in the pit with the bulk solution. The acidity of the pit solution can be important in other forms of attack such as hydrogen embrittlement or SCC.

Crevice Corrosion

In many aspects, crevice corrosion is similar to pitting, but its origin is somewhat different. Crevice corrosion occurs when access of the bulk solution to parts of the metal surface is limited and in environments when the metals are passive in the absence of crevices. In such solutions, passivity usually depends on the presence of an oxidizing agent, usually oxygen.

When such a metal with a crevice is first placed in an aerated solution, all surfaces (those freely exposed as well as those in crevice regions) are exposed to the same solution. However, because of the minute quantity of oxygen in the volume of solution in the crevice, only a very small amount of corrosion is required to consume all of the oxygen. Since mixing of the solution in the crevices with the bulk solution is very restricted, diffusion of oxygen into the crevice cannot keep up with the demand for it in the corrosion process. As a result, the anodic reaction within the crevice is maintained by cathodic reduction of oxygen on the surfaces outside of the crevice. To electrically balance the positive metal ions formed in the crevice, negatively charged ions, under influence of the potential field, migrate into the crevice. As with pitting, hydrolysis of the metal ions produces free acid in the crevice, and this leads to further acceleration of corrosion. Thus the

initiation of pitting and crevice corrosion is different, but once established the mechanisms that produce continued corrosion are essentially the same.

Stress-Corrosion Cracking

Stress-corrosion cracking is a form of failure experienced by alloys when subjected to a tensile stress during exposure to specific environments. In most cases, pure metals are not subject to SCC, but there are exceptions. Usually there is an apparent stress level below which cracking will not occur; often this level is considerably below the yield stress as determined in air. Stress-corrosion cracks have the appearance of a brittle failure in a ductile material. Generally, the alloy undergoing cracking is almost inert in the environment, with essentially all of the oxidation being concentrated in the crack. Not long ago, SCC was believed to be confined to only a few systems (combinations of metals and environments), but now it is recognized as a general phenomenon which occurs in all or nearly all types of alloys when the proper combination of heat treatment, stress, and environment exists.

There are two distinct phases to the SCC process: an incubation period before a detectable crack forms, followed by a period of crack growth. The incubation period can be extremely variable, in some cases lasting for years. The crack growth rate tends to be relatively fast and depends on the stress intensity at the tip of the crack and the environment.

Cracks frequently – but not always – originate from the base of pits. Most investigators have indicated that the major purpose of the pit is to provide a stress concentration, but at least one investigator² believes that in some cases the primary function of the pit is to produce a solution of low pH within the pit which then initiates the crack.

SCC, in the context used here, implies that at least part of the cracking process involves an electrochemical dissolution of the metal at the tip of the crack and is sometimes referred to as "active-path corrosion." (This is in contrast to hydrogen-embrittlement cracking to be discussed later.) That electrochemical processes are involved is

shown by the fact that cracking can usually be prevented, or even stopped once started, by cathodic polarization of the metallic object. In addition, as with crevice and pitting corrosion, the solution within the crack is of different composition from that of the bulk solution - in most cases more acid.

One major advance in studying SCC made during recent years has been the straining of test specimens at a very low constant rate while at the same time fixing the potential of the specimen relative to the environment.³ The effect of anodic polarization on most metals is to cause either active dissolution or passivation. In the electropotential range of active dissolution, the entire metal surface corrodes rather than developing isolated cracks. Similarly, in the potential region of stable passivity, the alloy is essentially inert and cracking does not occur. It is only in the potential regions where a transition between passivity and active dissolution occurs that cracking conditions are established. In these narrow potential regions the constant straining of the metal locally disrupts passive films that are being formed, and active-path corrosion cracking occurs if the environment is capable of producing cracks. Once the response of an alloy to a given environment has been characterized (in terms of dissolution or passivation), it is only necessary to alter the potential either to allow cracking or to prevent it. The potential may be altered by the addition of oxidizing or reducing substances to the solution, by polarization from an external source, or by electrically coupling it in the same solution to a metal or alloy of different electrochemical activity.

Other advances have been the use of precracked specimens to eliminate the incubation period and the application of linear elastic fracture mechanics.⁴ Application of the latter methodology allows the direct use of laboratory data for predicting the behavior of large structural components for which fracture is a critical design consideration.

Hydrogen Embrittlement

Hydrogen-embrittlement cracking results from the entry of hydrogen into the metal, which reduces its ability to deform. In the strictest sense, hydrogen embrittlement is not a corrosion process; that is,

oxidation does not occur along the fracture surface. However, entry of hydrogen into metal may result from corrosion on the metal surface. Whereas cathodic polarization stops active-path SCC, cathodic polarization of a stressed metal subject to hydrogen embrittlement usually either enhances cracking or has no effect on it.

Any process that generates atomic hydrogen on the surface of a susceptible metal can lead to hydrogen embrittlement. Cathodic polarization, either from internal or external sources, is the usual method of producing this hydrogen. The formation of molecular hydrogen involves the transitory existence of atomic hydrogen on the metal surface. Certain materials at the surface, notably H_2S and H_3As , inhibit the discharge of molecular hydrogen, thereby allowing a greater steady-state surface concentration of atomic hydrogen and, correspondingly, allowing a greater concentration of hydrogen to enter the metal. For example, H_2S cracking in sour gas and oil wells is not active-path SCC but is hydrogen-embrittlement cracking.

Hydrogen embrittlement of high-strength steels is a relatively low-strain-rate phenomenon, because the cracking mechanism involves diffusion of hydrogen to sites where failure initiates. Atomic hydrogen concentrates in the region of highest stress, and time is required for a critical quantity of hydrogen to arrive before crack growth begins. Consequently, hydrogen embrittlement of high-strength steels is not detected with impact loading. Generally, the greater the hardness of a steel, the more likely it is to be embrittled; consequently, cold-working a steel increases its susceptibility to hydrogen embrittlement.

CORROSION OF CARBON STEEL

Since prestressed steel tendons are expected to retain their integrity for many years, and since in most applications the tendons are stressed to about 75% of their yield point, it is clear that even low general corrosion rates can lead to ultimate failures by reduction of the cross-sectional area of the tendons. Thus, even though in the previous section it was indicated that most service failures result from localized attack, general or uniform attack must be considered

when long-term service life is required. Furthermore, under certain conditions, even moderate general attack of high-strength steels can lead to hydrogen embrittlement.

In this section a few observations will be made about the general corrosion of steel, and this will be followed by a brief review of stress-corrosion cracking of steels. Finally, some pertinent literature on the corrosion of steels in concrete and organic greases will be reviewed.

