CORROSION OF STEEL TENDONS USED IN PRESTRESSED CONCRETE PRESSURE VESSELS*

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ABSTRACT

The purpose of this investigation was to determine the corrosion behavior of a high strength steel (ASTM A416-74 grade 270), typical of those used as tensioning tendons in prestressed concrete pressure vessels, in several corrosive environments and to demonstrate the protection afforded by coating the steel with either of two commercial petroleum-base greases or portland cement grout. In addition, the few reported incidents of prestressing steel failures in concrete pressure vessels used for containment of nuclear reactors are reviewed. The susceptibility of the steel to stress corrosion cracking and hydrogen embrittlement and its general corrosion rate were determined in several salt solutions. Wires coated with the greases and grout were soaked for long periods in the same solutions and changes in their mechanical properties were subsequently determined. All three coatings appeared to give essentially complete protection but small flaws in the grease coatings were detrimental; flaws or cracks less than 1 mm wide in the grout were without effect.

Key Words: Prestressing steel, high-strength steel, grout, petroleum-base greases, stress-corrosion cracking, hydrogen embrittlement, corrosion, protective coatings.

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INTRODUCTION

Prestressed concrete pressure vessels (PCPVs) for nuclear reactor containment are massive structures. They are constructed of relatively high-strength concrete which is heavily reinforced by both conventional steel and a steel posttensioning system consisting of vertical tendons and circumferential wire-strand windings. Performance requirements for PCPVs dictate that extremely large capacity prestressing tendons fabricated from high-strength steels be utilized to reduce the concentration of steel as much as possible. The wires or strands used to make up the prestressing systems are often small in diameter (6 to 7 mm) and are used at stresses up to 75% of their ultimate tensile strength (UTS). These two facts make corrosion protection of the tendons imperative if the PCPVs are to operate safely throughout their 30 to 40 year design life.

Present practice for protecting the tendons in PCPVs is to fill the conduits which contain the tensioned tendons with either a portland cement grout or an organic substance composed of petroleum-based greases or waxes which contain specific additives. Although steels are normally quite compatible with these materials, water leakage into the ducts, particularly if impurities are present, could cause serious corrosion leading to failure of the load-carrying tendons. It was the inleakage of water into the ducts combined with other unusual circumstances that produced stress corrosion cracking failures of prestressing tendons in a small-scale model of a concrete pressure vessel at Oak Ridge National Laboratory.[1]

The present investigation was undertaken to determine the corrosion behavior of a typical prestressing steel in several environments and to demonstrate the protection afforded by two different organic materials and by a portland cement grout. Generally, the corrosive environments tested were more severe than those expected to occur in any PCPV. In addition to the experimental program, the few reported incidents of prestressing steel failures in PCPVs for containment of nuclear reactors are briefly reviewed.

EXPERIENCE WITH PRESTRESSING STEELS IN NUCLEAR POWER STATIONS

Prestressed concrete was first used for nuclear pressure vessels in 1960.[2] As of 1976, fifteen nuclear reactor concrete pressure vessels were scheduled for operation in Europe and the United States with additional PCPVs in various stages of design and construction.[3] Except for the Fort St. Vrain high-temperature gas-cooled reactor where a PCPV provides primary containment, concrete vessels are used only for secondary containment in water-cooled reactors in the United States. In both cases large number of tendons are used; e.g., in the Fort St. Vrain PCPV 448 tendons each with 169 wires 6.4 mm in diameter are used,[4] and in 800 to 1100 MW(e) water-cooled reactors up to 1.1×10^6 kg of prestressing steel are employed.[5] Despite the large number of tendons in use, incidents involving corrosion failures are extremely limited.

In 1962 and 1963 during periodic inspections of the tension in the longitudinal and transverse cables in the containment vessels of the Marcoule G2 and G3 reactors in France, it was noted that the initial tension in some of the cables had decreased by 30%.[6] Upon unloading and examining one of these cables it was found that approximately 50% of the wires had broken in brittle fracture with corrosion the apparent cause. Some parts of the circumferential cable which was coated with several layers of a bituminous material exhibited minor rust. Prior to examination, protection was provided by periodic sweeps of dried air to maintain the relative humidity of the air adjacent to the cables at 30 to 40%. Failure of the tendons was apparently due to hydrogen embrittlement caused by the excess humidity in the conduits. To prevent further corrosion, the relative humidity of the air was decreased to 10% and the air flow was changed from periodic to continuous. Since then two additional cables have been replaced, but corrosion has apparently been arrested.

A statutory inspection of prestressing tendons at Wylfa Power Station in the United Kingdom in 1971 revealed extensive pitting of exposed hoop tendons with some pits as deep as 0.3 mm.[7] Corrosion protection of the tendons was by a grease containing a proprietary corrosion inhibitor. Laboratory studies to identify the cause of the pitting concluded that pitting was due to the combined action of contaminating salt from the sea and moisture from the air. The corrosion inhibitor prevented corrosion only up to a threshold concentration of chloride at which point the inhibitor was unable to prevent attack at susceptible local areas. The corrosion rate was also dependent on the relative humidity with corrosion occurring only at relative humidities above 33%.

Despite the application of phosphate paints and heavy greases, a number of tendons installed in the bottom cap of the prestressed pressure vessel under construction at Dungeness "B" Power Station in Kent, United Kingdom, corroded badly after a short period of unstressed storage in conduits.[8] It was later found that water had entered the tendon ducts and emulsified the grease protecting the tendon wires. Ten tendons containing 1630 wires, each 7 mm in diameter, were removed and examined, and 1550 wires were found to be severly pitted. An investigation indicated that the cause of the pitting was electrolytic attack due to an impressed anodic current from dc welding equipment that had been grounded to metal components of the vessel. Since then dc welding has been prohibited in the vicinity of prestressing materials and subsequent examinations at Dungeness have revealed no further abnormal corrosion.

