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Corrosion Characterization and Response to Cathodic Protection of Eight Wire-Rope Materials in Sea Water

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The titanium alloy 13V-11Cr-3Al, the nickel-base alloy, and the aluminized steel were inherently corrosion resistant. Based solely on corrosion resistance, their use would be suitable for two years total immersion in sea water even without cathodic protection.

Unprotected phosphor bronze, galvanized steel, and copper-nickel clad stainless steels are not suitable for extended use in sea water. Phosphor bronze and galvanized steel would be satisfactory for long-term service if cathodically protected. The 90/10 copper-nickel clad Type 304L stainless steel was essentially corrosion free when cathodically protected. Pitting was not eliminated on unclad Type 304L stainless steel even when cathodically protected. The 90/10 copper-nickel clad Type 205 stainless steel showed localized corrosion on some of the wires when cathodically protected with a zinc anode.

Some problem areas in the use of wire rope in sea water include:

1. Cathodic protection may cause deterioration of hemp-fiber cores.
2. Certain exposure conditions may cause deterioration of the hemp-fiber core in a wire rope even when not cathodically protected.
3. The corrosion characteristics of a wire rope may be affected by the core material (e.g., hemp-fiber core vs independent wire-rope core — IWRC).
4. The condition of a wire rope in sea-water service cannot be determined by examination of only the external surface.
5. Zinc socketing of the nickel-base alloy may result in embrittlement.
6. Titanium-alloy ropes are subject to deterioration when used as working ropes over sheaves.

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ABSTRACT

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1. Cathodic protection may cause deterioration of hemp-fiber cores.

2. Certain exposure conditions may cause deterioration of the hemp-fiber core in a wire rope even when not cathodically protected.

3. The corrosion characteristics of a wire rope may be affected by the core material (e.g., hemp-fiber core vs independent wire-rope core — IWRC).

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5. Zinc socketing of the nickel-base alloy may result in embrittlement.

6. Titanium-alloy ropes are subject to deterioration when used as working ropes over sheaves.

PROBLEM STATUS

This report completes one phase of the task; work is continuing on other phases.

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CORROSION CHARACTERIZATION AND RESPONSE TO CATHODIC PROTECTION OF EIGHT WIRE-ROPE MATERIALS IN SEA WATER

INTRODUCTION

Wire ropes and armored cables are used for many applications in the Navy and are an essential component of many mooring systems in the deep ocean. These systems may include moorings for ships, data buoys, instrument packages, underwater weapons, or may be used in other oceanographic studies.

A considerable amount of general information on wire-rope service requirements, design parameters, operation, maintenance, and inspection has been published (1 — 5). Savastano (6) has published general information on selecting wire ropes for oceanographic applications. A study of wire ropes in sea water without cathodic protection has been reported by Peterson and Tamor (7). Groover (8) and Lennox (9) have reported on the corrosion analysis of in-service wire-rope moorings. There was, however, a definite lack of data on the corrosion characteristics of the newer wire-rope materials and their response to cathodic protection in sea water.

To obtain corrosion characterization data and determine the effectiveness of cathodic protection, eight different wire-rope materials were studied at the NRL Marine Corrosion Research Laboratory at Key West, Florida. The data obtained in these studies have been correlated in this report.

EXPERIMENTAL PROCEDURES

Some of the wire ropes studied had been fabricated from a single metal or alloy. In others, the base wire-rope metal was coated with a second metal, such as in zinc-coated steel (galvanized steel), aluminum-coated steel (aluminized steel), and copper-nickel clad stainless steels. In addition, some of the wire ropes had a fiber-strand core (FSC). The construction details of each material and the metallic-coating thickness, where applicable, are shown in Table 1. The first five wire ropes shown, with the exception of the titanium-alloy wire rope, had similar wire diameters. The latter five wire ropes had similar wire diameters and were similar in construction.

Three specimens of each material were studied as nonworking wire ropes. Two of these specimens were four feet long and were used for the total-immersion phase of this study. One of these two specimens was cathodically protected by a zinc anode, and the other was unprotected. The third specimen was 10 feet long and was partially immersed in sea water without cathodic protection. Approximately four feet were above mean low water (MLW), and six feet were below MLW.