General Corrosion of Steel in Aqueous Environments

The general or uniform corrosion of iron and steel in aqueous solutions is discussed in standard reference books, and only a few comments pertinent to more or less uniform corrosion of steel tendons are presented here. Most of the following information is based primarily on refs. 5-7. The most important variable in the corrosion of steel is the composition of the aqueous environment to which it is exposed. When steel corrodes in air-saturated water with neutral pH, the anodic reaction is the conversion of iron atoms to ferrous ions, and the cathodic reaction is primarily the reduction of dissolved oxygen to hydroxyl ions, but a small part of the cathodic process involves reduction of hydrogen ions to hydrogen. Removal of oxygen from such solutions significantly reduces the corrosion rate. Increasing the hydrogen ion concentration with a nonoxidizing acid increases the corrosion rate, and in deaerated solutions the formation of hydrogen becomes the cathodic process. Under these conditions, and probably even in air-saturated water, some hydrogen can enter the metal and under proper conditions lead to embrittlement. Increasing the alkalinity of water greatly reduces its corrosivity, and at high enough alkalinity the embrittlement of steels at room temperature is unlikely.

Aerated neutral saline solutions are particularly aggressive to steel, but if the solution is made sufficiently alkaline, essentially no attack occurs; that is, the metal is passive. However, at some intermediate alkali concentration where passivity is incomplete, severe pitting occurs. As indicated in the previous section, it is in those cases of borderline passivity where severe localized attack is to be expected.

Specific information on the general corrosion of steels with as much as 0.8% carbon was not found. However, in salt water, steels with carbon contents ranging from 0.05 to 0.2% carbon showed equivalent behavior, and it seems likely that this result would hold true for steels of still higher carbon content.

Steels sometimes undergo unexpected corrosion in oxygen-free environments that contain sulfate ions. These high corrosion rates are frequently caused by anaerobic bacteria, which reduce sulfate to hydrogen sulfide as part of their metabolic process. This point is raised here because some greases that have been used in contact with steel tendons contained organic sulfonates⁸ which may be reducible to sulfides by bacterial action.

Stress-Corrosion Cracking of Steel

It was formerly believed that carbon steels were only susceptible to active-path SCC in caustic or nitrate solutions, and many studies with steels have been carried out in these environments. In both sodium hydroxide⁷ and nitrate⁹ solutions the mode of failure has been shown to be active-path SCC. In caustic solutions the severity of cracking increases as both temperature and caustic concentration increase. Generally, at room temperature, caustic concentration must be above several percent to produce cracking.¹⁰ In nitrate solutions, cracking has been experienced at or near room temperature, but the severity increases as the temperature decreases.^{11,12} Generally, the time to produce cracks decreases with increasing nitrate concentration, but this is not universally true. For example, cracks formed in AISI 1080 steel in 0.2 M NH_4NO_3 at 70°C but not in a saturated solution at the same temperature.¹² Also, the time for cracking to occur increases as the pH of the solution increases.¹³

In recent years it has been shown that mild and low-alloy steels are susceptible to cracking in many different environments. Thus, cracking has been observed in liquid ammonia,¹⁴ in water containing both CO and CO₂,¹⁵ in solutions of carbonates and bicarbonates,¹⁶ in solutions containing acetate ions,¹⁷ in phosphate solutions,¹⁸ and in solutions of ammonium carbonate.¹⁹ In addition, cracking in aqueous solutions of

hydrocyanic acid has been reported,²⁰ but in this case it is probable that the cracks were due to hydrogen embrittlement. In most of these cases, cracking was demonstrated using the constant-strain-rate method combined with anodic polarization. The above list indicates that cracking can occur in many different environments, most of which were formerly considered to be innocuous.

Investigations with high-strength steels have been carried out by a number of investigators. Gilchrist and Narayan²¹ studied the behavior of a high-carbon (0.83% C) eutectoid steel in several different metallurgical conditions and showed that cracking occurred in all microstructures, with failures both by active-path corrosion and hydrogen embrittlement. In ferric sulfate solutions, failures did not occur without polarization, but either anodic or cathodic polarization produced cracks. In ammonium nitrate solutions, cracking occurred at the open-circuit potential and on anodic polarization, but cathodic polarization completely prevented attack. Hydrogen sulfide produced cracking under all conditions, but chloride solutions containing sodium arsenate did not produce cracking at the open-circuit potential; cracking did occur, however, with either anodic or cathodic polarization. In general, cold-drawn wires with a fine pearlitic structure were more resistant than quenched and tempered wires, although under the proper conditions both could be cracked.

Asphahani and Uhlig²² showed that when AISI 4140 steel was heat-treated to hardnesses greater than $R_c 42$, cracking occurred in short times in boiling distilled water. Cold-rolling to 60% reduction ($R_c 46.5$) resulted in immunity to cracking in boiling water and 3% NaCl, although in the latter environment, cracking could be produced by control of the potential. In another study by Uhlig et al.²³ a similar effect of cold-rolling was noted with furnace-cooled pearlitic steels. In this case, steels with up to 0.2% carbon were susceptible to cracking in ammonium nitrate solutions, but at greater carbon contents (up to 0.65%) cracking did not occur. Cold-rolling of these steels produced immunity to cracking at all carbon levels.

Phelps²⁴ noted that steels with yield strengths of about 200 ksi or greater are susceptible to cracking in a number of environments, including various natural atmospheres.

The published information generally indicates that the higher the yield strength or hardness of a steel, the greater its tendency to crack. Cold-working the steel reduces, but does not totally eliminate, its susceptibility to cracking.

Because of failures experienced over the years in sour gas and oil wells, a very large amount of information about H_2S cracking has been generated. In these cases, H_2S leads to hydrogen embrittlement of susceptible steels. A recent review article²⁵ summarizes the most significant facts on the subject, and only a few of the pertinent papers will be referenced here.

According to an NACE committee,²⁶ steels with hardnesses of $R_c < 22$ are not expected to be susceptible to H_2S cracking. It has been shown that cracking of susceptible steels occurs with as little as 1 ppm H_2S in solution, although failures take much longer than with higher concentrations.²⁷ It has also been shown that the active species in aqueous solution is the undissociated H_2S molecule, not HS^- or S^{2-} ions.^{27,28} As a result, sulfide cracking is much more likely in acid solution (pH of 2 to 6), where the major part of the sulfide exists as H_2S , than in more alkaline solutions, where dissociation of the H_2S takes place. However, failures have been observed at solution pH values as high as 9.5.^{27,29} The presence of chloride ions in H_2S solutions produces no detectable effect on cracking,^{21,30} and the time to failure is a minimum at 25°C according to Townsend,³¹ or 50°C according to Kawashima et al.²⁸ Generally, cold work has a detrimental effect on H_2S cracking.^{32,33} For example, Baldy³³ demonstrated that with an N-80 steel, 1% cold work lowered its load carrying ability from 70–75,000 psi to 40–45,000 psi in H_2S solutions.

Uhlig³⁴ noted that 3% NaCl solutions containing low concentrations of sulfites or thiosulfates produced cracks in stressed high-strength steels. Cracking did not occur with sulfate. He showed that sulfite and thiosulfate ions, but not sulfate ions, are reduced at a steel surface to hydrogen sulfide, which is the agent responsible for the cracking.

The evidence is very clear that even very low concentrations of H_2S in aqueous environments can produce cracking in high-strength steels. Fortunately, cracking is not likely to occur in strongly alkaline environments such as those associated with concrete. But in acid, neutral,

or slightly alkaline (pH of 7-9.5) solutions, cracking of such steels is highly probable with H_2S present. While H_2S facilitates hydrogen embrittlement of steels, it should be noted that embrittlement can be produced in its absence. Generation of hydrogen on a steel surface, either from corrosion reactions or by external polarization, may allow sufficient atomic hydrogen to enter the steel to embrittle it.