The condition and functional integrity of nongrouted tendons in secondary containment structures in the United States are assessed periodically. Five vessels prestressed with tendons containing 90 wires of 6.35 mm diam have been examined.[8] Of 7600 wires inspected, 7 discontinuities were found with all breaks being discovered prior to the completion of construction. A total of 86 wires were removed and only three of these showed evidence of metal loss (pitting) amounting to a cross-sectional area reduction of 1%. This attack occurred before application of the final corrosion protection. Metallurgical examination revealed no evidence of stress corrosion cracking or hydrogen embrittlement.

Corrosion observed in the prestressing steel tendons of PCPVs which provide containment for nuclear reactors has not resulted in serious failures to this time. In retrospect, most of the corrosion damage found could have been prevented if proper storage, handling, and construction practices had been followed and well established corrosion prevention practices had been employed.

EXPERIMENTAL PROCEDURES

This study involved two separate phases. In one the corrosion of an uncoated typical tendon steel was investigated in several environments, and in the second the behavior of the steel coated with either organic or cement grout coatings was examined in the same corrosive environments. The high strength AISI 1080 carbon steel used in this study was from different heats which conformed to ASTM specification A416-74, grade 270. The composition of the steel is shown in Table 1. Its minimum UTS is 1860 MPa (270,000 psi). The individual tendon wires were austenitized at approximately 815°C (1500°F), cooled in lead to about 500°C (930°F), and transformed at this temperature to lower pearlite. This pearlite structure was subsequently cold worked to provide the high strength.

Corrosion Testing with Uncoated Wires

A major concern from the corrosion standpoint was stress corrosion cracking. With the uncoated steel, stress corrosion cracking tests were conducted using the constant-strain-rate method developed by Humphries and Parkins.[9] With this technique, a tensile-type specimen while exposed to the test environment is strained at a very slow constant rate until fracture occurs, usually within a period of a few days. 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 gage section near the fracture can provide additional information about the fracture process.

Table 1. Composition range of ASTM A416 grade 270 steel used in tests.

Element	Wt percent[a]
Carbon	0.75 –0.81
Silicon	0.26 –0.28
Magnese	0.62 –0.84
Phosphorus	0.012–0.021
Sulfur	0.018–0.028
Copper	0.01 –0.02
Iron	Balance

[a] Material supplied from more than one heat.

For the stress-corrosion cracking tests the center straight 5 mm (0.20 in.) diameter wire of a seven-wire tendon was used. Light surface rust was removed with fine emory paper and the specimens were degreased in acetone before use. A gage section was not machined in the wires since we wanted to retain the original surface condition of the cold-drawn wire. The wire in the presence of the test environment was strained at a rate of 4.2×10^{-7}/s in an Instron tensile machine. 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. To prevent any unusual effects at the solution-air interface or in the crevice where the wire passed through a rubber stopper in the bottom of the bottle, all the wire except a 75-mm (3 in.) test length at the center was coated with a stop-off varnish. After fracture, one end of the specimen was mounted axially and metallographically polished to look for secondary cracks.

The corrosion rates of unstressed 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 the test solutions, which included dilute solutions of chloride, nitrate, and sulfate salts, and potable and distilled water. The total volume of solution was only about 500 mm^3. 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 h, but duplicate specimens were removed from test after 1000 h. All specimens were descaled in Clarke's solution[10] (2 g Sb_2O_3 and 5 g $SnCl_2$ dissolved in 100 ml of 37% HCl) before final weighing.

In another series of tests, single wires 0.3 m (12 in.) long were immersed in dilute solutions of Na_2SO_4 and NaCl and in distilled water at room temperature for 6500 h. The volume of solution was about 1 liter and was freely exposed to 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, and the diameter of the wire above and below the waterline was compared.

Testing with Coated Wires

To evaluate the effectiveness of coating materials in preventing corrosion of tendon steels, two different types of tests were conducted. In one case, the specimens after coating were stressed to 60% of the UTS while in contact with the corrosive solution, and in the second the coated specimens were first exposed to the solution for relatively long times without an applied stress and were subsequently strained to failure. In both cases the center straight wire from the tendon was used, and it had a diameter of 4.36 mm (0.17 in.) which was slightly less than that of the wires used in the previously described corrosion tests. The two organic coatings used in these tests, designated "A" and "B", are commercially available petroleum-based greases containing corrosion inhibitors and polar agents to facilitate wetting of the wires and displacement of moisture. They were applied according to the manufacturers' recommendations to a thickness of about 1 mm. Test specimens protected by grout were prepared by casting 15.9 mm (0.6 in.) diameter cylinders 3.8 mm (1.5 in.) long around the wires. The area of the wires not coated with a grout or grease that could be contacted with the test solutions was covered with a polyurethane insulating paint. All tests were conducted at ambient temperature except for those using ammonium nitrate solutions, and a conventional tensile machine was used to stress the specimens. In some cases the effect of flaws in the coatings was evaluated. Flaws were placed in the organic coatings by scraping the wire to which the coating had been applied with a similar wire so that a thin strip of unprotected wire resulted. Flaws were cast in grout ranging in width from 0.01 to 3.2 mm by using plastic shim stock which was removed after the grout hardened.

With the specimens stressed during exposure, only $0.1M$ H_2S (pH ∿4) was used as test solution. The organic coatings were applied to completely cover the wire surface over the 50.8 mm (2-in.) test length and the specimen was mounted in a plastic bottle as described above. The grout coated specimens were similarly mounted. The bottle was then filled with demineralized water and H_2S was bubbled through the water for about 15 min. The bottle was sealed and the specimen was loaded to 60% of its UTS and maintained at that level for 6 days unless the specimen failed before then. The length between the grips was 216 mm (8.5 in.). If failure did not occur within 6 days, the specimen was removed from the environment and pulled to failure at a cross head velocity of 0.51 mm/min to determine if the exposure reduced the UTS and ductility (time to failure) compared to control specimens exposed only to air.