Table 1
Wire-Rope Construction Details

Material	Construction Details			Metallic-Coating Thickness (Mils)
	Rope Diameter (in.)	Individual Wire Diameter (Mils)	Number of Wires per Strand	
Phosphor Bronze	5/16 6 X 19FSC Warrington	18 — 24	19	None
Galvanized Steel Source 1	1/2 6 X 37FSC Warrington-Seale	16 — 25 core: 40	41	0.1 — 0.9 zinc
Aluminized Steel Source 1	1/2 6 X 37FSC	19 — 26	37	0 — 0.7 aluminum
Nickel-Base Alloy	1/4 7 X 19	16 — 18 core: 19+	19	None
Titanium Alloy 13V-11Cr-3Al	1/8 7 X 19	8 — 11	19	None
90/10 Cu-Ni Clad Type 304L-SS	1/2 6 X 19 (IWRC)	20 — 40 core: 47	19	1.0 — 2.8 90/10 Cu-Ni
90/10 Cu-Ni Clad Type 205-SS	1/2 6 X 19 (IWRC)	20 — 40 core: 47	19	1.0 — 2.6 90/10 Cu-Ni
Type 304L-SS	1/2 6 X 19 (IWRC)	19 — 40 core: 47	19	None
Galvanized Steel Source 2	1/2 6 X 19 (IWRC)	19 — 40 core: 48	19	0.1 — 0.6 zinc
Aluminized Steel Source 2	1/2 6 X 19 (IWRC)	20 — 40 core: 48	19	0.1 — 0.9 aluminum

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None of the wire ropes were solvent or chemically cleaned before initiating the exposure phase of the study because some of the wire ropes had fiber-strand cores, and also the intent was to expose the wire ropes in the as-manufactured surface condition.

The bottom 2 — 3 inches of each specimen were covered with electrical insulation putty and polyvinyl chloride (PVC) electrical tape to prevent fraying of the ends. This putty and tape covering also served as an additional crevice area.

A No. 12, single-conductor, insulated, copper wire was connected at the top of each specimen. These wires were used for electrical contact to monitor the electro-chemical potential of each specimen, served as the electrical conductor from the zinc anodes for the cathodically protected specimens, and supported the specimens in the water. On wire ropes with fiber cores, approximately three inches of the fiber core were removed before attaching the lead wires. All electrical connections were sealed with epoxy resin that was very fluid

before curing, which allowed the epoxy to penetrate and seal crevices within the joint. The connections were further covered with electrical insulation putty and PVC electrical tape.

The zinc anodes used to cathodically protect the totally immersed specimens were 1/2 × 1-1/4 × 6 in. The electrical connection on the anode was sealed in a manner similar to the method used to seal the electrical connections to the wire rope. The zinc anodes were suspended in the water approximately 27 inches from the center of the 4-ft wire-rope section.

All specimens were suspended from beneath a pier and partially or totally immersed in sea water at NRL's Marine Corrosion Research Laboratory. The sea-water temperature ranged from 62° to 90°F and averaged 78°F. Water resistivity ranged from 17-21 ohm-cm and averaged 19 ohm-cm. The sea-water pH ranged from 8.1 to 8.5 and averaged 8.2 during the 790-day exposure period. Water velocity was relatively quiescent, and any flow was due only to tidal changes.

Interim inspections were made of each wire rope after 183 and 325 days. At the conclusion of the experiment, gross marine fouling was removed using a pressure washer, and specimens were chemically cleaned and solvent degreased by the procedures shown in Table 2.

Table 2
Procedures Used to Chemically Clean* Wire Ropes
After 790 Days in Sea Water at Key West, Florida

Metal	Chemical Cleaning Procedure
Phosphor Bronze	HCl (1:1) room temperature
Galvanized Steel	Generally used — 10% NH_4Cl at 120°-140°F Occasionally used — 40g/1 Sb_2O_3 in HCl at room temperature to strip the galvanized steel; required for the final evaluation of the specimens most severely corroded
Aluminized Steel	2 wt-% chromic acid (CrO_3) and 5 vol-% orthophosphoric acid (H_3PO_4, 85%) at 175°F
Titanium Alloy 13V-11Cr-3Al	Concentrated HNO_3 at room temperature
Nickel-base Alloy	HCl (1:1) at room temperature
90/10 Cu-Ni Clad Type 304L Stainless Steel	HCl (1:1) at room temperature
90/10 Cu-Ni Clad Type 205 Stainless Steel	HCl (1:1) at room temperature
Unclad Type 304L Stainless Steel	10% HNO_3 at 140°F

*Alternately degreased with xylene in ultrasonic cleaner

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Before the chemical cleaning, each wire rope was cut into 12- to 18-in. sections representing the immersed area for all exposure conditions and the tidal-zone, splash-zone, and above-splash-zone areas on the partially immersed wire ropes. Strands of each wire rope were physically separated for more efficient cleaning and for removal of the fiber-strand cores so that they would not be affected by the cleaning processes.