Corrosion of Steel in Concrete and in Organic Compounds

To understand corrosion of metals in concrete, one must have at least a qualitative knowledge of the chemical nature of concrete. The following paragraph taken directly from a translation of a recent paper by Rieche³⁵ is a brief description of the chemistry of concrete:

The setting and hardening of cement are consequences of chemical reactions between its components and the mixing water. The products of these reactions are gel-form, i.e., extremely fine-grained fiber, sheet, and tubular-shape particles which initially occur primarily in the water-filled spaces that occur between the cement particles and the additive particle grains. They form an initially local interwoven structure which is continuously strengthened by further products of hydration, and form a stiff bridgework connecting the solid particles. As a result of this, their mobility is increasingly restricted, and the cement grout, mortar, or concrete sets. This gel, which is formed in the process of hardening, which contains water, but is rigid, and which forms as the result of progressive hydration, is permeated by a large number of gel and capillary pores. The gel pores exhibit diameters of the order of magnitude of only a few molecular diameters (10^{-3} to 10^{-2} μm) and run throughout the entire cement stone in a matrix-like fashion. In contrast, the capillary pores are in the range from 10^{-2} to 1 μm . The $Ca(OH)_2$ formed in the hydration of the cement is deposited in both the gel pores and the capillary pores. Whereas the relatively wide capillary pores can dry out, depending on the humidity conditions of the environment, the gel pores of the cement-glue are always filled with water, which is itself saturated with calcium hydroxide. Just like the components of the concrete, the steel is also firmly surrounded by well-adhering cement gel. Thus the surface of a steel embedded in concrete is directly surrounded by saturated $Ca(OH)_2$ solution which exhibits a pH value of 12.6, and thus causes the well-known corrosion protection of the steel by passivation.

Thus it seems appropriate to perform corrosion tests in an aqueous lime solution which serves as a model for concrete, and some investigators have done this.

Because of the alkaline nature of concrete, reinforcing or prestressing steels have good corrosion resistance when the concrete is correctly formulated and applied. One method by which the alkalinity of the concrete is destroyed is through the process of carbonation, that is, the reaction of CO_2 (usually from air) with the Ca(OH)_2 in the concrete. This is a slow and continuing process and may, in time, penetrate the concrete to a depth of 1/4 to 1 in., depending on the quality of the concrete.³⁶ As a result of this reaction with CO_2 , the pH of the environment becomes as low as 9 to 9.5. At this pH, steel is no longer passive,³⁷ and corrosion of the steel is possible if water and oxygen are available. Furthermore, if the concrete contains sulfides, as in cases where blast-furnace slags are incorporated in it, H_2S cracking can be expected at pH's of 9 to 9.5.^{27,29}

It is the permeability of the concrete as well as its thickness over reinforcing or prestressing steel that determines how well the steel is protected. Obviously, highly permeable concretes will undergo carbonation and will allow the diffusion of corrosive materials in the environment (Cl^- , O_2 , H_2O , CO_2) to the steel surface much more readily than will very dense concretes. The water-cement ratio is the primary factor in determining the permeability of concrete. Szilard³⁷ recommends that the ratio not exceed 0.5, with the preferred value being 0.40. Even with dense, impermeable concretes, a minimum concrete thickness over the steel of 1 in. in mild environments and 2-1/2 in. in marine environments is recommended.

Chloride is an important cause of the corrosion of steels, and a number of investigators have studied the effect of this ion on corrosion of steel in concrete. Hausmann,³⁸ using saturated, as well as more dilute, lime solutions with chloride additions as test media, concluded that in aerated solutions, corrosion of steel does not occur if the molar ratio of chloride to hydroxide ions is less than 0.6; in saturated lime solutions, attack began at a chloride concentration of about 700 ppm,

but in the absence of oxygen much higher concentrations of chloride could be tolerated. Since Hausmann used unstressed specimens, SCC was not observed, but pitting and general corrosions were.

Monfore and Verbeck³⁹ studied corrosion of prestressing wire (composition unspecified) embedded in various concretes containing added CaCl_2 . The wires were externally loaded to 140 ksi, and after 28 days, corrosion in the form of pitting was observed on all specimens. Cold-drawn wires supplied by the manufacturer (presumably using cooled and lubricated dies) showed no tendency to crack, but wire cold-drawn in the laboratory, using an uncooled and unlubricated die, tended to develop longitudinal cracks, that is, cracks parallel to the direction of applied stress. No sign of conventional SCC was found. Treadaway⁴⁰ also studied the behavior of cold-drawn steel (0.8%C) stressed to 70% of its ultimate tensile strength in concrete containing 2 to 5% CaCl_2 . After periods ranging from 2 to 27 months, no cracks were found, although severe general corrosion and pitting occurred, the extent of attack being greater the higher the CaCl_2 concentration. Similar results were obtained by Godfrey.⁴¹

On the other hand, Rieche³⁵ showed that cracking as well as pitting of carbon steel (0.4% C) could occur in saturated limewater to which chloride was added, if the applied stress and chloride concentration were high enough. Over a large concentration range, open-circuit potentials fell within an SCC region of potential so that cracks in stressed materials could develop spontaneously. His data indicated that at chloride concentrations below about 0.01 M (350 ppm), cracking should not be possible. He therefore postulated that limiting the chloride concentration to a maximum of 300 ppm would prevent SCC. The reason why cracking was observed by Rieche and not by the other investigators³⁹⁻⁴¹ is not completely clear from the information presented. It has been noted by several investigators^{35,36,39} that the components of cements are capable of chemically binding chloride so that it is not available to produce corrosion, and this may partly explain the difference; that is, the "effective" chloride concentration in the concrete could have been much less than the total chloride, perhaps less than 0.01 M. Regardless of the reason, it is clear that calcium chloride should not be used as an additive to concrete that is to be in contact with steel, nor should seawater or unwashed sea sand be used in mixing the concrete.

Generally, H_2S cracking of steel in concrete is not expected because of the high alkalinity of concrete, but Rieche³⁵ and Cornet⁴² report apparent cases of embrittlement caused by the presence of H_2S where the alkalinity of the concrete was diminished or when cracks in the concrete allowed H_2S to come in contact with steel. On the other hand, Rieche³⁵ showed that in saturated lime solutions containing 0.02 M or greater CaS , cracking of high-strength steels could occur. Using two similar steels, each containing about 0.4% carbon, he showed that neither cracked on cathodic polarization, but both cracked on anodic polarization. One of the steels cracked at the open-circuit potential, whereas anodic polarization was necessary to produce cracking in the other. With only $Ca(OH)_2$ solutions, cracking could not be produced under any conditions. This appears to be the first time that active-path SCC has been reported in the presence of sulfide.