Coated specimens in the unstressed condition were exposed to solutions of 0.1*M* H_2S, 0.1*M* NaCl, and 0.2*M* NH_4NO_3. The first two were used at room temperature, but because of the stress corrosion cracking results (see later section), the ammonium nitrate solution was maintained at 66°C (150°F). A 63.5 mm (2.5-in.) diameter polyvinyl chloride pipe with stoppers in each end was used to expose the gage length of specimens to the H_2S solution. Holes were drilled through the pipe and the specimens were centered in these by appropriate sized rubber stoppers (Fig. 1). Water in the pipe was resaturated with H_2S at frequent intervals. Exposure to the other two solutions was carried out in stainless steel pans with holes drilled through the bottom, and the specimens were held in position by means of rubber stoppers. After various exposure times, specimens were removed from the test environment and pulled to failure at a cross head speed of 0.51 mm/min.

RESULTS

Stress Corrosion Cracking Tests

The results from the slow constant strain rate tests are shown in Table 2. Test 1 confirmed that the UTS conformed to ASTM A416 grade 270. Tests 2 through 6 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 evidence of cracks was found at 21 and 38°C, but cracks formed at 52 and 66°C. Figure 2 shows representative views along the axis of the specimens tested at the four temperatures. Even though cracks

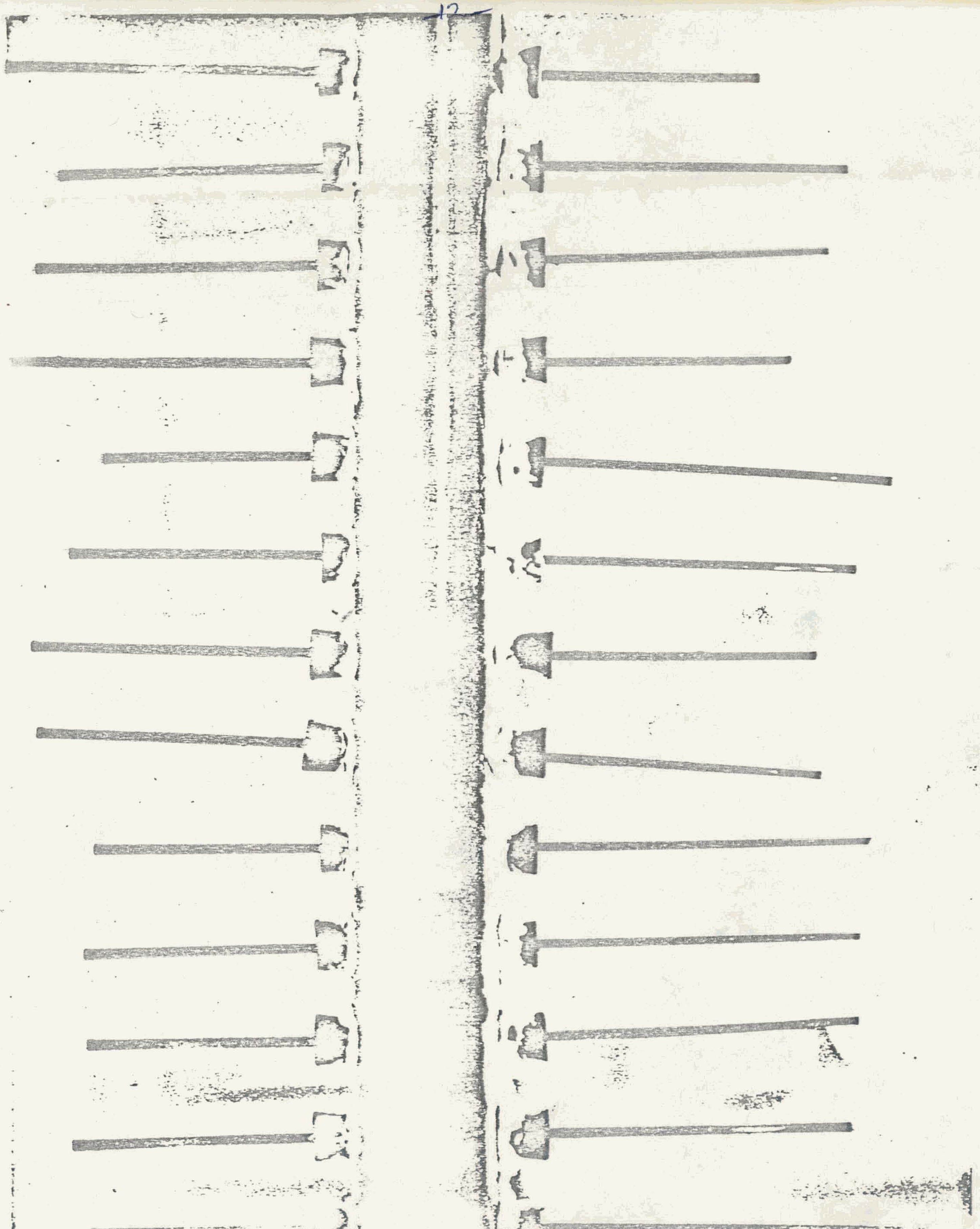

Fig. 1. Photograph of Test Specimens Mounted in Polyvinyl Chloride Pipe.

Table 2. Results obtained from constant-strain-rate tests with high-strength steel wires (Strain rate 4.2×10^{-7}/s)

	Test medium	Temperature °C	pH	Time to break (h)	Load (kN)	Cracks
1.	Air	21		55.5	41.9	No
2.	$0.2M$ NH_4NO_3	21	5.0	57.5	40.1	No
3.	$0.2M$ NH_4NO_3	21	5.3	66.5	39.3	No
4.	$0.2M$ NH_4NO_3	38	5.3	47.0	39.0	No
5.	$0.2M$ NH_4NO_3	52	5.3	49.5	38.9	Yes
6.	$0.2M$ NH_4NO_3	66	5.0	50.5	38.9	Yes
7.	$0.01M$ KCl + CaO	21	11.9	55.3	39.1	No
8.	$0.01M$ KCl	66	5.3	60.8	38.9	No
9.	$0.03M$ KCl	21	5.5	58.1	39.3	No
10.	$0.03M$ KCl + HCl	21	3.0	60.8	39.3	No
11.	$0.1M$ H_2S + HCl	21	3.0	6.6	15.0	Yes
12.	$0.1M$ H_2S	21	4	4.7	11.1	Yes
13.	$0.001M$ Na_2S	21	11.1	57.8	38.4	No
14.	$0.001M$ Na_2S + HCl	21	7.4	53.8	39.1	No
15.	$0.001M$ Na_2S + HCl	21	4.3	19.3	35.2	Yes
16.	$0.003M$ Na_2S + HCl	21	4.3	17.0	34.2	Yes
17.	$0.0003M$ Na_2S + HCl	21	6.3	52.0	39.3	No
18.	$0.0003M$ Na_2S + HCl	21	4.3	54.8	39.3	No
19.	Deionized water	21	6.0	57.5	39.0	No
20.	Deionized water + CO_2	21	4	55.8	39.3	No
21.	H_2O + CO_2 + 750 ppm H_3AsO_3	21	5.1	57.6	39.3	No
22.	Zn plate, H_2O	21	5.8	80.6	39.5	No
23.	Zn plate, $0.2M$ Na_2SO_4	21	5.7	54.9	39.5	No
24.	Corroded in water, 3 days	21	5.9	50.9	39.3	No