Each strand of the chemically cleaned wire rope was examined for corrosion at 20X magnification under a stereo microscope. Photographs showing corrosion details were obtained using Panatomic x film in a 35-mm Graflex Stereo Graphic camera.

Cross sections of each specimen were prepared metallographically and viewed at magnifications up to 60X to detect any corrosion that might not have been detected during the examination of the wire-rope strands.

Metallographically polished cross sections of pre-exposed wire-rope specimens were used to measure on a metallograph the original metallic-coating thicknesses.

Before the exposure of these wire ropes, the diameter of individual wires was measured to obtain baseline data. After completing the final microscopic examination of the specimens, it was evident that a comparison of initial and final individual-wire diameters would not produce meaningful data because of the highly localized corrosion that had occurred. It was therefore decided not to determine the final individual-wire diameters and also that a qualitative evaluation of the specimens would be adequate to characterize corrosion and the effectiveness of cathodic protection.

CORROSION ANALYSIS AND POTENTIAL VS TIME DATA

General Comments

The appearance of the corrosion observed on each wire-rope material has been detailed in Table 3. The particular strands of each material that showed the worst corrosion have been summarized in Table 4. Table 5 has indicated the degree of marine fouling, and Table 6 has summarized the corrosion characteristics of wire-rope materials judged to be suitable for long-term, i.e., two-year, service.

A qualitative summary of the degree of corrosion has been plotted as a function of exposure location with respect to mean low water (MLW) and mean high water (MHW) in Figs. 1 — 7. These data were based on the most severe corrosion observed on each material under the exposure conditions indicated. The electrochemical potential of the materials, measured to a Ag/AgCl reference electrode,* has been plotted in Figs. 8 — 11.

Figures 12 — 54 have been used to show the seriousness and degree of corrosion observed and the response of the various wire-rope materials to cathodic protection.

*All potentials in this report were measured to the Ag/AgCl reference electrode.

Table 3
Degree and Type of Corrosion on Wire Rope Specimens* After 790 Days in Sea Water at Key West, Florida