Rieche³⁵ also examined the effect of nitrate concentration in saturated $Ca(OH)_2$ solutions on the cracking of steel and showed that at nitrate concentrations greater than 0.01 M (620 ppm NO_3^-), cracking occurred only on anodic polarization. Regardless of potential, no failures occurred at concentrations of 0.01 M or less.

The importance of pockets of air in concrete that are in contact with steel has been pointed out by several investigators.^{36,38,39,43} All data indicate that steel corrodes more severely at voids in the concrete than on adjoining areas covered with cement. Thus in filling conduits containing prestressing steel tendons, care must be taken to prevent such air pockets from forming; compressed air should never be used to force grouts into conduits.

One form of failure that is possible with grouted tendons is dissimilar-metal (galvanic) corrosion. If, for example, a stressed tendon embedded in grout is electrically coupled with a more active metal such as aluminum or zinc, the tendon becomes the cathode of the cell and under some conditions hydrogen can be liberated on its surface, enter the metal, and embrittle it. Examples of such failures are presented in the literature.^{35,44} The hydrogen embrittlement of galvanized high-strength steels has also been studied;⁴⁵ when zinc was removed from small areas of the surface and the steel placed in concrete, cracking

usually occurred at about 80% of the yield stress. Furthermore, examples of cracking of prestressed steels coupled to more noble metals have been cited by Rieche,³⁵ and in these cases the cracking was apparently due to active-path SCC. In addition to dissimilar-metal cells, similar types of electrochemical cells may develop because of differences in concentration of chloride, oxygen, acidity, and possibly other materials along a wire. Stray dc currents such as from an improperly grounded welding machine can also produce corrosion.

From the above considerations it is apparent that the corrosion of steels in concrete is not a problem if simple and reasonable precautions are taken in making and applying the grout or concrete.

In one reported incidence of corrosion of steel tendons that were presumably protected by an organic substance, stray currents appear to have been responsible for the observed damage.⁸ A heavy petroleum grease containing a sodium petroleum sulphonate as a wetting agent coated all surfaces. Contamination of the coated tendons with water resulted in emulsification of the grease on part of each tendon. Examination of these tendons six months after installation in the ducts showed pits up to 2 mm deep under both emulsified and sound grease. In laboratory tests with identical tendons, some coated with emulsified grease and some with sound grease, no pits or other forms of attack occurred, but on anodic polarization, pits formed identical to those observed in the ducts.

The only other case of failures of tendons protected by organic materials that we are aware of are those observed in a concrete thermal cylinder test at Oak Ridge National Laboratory and referred to in the Introduction.¹ In that case the tendons were protected by a wax, but water inadvertently entered some of the ducts containing the tendons. In addition, improperly formulated epoxy resin in the cylinder added high concentrations of nitrogen compounds to the environment. It was suspected that a nitrogen compound, possibly ammonium nitrate, was the responsible agent.

Unfortunately, the information available on the behavior of steels when coated with greases or other protective organic compounds is very limited. Also, the chemical stability of these compounds over very long periods of time and the effects of any degradation products on corrosion products on corrosion are not well known.

EXPERIMENTAL INVESTIGATION

Experimental Considerations

The approach to studying stress-corrosion cracking that was used in many former investigations involved exposing candidate materials, stressed to some predetermined level, in a given environment, and measuring the time to failure. When specimens cracked in less time than the duration of the test, the susceptibility of the material to cracking was established. If the material did not crack during the test, the material was considered resistant to cracking in the environment. To be sure of immunity, however, one would have to expose the stressed material for very long times — probably as long as the intended use of the object. Obviously this is not practical in most cases. Furthermore, cracking is statistical in nature, and to obtain significant data, relatively large numbers of specimens should be exposed under each test condition, yielding a distribution of failure times. Thus, with conventional stress-corrosion cracking tests, one is usually faced with large numbers of tests conducted for long periods of time if one is to have confidence in knowing the susceptibility of a given alloy to cracking in a specific environment.

Another approach to the study of stress-corrosion cracking uses the constant-strain-rate method as described by Humphries and Parkins.³ With this technique, a tensile-type specimen is exposed to the test environment and is pulled at a very slow constant rate until fracture occurs, usually within a period of a few days at most. By comparing reduction in area, elongation, and/or time to failure under different conditions, the relative susceptibility of a material to cracking in different environments can be established. Examination of the fracture surface and metallographic examination of the surface in the gage section can provide additional information about the fracture process. Additional insight into the cracking process and the influence of changes in the oxidizing potential of the solution can be obtained by impressing an electrochemical potential on the specimen using a potentiostat and studying the time to failure at different potentials. Even though all

the subtleties of the constant-strain-rate technique may not be fully understood, the data obtained from these tests provide engineering information on the properties of materials under controlled environmental conditions. While this test method provides information on the tendency of a material to crack, it does not provide direct information on the statistical probability of cracking at a specific stress level.

In view of the above considerations and because of budgetary and time limitations, the slow-strain-rate method was used to examine the cracking tendency of cold-worked AISI 1080 steel tendon wires in selected environments. The general corrosion rate of the steel under several conditions was also determined. Most of the experiments were conducted in near neutral environments because at these pH values attack is usually more severe than in alkaline solutions such as exist in concretes. Also, no attempt was made to study pitting and the cracking that frequently originates at the base of pits.

Experimental Procedures

The tensile tests described here were conducted on the center straight wire of a seven-wire tendon made from cold-worked AISI 1080 steel and conforming to ASTM A 416, grade 270. The diameter of the wire was 5 mm (0.20 in.), and for the present test the surface of the wire was used as received, except surface rust was removed with fine emery paper. For the stress-corrosion tests, the wire in the presence of the test environment was strained at a constant rate in an Instron tensile machine which had a maximum capacity of 4500 kg (10,000 lb). The length between the grips was 0.20 m (8 in.), but only the center 75-mm (3-in.) length was exposed to the solution, which was held in a polyvinyl chloride bottle. A gage section was not machined in the wire, since we wanted to retain the original surface condition of the cold-drawn wire. To prevent any unusual effects at the solution-air interface or in the crevice when the wire passed through a stopper in the bottom of the bottle, the 75-mm test length was defined by the use of a stop-off varnish and was covered with solution both above and below the test section. All tests were conducted at the open-circuit corrosion potential.

The minimum crosshead speed of the tensile machine was $8.33 \times 10^{-2} \mu\text{m/s}$ (0.0002 in./min) and with the 0.20-m length of the specimen corresponded to a strain rate of $4.17 \times 10^{-7}/\text{s}$. This minimum strain rate was used in all tests except two. After a specimen failed a 25-mm (1-in.) length, including one failed end, was metallographically polished along the axis to look for cracks on the surface exposed to the solution.