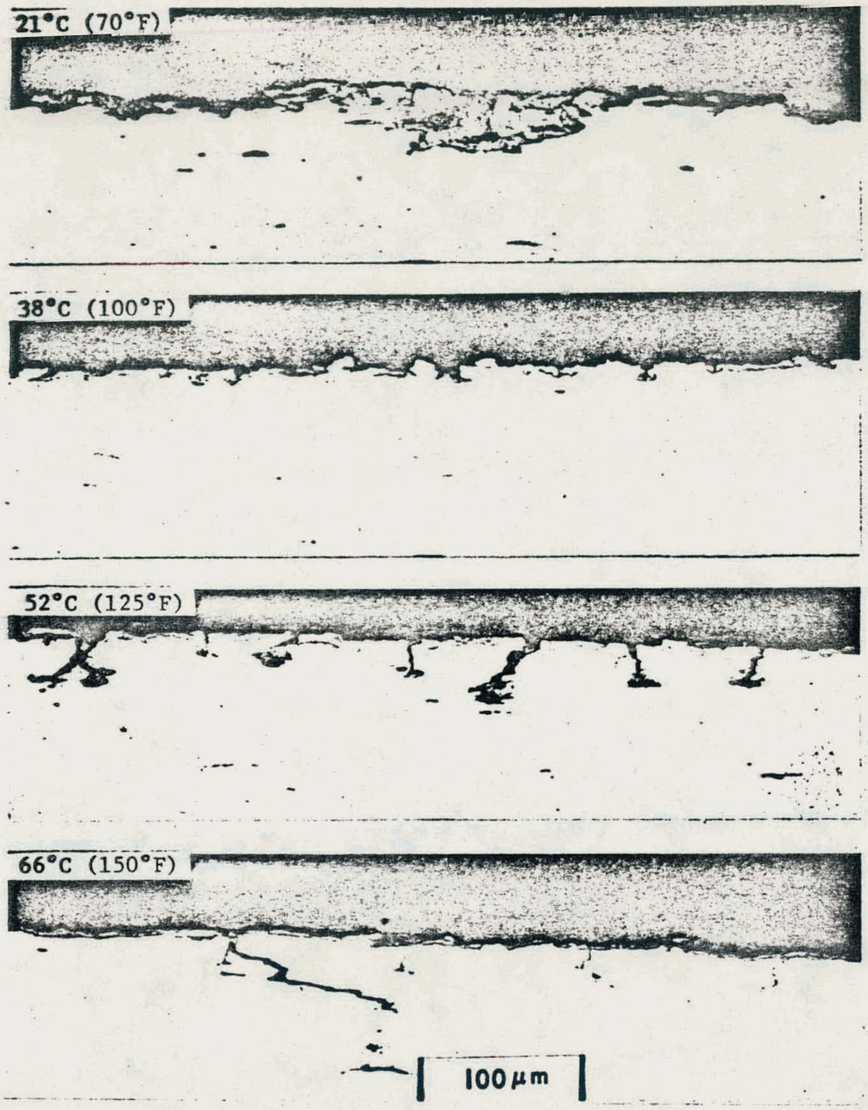

Fig. 2. Attack on Steel Tendons Wires in $0.2M$ NH_4NO_3. Strain rate, 4.17×10^{-7}/s.

were evident in the steel at the two higher temperatures, no effect on either time to failure or on the load at failure was apparent. The large diameter of the wire and the slow rate of crack propagation were responsible for this observation. The formation of cracks at 66°C and the absence of cracks at 21°C agree with the results from U-bend specimens exposed to the same solution; U-bends cracked in a few days at 66°C but remained intact at 21°C during 100-day tests.[1]

Cracks were not found in any of the specimens exposed to chloride-containing solutions (tests 7 to 10), regardless of the pH of the solution. These results are in conformance with the generally-accepted belief that chloride ions do not produce cracking in steels of this type.

As expected, H_2S produced rapid failure in the test specimens when the pH was low and the H_2S concentration was relatively high (tests 11 and 12). Figure 3 shows cracks observed in test 12. In 0.001*M* Na_2S at a pH of 11.1 or 7.4 (tests 13 and 14), no cracking was observed, but when the pH was adjusted to 4.3 (test 15), cracking occurred. At this lower concentration, failure took longer than at the higher sulfide concentration. Cracking occurred slightly faster when the Na_2S concentration was increased to 0.003*M* (test 16). When the sulfide concentration was reduced to 0.0003*M* (test 17 and 18), no cracking was observed even though the pH of the solutions was less than 7. 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 to sulfur early in the test by traces of oxygen in the bottle.