Material	Total Immersion		Partial Immersion – No Cathodic Protection				
	No Cathodic Protection	Cathodic Protection Zinc Anode	Immersed Zone	Immersed – Near Surface Zone	Tidal Zone	Splash Zone	Above Splash Zone
Phosphor Bronze	Very severe corrosion; wires broken	Slight intermittent evidence crevice corrosion	Severe general and pitting corrosion; necked down	Wires badly thinned; severe pitting	All wires severely corroded and broken	Quite severe to 6" above mean high water	Laminar, generalized corrosion
Fiber core	Could not be broken by hand	Could be broken by hand	Could not be broken by hand	Could not be broken by hand	–	Could not be broken by hand	Could not be broken by hand
Galvanized Steel Source 1	Very severe corrosion; wires broken	Slight rust and roughened surface	Very severe corrosion; broken wires	Very severe corrosion; broken wires	Wires broken	Badly whiskered and reduced wire diameter	Very severe
Hemp fiber core	Could not be broken by hand	Could be broken by hand	Could not be broken by hand	Could not be broken by hand	Could not be broken by hand	–	Could not be broken by hand
Galvanized Steel Source 2	Slight-to-moderate corrosion and pitting	No corrosion	Moderate-to-severe corrosion	Considerable general corrosion	Moderate-to-severe corrosion	Very severely corroded	Severe general corrosion; broken wires
IWRC	Essentially no corrosion	No corrosion	Relatively small amount corrosion	Wires thinned	Moderate-to-severe corrosion; some broken wires	Very severely corroded	Severe general and local corrosion
Aluminized Steel Source 1†	Rust stained; essentially no bright aluminum remained	Small amount of superficial rusting†	Some scattered rust areas	Scattered superficial rust	Top 3"—quite severe rusting	Very severe corrosion to 5" above mean high water	No rust; 30 – 80% bright aluminum present
Hemp fiber core	Could not be broken by hand	Could be broken by hand	Could not be broken by hand	Could not be broken by hand	Could be broken by hand	Could not be broken by hand	Could not be broken by hand
Aluminized Steel Source 2	Scattered rusted areas	95% bright aluminum remaining, except under tape	Scattered flaking and corrosion	Scattered rust-stained areas	Scattered superficial rusting; <40% bright aluminum	Rust stains scattered areas; 50% bright aluminum	Localized flaking and corrosion
IWRC	Scattered rusted areas	95% bright aluminum remaining, except under tape	Scattered flaking and corrosion	Scattered rust-stained areas	Scattered superficial rusting; essentially no bright aluminum	Rust stains scattered areas; 30% bright aluminum present	Localized flaking and corrosion
Type 304L Stainless Steel	Severe crevice corrosion under tape	Slightly etched and some shallow pitting	Severe crevice corrosion and tunneling	Rusting, etched and pitting	Considerable crevice corrosion and pitting	Severe crevice corrosion and pitting	Crevice corrosion and pitting
IWRC	Very severe tunneling	Etched and slight crevice corrosion	Badly thinned by crevice corrosion	Tunneling	Some local corrosion	Crevice corrosion, pitting and tunneling	Crevice corrosion and pitting
90/10 Cu-Ni Clad Type 304L Stainless Steel	Irregular corrosion	No corrosion and some mechanical deformation	Tunneling	Crevice corrosion	Severe tunneling	Mechanical deformation	Crevice corrosion and blistering
IWRC	Crevice corrosion and tunneling; Cu-Ni present	No corrosion and some mechanical deformation	Tunneling	Severe tunneling	Severe tunneling	Very severe tunneling	Very severe tunneling
90/10 Cu-Ni Clad Type 205 Stainless Steel	Crevice corrosion and pitting	Discolored and some mechanical deformation	Crevice corrosion	Crevice corrosion	Some crevice corrosion and pitting	Severe tunneling	Very severe corrosion and tunneling to 3' above mean high water
IWRC	Very severe tunneling	Some crevice corrosion	Severe tunneling	Very severe tunneling	Very severe tunneling	Very severe tunneling	Very severe corrosion and tunneling to 3' above mean high water
Nickel-Base Alloy	Slight crevice corrosion with mechanical delamination	Slight crevice corrosion and microscopic pitting	Crevice corrosion and pitting; necked down under tape	Intermittent and slight crevice corrosion	Intermittent and slight crevice corrosion and microscopic pitting	Intermittent and slight crevice corrosion	Intermittent and slight crevice corrosion
WSC	Slight to moderate crevice corrosion under tape with mechanical delamination	No corrosion	Crevice corrosion pitting; necked down under tape	Etched	Evidence slight general corrosion and microscopic pitting	No corrosion	No corrosion
Ti-13V-11Cr-3Al Alloy	Etched; occasional microscopic pitting	Bright and corrosion free†	Etched	Etched; occasional microscopic pitting	Etched; occasional microscopic pitting	Etched; occasional microscopic pitting	Etched
WSC	Etched; occasional microscopic pitting	Bright and corrosion free†	Etched	Etched; occasional microscopic pitting	Etched; occasional microscopic pitting	Etched; occasional microscopic pitting	Etched

*Examined at 20X magnification
†Cross section

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Table 4
Position of the Wire-Rope Strands Showing the Worst Corrosion
After 790 Days in Sea Water at Key West, Florida

Material	Total Immersion		Partial Immersion — No CP*				Remarks
	No CP	CP Zinc Anode	Immersed	Tidal	Splash	Above Splash	
Phosphor Bronze	OS†	Fiber core (hemp) severely deteriorated	OS	OS	OS	OS	No metallic center strand
Galvanized Steel Source 1	OS	Fiber core (hemp) severely deteriorated	OS	OS	OS	OS	No metallic center strand
Source 2	OS	OS & CS,‡ no corrosion	OS & CS	OS & CS	OS & CS	OS & CS	IWRC
Aluminized Steel Source 1	OS	Fiber core (hemp) severely deteriorated	OS	OS; fiber core severely deteriorated	OS	OS	No metallic center strand
Source 2	OS & CS	OS & CS, no corrosion	OS & CS	OS & CS	OS & CS	OS & CS	Corrosion slight to moderate without CP
Type 304L Stainless Steel	CS	Some pitting OS & CS	OS & CS	OS	OS & CS	OS & CS	—
90/10 Cu-Ni Clad Type 304L Stainless Steel	CS	OS & CS, no corrosion	OS & CS	OS & CS	CS	OS & CS	—
90/10 Cu-Ni Clad Type 205 Stainless Steel	CS	Slight-to-moderate corrosion	CS	CS	OS & CS	OS & CS	—
Nickel-Base Alloy	OS & CS	OS & CS, no corrosion	OS & CS	OS & CS	OS	OS	Only slight corrosion without CP; limited to tape area
Ti-13V-11Cr-3Al Alloy	Corrosion limited to etching or microscopic pitting without CP					No corrosion	—