The general corrosion rates of AISI 1080 steel tendon wires were determined in several different aqueous environments. In one series of tests, weighed 25-mm (1-in.) lengths of wire were totally immersed in different solutions. In these tests the 5-mm-diam wires were placed in 6-mm-diam glass test tubes and were immersed to a depth of about 10 mm above the specimen height in different test solutions, which included dilute solutions of chloride, nitrate, and sulfate, and potable and distilled water. The total volume of solution was only about 500 mm³, and these conditions were intended to simulate those that could exist in the interstices of wires in the tendons. Evaporative losses were replaced periodically with distilled water. Although the tubes were open to the air, the small clearance between the tube wall and the specimen restricted access of oxygen to the specimen. As corrosion proceeded, the buildup of corrosion products on the specimen further limited access of oxygen. These tests lasted for 2000 hr, but duplicate specimens were removed from test after 1000 hr. All specimens were descaled in Clarke's solution⁴⁶ (2 g Sb₂O₃ and 5 g SnCl₂ dissolved in 100 ml of 37% HCl) before final weighing. Other specimens that had been exposed to some of the solutions for 2000 hr were analyzed for their hydrogen content. In these cases the specimens remained in test until analyzed. The corrosion product was then removed with emery paper, and the hydrogen in the steel was determined by vacuum fusion.

In another series of tests, single wires 0.3 m (12 in.) long were immersed in dilute solutions of Na₂SO₄ and NaCl and in distilled water at room temperature for nine months. The volume of water was about 1 liter and was exposed to the air; water lost by evaporation was replaced every few days. The test specimens extended above the water level so that attack at the water-air interface could be examined. At the end of the test the specimens were descaled in Clarke's solution, and the diameter of the wire above and below the waterline was compared.

Results

The results obtained from the constant-strain-rate tests are shown in Table 1. Tests 1 and 2 confirmed that the tensile strength conformed to ASTM A 416 grade 270 (minimum tensile strength of 190 kg/mm^2). Since

Table 1. Results Obtained from Constant-Strain-Rate^a
Tests with AISI 1080 Steel Wires

Test	Test Medium	Temperature (°C)	pH Start/Finish	Time to Break (hr)	Load (kg)	Cracks
1	Air	21		0.2	3990	No
2	Air	21		55.5	4280	No
3	0.2 M NH_4NO_3	21	5.0/7.0	57.5	4100	No
4	0.2 M NH_4NO_3	21	5.3/7.0	66.6	4010	No
5	0.2 M NH_4NO_3	38	5.3/7.7	47.0	3980	No
6	0.2 M NH_4NO_3	52	5.3/7.3	49.5	3970	Yes
7	0.2 M NH_4NO_3	66	5.0/7.4	50.5	3970	Yes
8	0.2 M NH_4NO_3	66	5.0/7.0	5.2	3950	Yes
9	0.01 M KCl + Ca^{+}	21	11.9/11.5	55.3	3990	No
10	0.01 M KCl	66	5.3/6.3	60.8	3970	No
11	0.03 M KCl	21	5.5/6.4	58.1	4010	No
12	0.03 M KCl + HCl	21	3.0/3.1	60.8	4010	No
13	0.1 M NaHSO_3	21	4.5/6.5	44.0	3920	Yes
14	0.1 M H_2S + HCl	21	3.0/3.0	6.6	1530	Yes
15	0.1 M H_2S	21	4	4.7	1130	Yes
16	0.001 M Na_2S	21	11.1/11.2	57.8	3920	No
17	0.001 M Na_2S + HCl	21	7.4/7.7	53.8	3990	No
18	0.001 M Na_2S + HCl	21	4.3/6.0	19.3	3600	Yes
19	0.003 M Na_2S + HCl	21	4.3/7.0	17.0	3490	Yes
20	0.003 M Na_2S + HCl	21	6.3/	52.0	4010	No
21	0.003 M Na_2S + HCl	21	4.3/	54.8	4010	No
22	Deionized H_2O	21	7	57.5	3980	No
23	Deionized H_2O + CO_2	21	4.0/4.0	55.8	4010	No
24	H_2O + CO_2 + 750 ppm H_3AsO_3	21	5.1/5.1	57.6	3980	No
25 ^b	Zn plate, H_2O	21	5.8/6.3	60.6	4030	No
26 ^c	Zn plate, 0.2 M Na_2SO_4	21	5.7/6.0	54.9	4030	No
27 ^c	Corroded in H_2O , three days	21	5.9/6.5	50.9	4010	No

^aThe strain rate was 4.17×10^{-2} /s except in test 1, where it was 1.08×10^{-4} /s, and in test 8, where it was 4.17×10^{-4} /s.

^bSpecimen except center 12.5 mm (0.5 in.) was zinc-plated before test.

^cSpecimen was placed in 8-mm glass tubing and surrounded by tap water for three days before straining.

the entire wire was of constant diameter, there was concern that failure would occur preferentially at the grips, but this problem was not encountered. Tests 3 through 8 were conducted with 0.2 M NH_4NO_3 , since this reagent was suspected of causing failure in the thermal cylinder test at Oak Ridge National Laboratory.¹ No signs of cracks were found in specimens tested at 21 and 38°C, but cracks were found at 52 and 66°C.

Figure 1 shows representative views of the specimens tested at the four temperatures when the strain rate was $4.17 \times 10^{-7}/s$. At a tenfold greater strain rate (test 6), cracks were noted, but the depth of penetration was less than at the lower strain rate. Even though cracks were evident in the steel at the two higher temperatures, no effect on either the time to failure or on the load at failure was noted. The large diameter of the wire and the relatively slow rate of crack propagation were responsible for this observation. With a smaller-diameter test section and a slower strain rate, the effect of the cracks on the time to failure would have been obvious. The formation of cracks at $66^{\circ}C$ and the absence of cracks at $21^{\circ}C$ agree with the results obtained with U-bend specimens exposed to the same solution; U-bends cracked in a few days at $66^{\circ}C$ but remained intact at $21^{\circ}C$ during 100-day tests.¹

No cracks were found in any of the specimens exposed to chloride-containing environments (tests 9-12), regardless of the pH of the solution. This is in conformance with the generally accepted belief that chloride ion is not an aggressive cracking agent for steels of this type, although Rieche³⁵ did observe cracking in a steel of 0.4% carbon content in the presence of chloride ions.

There appeared to be some evidence of cracking in 0.1 M NaHSO₃ (test 13) as illustrated in Fig. 2, which shows one of several localized penetrations along the surface of the wire near the failed region. Only in the case of ammonium nitrate solutions were similar penetrations observed. Obviously, the ammonium bisulfite was not reduced to hydrogen sulfide at a rate fast enough to produce hydrogen embrittlement as reported by Uhlig.³⁴

As expected, H₂S produced rapid failure in the test specimens when the pH was low and the H₂S concentration was relatively high (tests 14 and 15). Figure 3 shows cracks observed in test 15. In 0.001 M Na₂S at a pH of 11.1 or 7.4 (tests 16 and 17), no cracking was observed, but when the pH was adjusted to 4.3 (test 18), cracking occurred. At this lower concentration, failure took longer than at the higher sulfide concentrations, and the cracks were generally finer (Fig. 4). Cracking occurred slightly faster when the Na₂S concentration was increased to 0.003 M (test 19), but the nature of the cracks was the same as shown

Fig. 1. Attack on AISI 1030 Steel Tendon Wire in 0.2 M NH_4NO_3 at Different Temperatures. Strain rate, $4.17 \times 10^{-7}/\text{s}$. 250 $\times$.