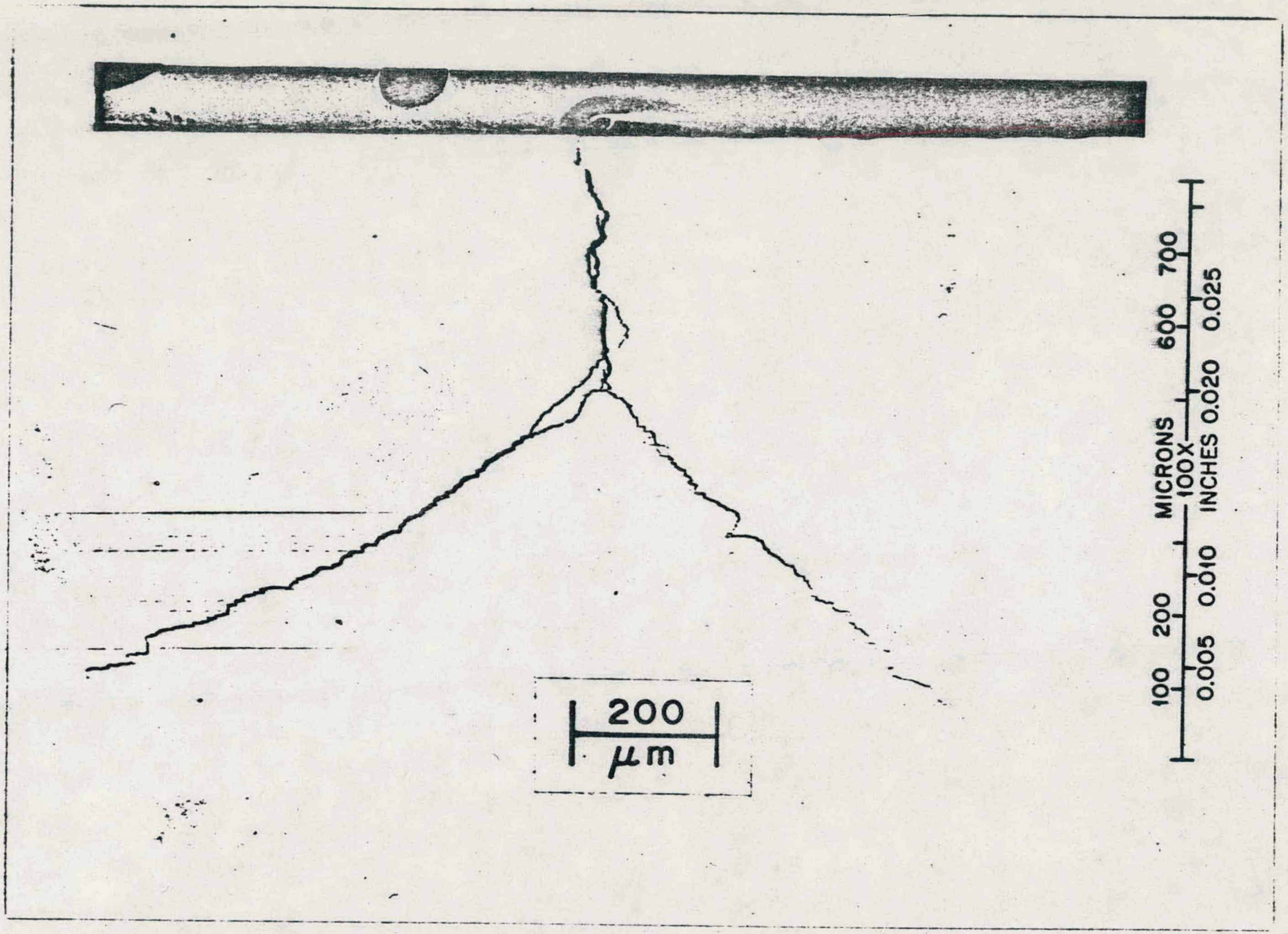

Fig. 3. Cracks in Tendon Wire Formed During Constant-Strain-Rate Test in 0.1*M* H_2S.

The rest of Table 2 shows that cracking was not produced in distilled water with carbon dioxide or when arsenious acid was added to the water. 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. Electroplating the specimen with zinc, except for an area 200 mm^2 in the middle of the wire, also had no effect on cracking in either water or a dilute sodium sulfate solution.

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 2, when it was 47%. In tests 11 and 12, no reduction in area could be measured, and in tests 15 and 16 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.

General Corrosion Rate Determinations

The corrosion rates observed for the tendon wires exposed to very small volumes of solutions are shown in Table 3. Each value represents a single specimen. After 1000 h in some cases and after 2000 h in most cases, the volume of corrosion products prevented removal of the specimen from the glass tube, and it was necessary to break the tube to recover the specimen. Table 3 shows that under these conditions, corrosion rates were low and nearly independent of the environment. There was no significant localized attack in any case. Vacuum fusion analysis of specimens exposed to each solution for 2000 h showed hydrogen content increases ranging from less than 1 ppm to a maximum of 2.4 ppm.

Table 3. Corrosion of tendon wires in different environments with restricted access to oxygen.

Test environment	Corrosion rate (μm/year)[a]	
	1000 H	2000 H
Potable water	5.8	5.3
Distilled water	5.1	5.3
0.01*M* NaCl	6.4	9.7
0.03*M* NaCl	6.6	7.9
0.001*M* $NaNO_3$	7.4	23.1
0.01*M* $NaNO_3$	11.2	8.1
0.002*M* Na_2SO_4	5.8	7.6
0.02*M* Na_2SO_4	7.6	13.2
0.2*M* Na_2SO_4	8.9	13.5

[a] 1 mpy = 25.4 μm/year.

The 0.3 m (12-in.) long wires exposed to large volumes of solution that was freely exposed to air corroded more than the specimens with limited air exposure. Corrosion rates calculated from differences in diameter above and below the water line after 6500 h were 76, 152, and 254 μm/yr (3, 6, 10 mils/yr), respectively, for distilled water, 0.05*M* NaCl, and 0.1*M* Na_2SO_4. Attack was greatest at the solution-air interface, but localized attack in the form of broad elongated pits was noted below the waterline in all cases. Therefore, maximum penetration rates were considerably greater than indicated above. Comparison of these corrosion rates with those shown in Table 3 clearly shows that free access to oxygen greatly accelerates corrosion.

Coated Wires Stressed During Exposure

A series of tests with bare wires exposed to 0.1*M* H_2S showed that as the stress level increased both the time to failure and the scatter in the data decreased up to about 50% of the failure stress (Fig. 4). From 50 to 90%, failures occurred in 1 to 2 hours, independent of stress level.

Results obtained with the coated specimens that were stressed during exposure to 0.1*M* H_2S are summarized in Table 4. None of the specimens covered with unflawed coatings of either of the organic greases or grout cracked during approximately 6-day exposures at 60% UTS, and subsequent tensile tests showed that no degradation of either load carrying capacity or ductility (time to failure) had occurred. Flaws in either organic coating resulted in fracture of the wires in short times. On the other hand,

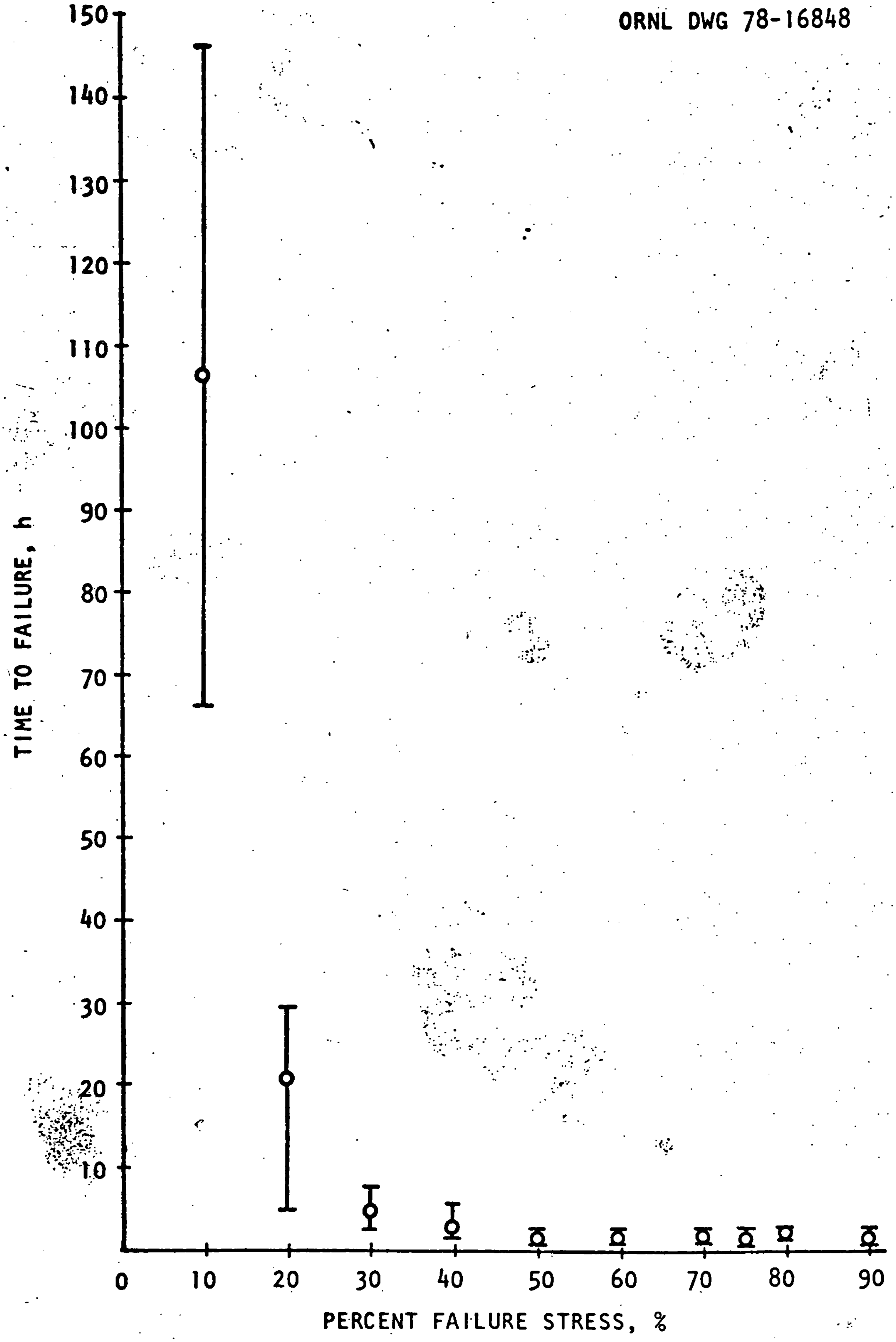

Fig. 4. Effect of Stress (% UTS) on Time to Failure for Tendon Wire in 0.1*M* H_2S.

Table 4. Loads at failure and failure times for specimens exposed in 0.1*M* H_2S at room temperature.

Coating material	Average failure load[a] (kN)	Average failure time[b] (h)
Organic "A"		
Unflawed	28.58	152.0
Flawed	17.17	14.0
Organic "B"		
Unflawed	28.63	149.0
Flawed	17.17	63.8
Portland cement grout		
Unflawed	28.36	162.7
0.1-mm flaw	28.60	260.0
0.3-mm flaw	27.86	180.9
1.3-mm flaw	17.17	118.3
1.6-mm flaw	17.17	48.1
3.2-mm flaw	17.17	34.6

[a] Average load and time to failure for control specimens were 28.62 kN and 34.7 min., respectively.

[b] No failure occurred for indicated exposure at 60% UTS; failure load obtained from standard tensile test.

flaw widths of 0.1 and 0.3 mm in the grout produced no detrimental effects, but as the flaw width increased beyond 0.3 mm cracking failures at 60% UTS occurred in progressively shorter times.

Coated Wires Unstressed During Exposure

Tables 5, 6, and 7, summarize the results obtained with both coated and uncoated wires that were exposed for various times to 0.1*M* H_2S, 0.2*M* NH_4NO_3, and 0.1*M* NaCl, respectively, without applied stress and then subsequently tensile tested. The average failure load and time to failure for unexposed specimens were 28.62 kN and 34.65 min, respectively.

Table 5 shows that for wires completely covered with either organic material or cement grout, exposure to H_2S-saturated water for up to 120 days had little or no effect on UTS or ductility. Completely unprotected specimens under the same condition showed a minor decrease in UTS and a major loss of ductility. Specimens with flaws in the organic coatings showed significant losses in both ductility and UTS after 119 days and proportionately smaller losses at shorter times (not shown in Table 5). On the other hand, flaws up to 0.76 mm wide in portland cement grout produced only very minor effects even after 119 days.