Fig. 2. Attack on AISI 1080 Steel Tendon Wire in 0.1 M NaHSO₄ at Room Temperature. 100 $\times$.

[REDACTED] Y-141620

[REDACTED] Y-141619

Fig. 3. Cracks Formed in AISI 1060 Steel Wire in 0.1 M H₂S (pH ~ 4) at Room Temperature. 100×.

Fig. 4. Cracks Formed in AISI 1080 Steel Vendon Wire in 0.001 M Na_2S with pH Adjusted to 4.3.

in Fig. 4. When the sulfide concentration was reduced to 0.0003 M (tests 20 and 21), no cracking was observed. Although the solutions were sparged with nitrogen before the Na_2S was added and the polyvinyl chloride bottle containing the solution was stoppered, it is probable that the small amount of sulfide in the solution was oxidized early in the test to sulfur by traces of oxygen in the bottle. Certainly, at the end of the test no odor of hydrogen sulfide could be detected above the solution.

Deionized water either by itself (test 22) or with carbon dioxide bubbling through it (test 23) did not produce cracking. Cracking also did not occur when the steel was corroded in water for three days before the specimen was pulled. Similarly, the presence of carbon dioxide and 750 ppm arsenious acid in water failed to produce cracks (test 24). In the latter case the wire was heavily pickled in uninhibited hydrochloric acid and remained in the test solution overnight before the specimen was pulled.

Two specimens (tests 25 and 26) were electroplated with 0.013 mm (0.0005 in.) of zinc except for a 12.5-mm (0.5-in.) length in the middle of the wire. When exposed to the aqueous environment, the unplated area was cathodic to the zinc, and the possibility of hydrogen embrittlement existed. However, neither in pure water nor in 0.2 M Na₂SO₄ did cracking occur.

In all cases except where cracking occurred in the presence of sulfide, cup-cone-type failures were observed, and the reduction in area varied randomly between 36 and 43% except in test 3, when it was 47%. In tests 14 and 15, no reduction in area could be measured, and in tests 18 and 19 the reduction in area was only 4%. Even though cracks were not observed in most cases, most of the failures occurred in the 75-mm (3-in.) length exposed to the test solution. Only in tests 12, 16, 20, 21, 25, 26, and 27 did the wire break outside the solution-exposed length, and in tests 25 and 26 the exposed steel was cathodically protected by zinc. The above observation suggests that general corrosion of the steel contributed to the failure process, although the amount of corrosion that occurred during the test period must have been very small.

The corrosion rates observed on the tendon wires exposed to the very small volumes of solutions are shown in Table 2. After 1000 hr in some cases and in most cases after 2000 hr, the volume of corrosion products that had formed prevented removal of the specimen from the glass tube, and it was necessary to break the tube to recover the specimen. Table 2 shows that under these conditions, corrosion rates were low and nearly independent of the environment except in one case; both specimens exposed for 2000 hr in 0.001 M NaNO₃ corroded at rates of nearly 25 µm/year (1 mpy). There was no significant localized attack in any case.

The hydrogen content of specimens exposed for 2000 hr are shown in Table 3. The control specimen had been exposed only to air. The hydrogen content of the steel was low, but exposure to any of the environments produced a detectable increase of the hydrogen content. Comparison of these results with those in Table 2 shows that the amount of hydrogen in the steel was not proportional to the corrosion rate. However, the smaller hydrogen content in the nitrate solution may be related to the oxidizing nature of the nitrate ion.

Table 2. Corrosion of AISI 1080 Steel
Tendon Wires in Different
Environments

Test Environment	Time (hr)	Average Corrosion Rate ($\mu\text{m}/\text{year}$)
Potable water	1000	5.8
	2000	5.3
Distilled water	1000	5.1
	2000	5.3
0.03 M NaCl	1000	6.6
	2000	7.9
0.01 M NaCl	1000	6.4
	2000	9.7
0.01 M NaNO ₃	1000	11.2
	2000	8.1
0.001 M NaNO ₃	1000	7.4
	2000	23.1
0.2 M Na ₂ SO ₄	1000	8.9
	2000	13.5
0.02 M Na ₂ SO ₄	1000	7.6
	2000	13.2
0.002 M Na ₂ SO ₄	1000	5.8
	2000	7.6

Table 3. Hydrogen Content of AISI
1080 Steel Tendon Wires Exposed
to Different Environments
for 2000 hr at Room
Temperature

Environment	Hydrogen Content (ppm)
Control	1.14
Potable water	1.99
0.03 M NaCl	3.51
0.01 M NaNO ₃	1.65
0.2 M Na ₂ SO ₄	2.89

The wires (0.30-m lengths) exposed to large volumes of solution that was freely exposed to air showed considerably more corrosion than did the short specimens exposed to small volumes of solution with restricted access to oxygen (air). Table 4 shows the corrosion rate calculated from the difference in diameter above and below the waterline after exposures of nine months.

Table 4. Corrosion Rates for
AISI 1080 Steel Tendon Wires
Exposed for Nine Months to
Solutions with Free
Access to Air

Environment	Corrosion Rate (mm/year)
Distilled water	76
0.05 M NaCl	152
0.1 M Na ₂ SO ₄	254

Table 4 also shows that with free access of oxygen the steel corroded at a greater rate than when access to oxygen was limited. In all of the above cases, attack was greatest at the solution-air interface, but localized attack in the form of pitting was noted below the waterline in all cases. Figures 5, 6, and 7 show the corrosion observed. In each figure (a) shows attack at the waterline, (b) shows representative attack on the submerged part of the wire, and (c) compares a cross section through the steel at the waterline with one above the waterline and illustrates the maximum reduction in cross sections produced by corrosion.

DISCUSSION

The experimental results obtained with the AISI 1080 steel are in general agreement with published data. Cracking was observed in the solutions containing H₂S when the pH was low but not when the pH was 7 or above. Thus, steel tendons surrounded by correctly formulated and

Fig. 5. Corrosion of AISI 1080 Steel Tendon Wire During a 9-Month Exposure to Distilled Water at Room Temperature. (a) Attack at waterline; (b) attack on submerged wire; (c) comparison of cross sections at the waterline and above the waterline. Diameter of wire is 5 mm.

applied concrete in which the pH of the incorporated water is greater than 12 should not become embrittled, even if the concrete contains appreciable concentrations of sulfide. On the other hand, it is doubtful that water in contact with greases or waxes would develop pH values greater than 9.5. Below this value, cracking has been observed.

The only other environments in which cracking was experienced were ammonium nitrate and sodium bisulfite solutions. In both cases it is likely that cracking could have been eliminated if the pH of the solution had been increased. In the nitrate solution, temperatures also had to be above 38°C (100°F) to produce cracks. In the case of the sodium bisulfite solution, there was only superficial evidence of cracking, and additional testing should be conducted before any definite conclusion is drawn about the susceptibility of AISI 1080 steel to cracking in bisulfite solutions. However, sodium bisulfite would not exist in strongly alkaline solutions (sodium sulfite becomes the stable form), and in the alkaline environment, reduction to hydrogen sulfide would be unlikely. All other attempts to produce cracks in AISI 1080 steel were unsuccessful.