In the ammonium nitrate solutions (Table 6) the unprotected wires lost about 14% in UTS and 66% in ductility after 42 days and no further changes were noted for the remainder of the 132-day test. Both organic materials provided complete protection for the duration of the test, but the protectivess of the grout seemed to decrease slowly with time. The ammonium

Table 5. The average load at failure and time to failure for wires exposed to $0.1M$ H_2S without applied stress and subsequently pulled to failure.

Coating material	Exposure time (days)	Average load at failure[a] (kN)	Average time to failure[a] (min)
None	33	26.28	13.2
Organic "A"	33	27.84	34.2
Organic "B"	33	27.98	32.6
Portland cement grout	33	27.95	32.5
None	77	26.37	13.8
Organic "A"	77	27.65	31.9
Organic "B"	77	28.06	35.9
Portland cement grout	77	28.02	32.9
None	120	25.36	10.4
Organic "A"	120		
Organic "B"	120	28.65	29.8
Portland cement grout	120	28.43	30.6
Flawed organic "A"	119	23.91	10.5
Flawed organic "B"	119	24.24	12.5
Portland cement grout			
0.01-mm flaw	119	26.71	33.3
0.10-mm flaw	119	26.82	34.8
0.51-mm flaw	119	26.13	32.8
0.76-mm flaw	119	25.58	32.0

[a] Average load and time to failure for control specimens were 28.62 kN and 34.7 min., respectively.

Table 6. The average load at failure and time to failure for wires exposed to 0.2*M* NH_4NO_3 at 66°C without applied stress and subsequently pulled to failure.

Coating material	Exposure time (days)	Average load at failure[a] (kN)	Average time to failure[a] (min)
None	42	24.58	11.5
Organic "A"	42	27.32	36.2
Organic "B"	42	27.24	35.1
Portland cement grout	38	28.62	34.7
None	78	26.77	14.7
Organic "A"	78	28.36	34.1
Organic "B"	78	38.39	37.1
Portland cement grout	87	38.14	27.2
None	132	25.91	11.7
Organic "A"	132	28.65	35.6
Organic "B"	132	28.47	34.3
Portland cement grout	122	26.47	25.2
Flawed organic "A"	130	26.47	36.0
Flawed "B"	130	26.80	33.3
Portland cement grout			
0.03-mm flaw	130	26.36	25.0
0.25-mm flaw	130	25.80	23.0
0.76-mm flaw	130	25.69	22.3
3.18-mm flaw	130	25.91	19.3

[a] Average load and time to failure for control specimens were 28.62 kN and 34.7 min., respectively.

Table 7. The average load at failure and time to failure for wires exposed to 0.1M NaCl without applied stress and subsequently pulled to failure.

Coating material	Exposure time (days)	Average load at failure[a] (kN)	Average time to failure[a] (min)
None	71	27.53	17.8
Organic "A"	71	28.62	36.1
Organic "B"	71	28.47	36.4
Portland cement grout	71	28.51	37.8
None	107	25.72	13.9
Organic "A"	107	27.13	30.4
Organic "B"	107	26.99	29.5
Portland cement grout	107	27.02	32.9
None	164	24.76	12.6
Organic "A"	164	26.34	33.0
Organic "B"	164	26.43	32.8
Portland cement grout	164	26.80	32.4
Flawed organic "A"	153	25.58	34.8
Flawed organic "B"	153	25.13	30.3
Portland cement grout			
0.03-mm flaw	153	26.58	31.5
0.25-mm flaw	153	26.91	36.5
0.76-mm flaw	153	26.24	37.3
3.18-mm flaw	153	23.58	8.8

[a] Average load and time to failure for control specimens were 28.62 kN and 34.7 min., respectively.

nitrate solution at 66°C causes degradation of grout, a fact which probably allowed ammonium nitrate to come in direct contact with the steel after some time. Specimens with flaws in the grout showed about the same result. On the other hand, specimens with flaws in the organic coatings showed little if any loss in properties, possibly because at 66°C the organic greases flowed over the defected areas early in the test and protected them.

In the 0.1*M* NaCl solution (Table 7) wires protected by all three materials seemed to slowly decrease in UTS and time to failure so that after 164 days the loss was 5 to 7% in both cases. Unprotected specimens behaved in a similar fashion but the percentage loss in UTS and time to failure were 13 and 64%, respectively, after 164 days. Specimens in which the organic coatings contained flaws showed about the same behavior as the unflawed materials. Flaws from 0.03 to 0.76 mm wide in grout coatings had no significant effect, but for a flaw 3.18 mm wide the mechanical properties of the steel were slightly poorer after 153 days than totally unprotected specimens exposed for 164 days.

DISCUSSION

The steel wires used in this study were made from AISI 1080 steel which was tempered and cold drawn to obtain the high strength required of tendon steels. At room temperature this steel was not susceptible to conventional stress corrosion cracking in the presence of impurities usually found in grouts or organic coatings (sulfates, nitrates, chlorides) but under some conditions this steel was subject to hydrogen embrittlement. Cracks were produced in ammonium nitrate solution but temperatures had to be above room temperature. Aqueous environments produced within grouts or organic greases or waxes containing alkaline-producing additives have high pH values, and its doubtful that cracking would occur in alkaline ammonium nitrate solutions even at higher temperatures. It should be noted, however, that the addition of substantial amounts of calcium chloride (2—5%) to concrete produces severe pitting in steel embedded in concrete.[11,12]

Test wires failed in short times when strained in solutions of H_2S in water at a pH of 4 or less, but where the pH was raised to 7 or above cracking failures did not occur. There are, however, reported incidents of cracking occurring at pH values as high as 9.5.[13,14] Cracking of high-strength steels in the presence of H_2S is due to hydrogen embrittlement, the H_2S facilitating the entry of hydrogen into the steel by interferring with the formation of molecular hydrogen in the cathodic part of the corrosion reaction.[15] Only molecular hydrogen sulfide is effective,[13,14] and as the pH of a solution is increased H_2S dissociates into HS^- and $S^=$ ions and cracking does not occur. At the pH of correctly formulated concrete (>12) H_2S in the cement is without effect on the mechanical properties of the steel. A similar situation should exist with those greases that contain alkaline-producing additives.

The corrosiveness of several dilute solutions to bare high-strength steel wires depended on the availability of oxygen. With restricted access to oxygen corrosion rates were significantly lower than when the solutions were freely exposed to air. Although we did not investigate the effect of pH on the corrosion rate of these steels, it is likely that even in the presence of oxygen the corrosion rates would be very low in alkaline solutions.

Therefore, if pockets of water in contact with tendons should develop in grout- or grease-filled conduits, corrosion of the steel would be low because of limited availability of oxygen and because of the alkalinity of the solution in contact with grouts or organic materials containing alkaline additives. In such cases hydrogen embrittlement produced by the corrosion reaction is unlikely since even in neutral solutions very little hydrogen was picked up by the steel in 2000-h tests.

All coatings applied to the test specimens provided almost complete protection even though they were tested in environments much more aggressive than would be expected in a PCPV. Those specimens coated with either of the two organic materials selected for study, showed no signs of attack on exposure to $0.1M$ H_2S when stressed at 60% UTS for about 6 days. Subsequent tensile tests showed no degradation of mechanical properties. However, if a small amount of coating was removed, failures occurred in relatively short times. Portland cement in the same type of test also provided complete protection, and with flaws up to 0.3 mm wide no failures occurred; however with flaw widths of 1.3 mm or greater, failures took place in less than 6 days. It seems probably that with a sufficiently small flaw or crack in the relatively thick concrete coating, the pH of the small volume of solution within the crack remained high enough so that the H_2S dissociated and cracks could not form.

Exposure of unstressed coated specimens to $0.1M$ H_2S and subsequent tensile testing also showed the coatings to be completely effective. However, exposure of uncoated specimens and organic coatings with flaws to $0.1M$ H_2S caused slight losses of load-carrying capacity and substantial reductions in times to failure during tensile tests. On the other hand, concrete coatings with flaws as wide as 0.76 mm resulted in only very small losses in mechanical properties after exposure to H_2S. Similar results were obtained in ammonium nitrate and sodium chloride solutions. In the ammonium nitrate solution flaws in either organic coating did not cause loss of mechanical properties, apparently because at the test temperature of 66°C the organic materials flowed over the flaws and protected them.

SUMMARY

The stress-corrosion cracking susceptibility of a typical cold-drawn high-strength steel (ASTM A416 steel 270) to several solutions was determined using a slow constant strain rate technique. The steel developed cracks in 0.2*M* NH_4NO_3 but only at temperatures above 38°C (100°F). Brittle failures, apparently because of hydrogen embrittlement, also occurred in hydrogen sulfide solutions if the pH was less than 7. Cracking did not occur in chloride solutions regardless of pH. The corrosion rate of the steel was low in dilute solutions of NaCl, $NaNO_3$, Na_2SO_4 when access to oxygen was restricted, but it was substantially higher with free access to air; in the latter case broad pits formed, even in pure water.

Both organic coating materials tested and portland cement grout provided complete protection to the steel in the above aggressive environment, provided the coating remained intact. With portland cement crack widths up to 0.76 mm did not result in loss of protection. These results indicate that in a PCPV the use of certain commercial organic greases or portland cement grout for filling the conduits containing high-strength steel tendons should provide protection to the tendons even if low concentrations of aggressive salts inadvertantly get into the conduits during filling.

REFERENCES

1. Canonico, D.A., Griess, J.C., and Robinson, G.S., "Final Report on PCRV Thermal Cylinder Axial Tendon Failures," ORNL-5110, Jan. 1976.
2. Germain, F., *Journal of the Prestressed Concrete Institute*, Vol. 12, No. 4, Aug. 1967, pp. 43–52.
3. Hannah, I.W., "Prestressed Concrete Pressure Vessels in the United Kingdom," Paper 121/75, *Experience in the Design, Construction, and Operation of Prestressed Concrete Pressure Vessels and Containments for Nuclear Reactors*, University of York, England, Sept. 8–12, 1975.
4. Hildebrand, J.F., "Evaluation of Corrosion Inhibiting Compounds for Protection of Prestressing Systems," Paper 150/75, *ibid.*
5. Schupack, M, *Journal of the Prestressed Concrete Institute*, Vol. 17, No. 3, May/June, 1972, pp. 14–28.
6. Poitevin, P., *Containers of the G2 and G3 Reactors: Protection of Prestressing Cables*, Technical Information Note Campagnie Industrielle de Travaux (Engerprises Schneider), ORNL translation STS 5651, March 21, 1966.
7. Fontain, M.J. et al., "Corrosion Protection of Prestressing Tendons," Paper 149/75, *Experience in Design, Construction, and Operation of Prestressed Concrete Pressure Vessels and Containments for Nuclear Reactors*, University of York, Sept. 8–12, 1975.
8. Rotz, J.V., "Inservice Surveillance of Unbonded Post-Tensioning Systems in Prestressed Concrete Containment Structures," Paper 172/75, *ibid.*

9. Humphries, M.J. and Parkins, R.N., in *Fundamental Aspects of Stress Corrosion Cracking*, R. W. Staehle, Ed., National Association of Corrosion Engineers, Houston, 1969, pp. 384—392.

10. Clarke, S.C., *Transactions of the Electrochemical Society*, Vo. 69, 1936, pp. 131—144.

11. Monfore, G.E. and Verbeck, G.J., *American Concrete Institute Journal*, Vol. 57, No. 11, 1960, pp. 491—515.

12. Treadaway, K.W.T., *British Corrosion Journal*, Vol. 6, 1971, pp. 66—72.

13. Hudgins, C.M. et al, *Corrosion*, Vol. 22, 1966, pp. 238—251.

14. McCord, T.G. et al, *Materials Performance*, Vol. 15, No. 2, 1976, pp. 25—34.

15. Greer, J.B., *Materials Performance*, Vol. 14, No. 3, 1975, pp. 11—22.