On the other hand, AISI 1080 steel has poor corrosion resistance to most aqueous neutral solutions and water when exposed to air, and in such environments reduction in cross-sectional area could lead to tendon failures. In tests reported here, attack was particularly severe at the waterline. Although tests were not conducted under alkaline conditions, attack would undoubtedly have been much less. In small volumes of solution with limited access to oxygen, corrosion was much less, and only a small amount of the corrosion-product hydrogen entered the steel. The amount was probably so small that it would have no effect on embrittlement of AISI 1080 steel. One of the reasons for using tendons made from this steel is that it is less susceptible to hydrogen embrittlement than many other more highly alloyed high-strength steels.

The corrosion of steel in concrete has been the subject of many investigations, and the literature indicates that with reasonable precautions, corrosion is not a serious problem. One of the necessary precautions is to limit the concentration of chloride ions to a maximum of 300 ppm (approximately 0.01 M), nitrate to no more than 620 ppm (0.01 M), and the sulfide (as metal sulfide) to 640 ppm (0.02 M). These are maximum values

recommended by Rieche³⁵ and are appreciably higher than those specified in U.S. Nuclear Regulatory Guide 1.107 [100 ppm Cl (200 ppm if pH > 12), 100 ppm NO₃, 2 ppm S (soluble)]. To achieve these lower values should present no undue hardship or expense, and therefore it appears reasonable to take advantage of the added safety factor. Another precaution is to use minimum water in preparing the grout (water/cement ratio = 0.40). This produces a grout with minimum porosity and greatly reduces carbonation, which could possibly lead to hydrogen embrittlement in extreme cases. Application of appropriate standards and procedures should result in tendon lifetimes at least equal to the design life of the vessel. The fact that many prestressed concrete vessels, bridges, and other structures are in use, many of them for many years, is proof that corrosion of prestressing steel in grouts can be reduced to an insignificant level.

There appears to be much less experience using greases or other organic compounds in protecting tendons in prestressed structures, and therefore the problem of assessing the potential for corrosion is not an easy one. Generally, such organic materials provide a very protective environment so long as they remain intact and free of water. Even with low levels of impurities, the greases are nonconductors (if dry) and as such should produce negligible corrosion. However, the chemical stability of these materials over very long periods of time — in a low radiation field if used in nuclear reactor containment vessels — and the nature and corrosivity of the degradation products are not well documented. One apparent point is that if water is present in the grease-filled ducts containing the tendons, the pH of the water will not be as alkaline as the water in a grout, and, therefore, the potential for corrosion would be greater with grease than with grout.

Two areas of tendon corrosion that have been inadequately investigated are (1) the initiation of cracks from the base of pits or in crevice regions, and (2) cracking that could occur because of galvanically coupling stressed tendons to a metal or alloy of different electrochemical activity. As noted earlier, the solutions that exist in active pits or crevices tend to be acid, and if a sulfide inclusion in the steel were exposed to such a solution, a relatively high concentration of H₂S would exist locally, possibly enough to cause failure; or even in the absence of

H₂S the acid environment may be able to produce active-path SCC as postulated by Brown.² Ideal sites for crevice corrosion exist among the strands of tendons.

In the case of galvanic couples, two questions that have not been answered are (1) how readily are high-strength steel tendons embrittled by coupling to more active metals, and (2) can coupling to more noble metals lead to active-path SCC in an otherwise innocuous environment? The fact that tendon steels are usually cold drawn should retard active-path SCC, but probably facilitate hydrogen embrittlement.

SUMMARY

The general forms of localized corrosion were discussed, and the recent literature concerning the general corrosion and stress-corrosion cracking of carbon steel was reviewed. The behavior of high-strength steels used as prestressing tendons in either concrete grouts or protective organic materials (waxes or greases) was also reviewed. Although very little information exists about corrosion of steels in the latter environment, organic substances normally produce insignificant attack on steel; there is however, a dearth of information on the long-term stability of such compounds and the corrosiveness of their degradation products. The literature shows that the corrosion of high-strength steels in correctly formulated and applied concrete is very low, even if appreciable concentrations of chloride, nitrate, or sulfide salts are present.

Stress-corrosion cracking tests carried out with AISI 1080 steel tendon wires, using the constant-strain-rate method, produced the results expected from literature-reported information. Thus, steel wires cracked rapidly in solutions containing hydrogen sulfide if the pH of the solution was 7 or less but not in alkaline solutions. Cracks also formed in 0.2 M ammonium nitrate but only if the temperature was above 38°C (100°F). Indications of cracking were also found in a sodium bisulfite solution.

AISI 1080 steel wires corroded appreciably in air-saturated solutions of 0.2 M Na₂SO₄, 0.05 M NaCl, and in distilled water; attack was particularly severe at the waterline. Attack such as noted could lead to failures due to reduction in the cross section of the load-carrying tendons. In

small volumes of similar solutions that had only limited access to air, AISI 1080 steel showed lower corrosion rates and only very small uptake of hydrogen. The severity of attack on steel tendons in the event water pockets form around them will depend to a large measure on the availability of oxygen.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge assistance from the following people in the preparation of this report: E. J. Lawrence, L. T. Ratcliff, and Steve Anderson for help in conducting the experiments; M. D. Allen for preparation of the metallographic specimens; Adroit for editing the report; and Kathryn A. Witherspoon for typing the manuscript.

REFERENCES

1. D. A. Canonico, J. C. Griess, and G. C. Robinson, *Final Report on PCRV Thermal Cylinder Axial Tendon Failures*, ORNL-5110 (January 1976).
2. B. F. Brown, Ed., *Stress-Corrosion Cracking in High Strength Steels and Titanium and Aluminum Alloys*, Naval Research Laboratory, Washington, D.C., 1972, pp. 4-5.
3. M. J. Humphries and R. N. Parkins, "The Influence of Oxide Films on Stress Corrosion Cracking of Carbon Steels," pp. 384-92 in *Fundamental Aspects of Stress Corrosion Cracking*, R. W. Staehle, Ed., National Association of Corrosion Engineers, Houston, 1969.
4. B. F. Brown, *Ibid.* pp. 18-77.
5. L. L. Shrier, *Corrosion*, Vol. 1, pp. 3.3-3.23, Wiley, New York, 1963.
6. H. H. Uhlig, *Corrosion and Corrosion Control*, 2nd. ed., Wiley, New York, 1971, pp. 93-126.
7. H. H. Uhlig, Ed., *The Corrosion Handbook*, Wiley, New York, 1948, pp. 124-43.
8. P. J. Hollingum, *Corrosion of Pre-Stressing Wires of Concrete Pressure Vessels*, Tech. Report of British Engine Boiler and Electrical Insurance Co., Ltd., New Series, Vol. X, pp. 87-93 (1971).

9. R. N. Parkins, "Stress Corrosion Cracking of Low-Strength Ferritic Steels," pp. 167-85 in *The Theory of Stress Corrosion Cracking in Alloys*, J. C. Scully, Ed., NATO, Brussels, 1971.
10. J. E. Reinoehl and W. E. Berry, "Natural Conditions for Caustic Cracking of Mild Steel," *Corrosion* 28: 151-60 (1972).
11. H. Mazille and H. H. Uhlig, "Effect of Temperature and Some Inhibitors on Stress Corrosion Cracking of Carbon Steels in Nitrate and Alkaline Solutions," *Corrosion* 28: 427-33 (1972).
12. J. Flis, "Role of Temperature in Stress Corrosion Cracking of Iron in Nitrate Solutions," *Br. Corros. J.* 10: 79-84 (1975).
13. R. N. Parkins and R. Usher, "The Effect of Nitrate Solutions in Producing Stress-Corrosion Cracking in Mild Steel," pp. 289-95 in *First International Congress on Metallic Corrosion*, London, Apr. 10-15, 1961, Butterworths, London, 1962.
14. A. W. Loginow and E. H. Phelps, "Stress-Corrosion Cracking of Steels in Agricultural Ammonia," *Corrosion* 18: 299-309 (1962).
15. M. Kowaka and S. Nagata, "Transgranular Stress Corrosion Cracking of Mild Steels and Low-Alloy Steels in the $H_2O-CO-CO_2$ System," *Corrosion* 24: 427-29 (1968).
16. J. M. Sutcliffe, R. R. Fessler, W. K. Boyd, and R. M. Parkins, "Stress Corrosion Cracking of Carbon Steel in Carbonate Solutions," *Corrosion* 28: 313-20 (1972).
17. J. G. Parker and W. G. Pearce, "Stress Corrosion Cracking of a Low Alloy Steel in Acetate Solutions," *Corrosion* 30: 18-23 (1974).
18. W. R. Middleton, "Stress Corrosion Cracking of Mild Steel in a Phosphate Solution," *Br. Corros. J.* 8: 62-65 (1973).
19. D. Hixon and H. H. Uhlig, "Stress Corrosion Cracking of Mild Steel in Ammonium Carbonate Solution," *Corrosion* 32: 56-59 (1976).
20. H. Buchholtz and R. Pusch, "Contribution on the Transcrystalline Stress Corrosion Cracking of Steel," *Stahl Eisen* 62: 21-30 (1942).
21. J. D. Gilchrist and R. Narayan, "Environmental Cracking of Eutectoid Steel," *Corros. Sci.* 11: 281-96 (1971).
22. A. Asphahani and H. H. Uhlig, "Stress Corrosion Cracking of 4140 High Strength Steel in Aqueous Solutions," *J. Electrochem. Soc.* 122: 174-79 (1975).

23. H. H. Uhlig, K. E. Perumal, and M. Talerman, "Stress Corrosion Cracking of Iron in Nitrates: Effect of Carbon and Low Alloying Additions," *Corrosion* 30: 229-31 (1974).
24. E. H. Phelps, "A Review of the Stress Corrosion Behavior of Steels with High Yield Strengths," pp. 398-410 in *Fundamental Aspects of Stress Corrosion Cracking*, R. W. Staehle, Ed., National Association of Corrosion Engineers, Houston, 1969.
25. J. B. Greer, "Factors Affecting the Sulfide Stress Cracking Performance of High Strength Steels," *Mater. Perform.* 14(3): 11-22 (1975).
26. NACE Committee T-1F, "Sulfide Cracking Resistant Metallic Materials for Valves for Production and Pipeline Service," *Mater. Prot.* 5(9): 81-82 (1966).
27. C. M. Hudgins, R. L. Glasson, P. Mehdizodeh, and W. M. Rosborough, "Hydrogen Sulfide Cracking of Carbon and Alloy Steels," *Corrosion* 22: 238-51 (1966).
28. A. Kawashima, K. Hashimoto, and S. Shimodaira, "Hydrogen Electrode Reaction and Hydrogen Embrittlement of Mild Steel in Hydrogen Sulfide Solutions," *Corrosion* 32: 321-31 (1976).
29. T. G. McCord, B. W. Bussert, R. M. Curran, and G. C. Gould, "Stress Corrosion Cracking of Steam Turbine Materials," *Mater. Perform.* 15(2): 25-34 (1976).
30. L. M. Dvorack, "Sulfide Stress Corrosion Cracking of Steel," *Corrosion* 26: 177-88 (1970).
31. H. E. Townsend, Jr., "Hydrogen Sulfide Stress Corrosion Cracking of High Strength Steel Wire," *Corrosion* 28: 39-46 (1972).
32. R. S. Treseder and T. M. Swanson, "Factors in Sulfide Corrosion Cracking of High Strength Steels," *Corrosion* 24: 31-39 (1968).
33. M. F. Baldy, "Sulfide Stress Cracking of Steels for API Grade N-80 Tubular Products," *Corrosion* 17: 509t-13t (1961).
34. H. H. Uhlig, "Effect of Aqueous Sulfides and Their Oxidation Products on Hydrogen Cracking of Steel," *Mater. Perform.* 16(1): 22-25 (1977).
35. G. Rieche, "Model Experiments on Stress Corrosion in High-Strength Steels in Non-Carbonated Concrete," *Werkst. Korros.* 26: 19-32 (1975); ORNL-tr-4277.

36. G. J. Verbeck, "Mechanisms of Corrosion of Steel in Concrete," pp. 21-38 in *Corrosion of Metals in Concrete*, Publication SP-49, American Concrete Institute, 1975.
37. R. Szilard, "Corrosion and Corrosion Protection of Tendons in Prestressed Concrete Bridges," *Am. Concr. Inst. J.* 66(1): 42-59 (1969).
38. D. A. Hausmann, "Steel Corrosion in Concrete," *Mater. Prot.* 6(11): 19-23 (1967).
39. G. E. Monfore and G. J. Verbeck, "Corrosion of Prestressed Wire in Concrete," *Am. Concr. Inst. J.* 57(11): 491-515 (1960).
40. K.W.J. Treadaway, "Corrosion of Prestressed Steel Wire in Concrete," *Br. Corros. J.* 6: 66-72 (1971).
41. H. G. Godfrey, "Corrosion Tests on Prestressed Concrete Wire," *Corrosion* 17: 24-25 (1961).
42. I. Cornet, "Corrosion of Prestressed Concrete Tanks," *Mater. Prot.* 3(1): 90-100 (1964).
43. G. N. Scott, "Corrosion Protection Properties of Portland Cement Concrete," *J. Am. Water Works Assoc.* 57: 1038-52 (1965).
44. N. Krishna Raju, "Corrosion of High Tensile Steel in Structural Concrete," *J. Electrochem. Soc. India* 22: 100-105 (1973).
45. P. Heiligenstaldt and K. Bohnenkamp, "Investigations on the Hydrogen-Induced Brittle Failure of Galvanized Prestressed Steels in Concrete," *Arch. Eisenhuettenwes.* 47: 107-12 (1976); *Corros. Abstr.* 16(2): 87 (1977).
46. S. G. Clarke, "The Use of Inhibitors (with Special Reference to Antimony) in the Selective Removal of Metallic Coatings and Rust," *Trans. Electrochem. Soc.* 69: 131-44 (1936).