NOTE: *CP = Cathodic Protection; †OS = Outer Strand; ‡CS = Center Strand

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Table 5
Summary of Marine Fouling Characteristics of Wire Ropes
After 531 Days in Sea Water at Key West, Florida

Material	Degree of Marine Fouling
Phosphor Bronze 90/10 Cu-Ni Clad Type 304L Stainless Steel 90/10 Cu-Ni Clad Type 205 Stainless Steel	Slight to Moderate
Type 304L Stainless Steel Ti-13V-11Cr-3Al Alloy Nickel-Base Alloy Galvanized Steel	Moderate
Aluminized Steel	Severe

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Table 6
Summary of Corrosion Characteristics and Response to Cathodic Protection of Nonworking Wire Ropes in Sea Water

Service Condition	Materials Judged Suitable for Long-Term (e.g., 2-yr) Service	Remarks
Partial immersion; rope extends from well below the tidal zone to above the splash zone	Aluminized Steel	Avoid hemp FSC; worst corrosion in splash zone
	Nickel-Base Alloy	Slight-to-moderate corrosion seen under the tape in the immersed zone; avoid Zn socketing (embrittles)
	Titanium Alloy 13V-11Cr-3Al	Working over sheaves may cause rapid deterioration
Totally immersed; no cathodic protection	Aluminized Steel	FSC or IWRC; both suitable
	Nickel-Base Alloy	Slight-to-moderate corrosion seen under the tape; avoid Zn socketing (embrittles)
	Titanium Alloy 13V-11Cr-3Al	Working over sheaves may cause rapid deterioration
Totally immersed; cathodic protection from Zn anode	Phosphor Bronze, Galvanized Steel, and Aluminized Steel	Avoid hemp FSC
	Type 304L Stainless Steel	Pitting not eliminated
	90/10 Cu-Ni Clad Type 304L Stainless Steel	—
	Nickel-Base Alloy	Avoid Zn socketing (embrittles)
	Titanium Alloy 13V-11Cr-3Al	Working over sheaves may cause rapid deterioration

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Phosphor Bronze

Phosphor bronze wire rope was one of the least-corrosion-resistant materials studied. The most severe corrosion occurred at the tidal zone (Figs. 1 and 12) of the partially immersed specimen, but this material was also severely corroded in all the unprotected-exposure conditions, Fig. 13 and top of Fig. 14. The cathodically protected specimen was only slightly corroded during the 790-day exposure period (Figs. 1 and 14), but the cathodic protection severely deteriorated the fiber-strand core. Compare the fiber cores without and with cathodic protection, Figs. 15 and 16.

The electrochemical-potential data for the phosphor bronze wire rope have been plotted in Fig. 8. The potential of the unprotected specimens varied from —0.14 to —0.24 volt, and there was nothing specific in the potential data that indicated how severely or at what specific period, if any, this wire rope corroded. The potential of the cathodically protected specimen was —1.0 volt or more electronegative, and the final examination showed that cathodic protection was effective and that it significantly reduced the corrosion to an acceptable level.

There was visual evidence after 183 days exposure that the unprotected phosphor bronze wire rope had corroded. The totally immersed specimen showed localized reduction in wire diameters, and the partially immersed specimen had a considerable quantity of green corrosion products in the immersed zone and the above-water zone. After 325 days exposure, multiple broken wires were observed in the tidal-zone area of the partially immersed specimen, and heavy green corrosion products were evident on the other specimens, except the one cathodically protected.

Galvanized Steel

There was evidence (Figs. 2 and 17 through 23) that the severity of corrosion was different on the source 1 (fiber-strand core — FSC) and the source 2 (independent wire-rope core — IWRC) unprotected galvanized-steel wire ropes. The source 2 material was less severely corroded than the source 1 material, except in the splash zone where severe corrosion occurred on both materials.

Differences in the corrosion behavior were also observed at the time of the interim inspections. Corrosion in the form of rust was evident on both the partially immersed and totally immersed, unprotected, source 1 specimens after 183 days. The unprotected source 2 material also showed heavy rust at the 183-day inspection, but the corrosion was limited to the splash-zone area of the partially immersed specimen. Corrosion was not evident on the unprotected, totally immersed, source 2 specimen at the 325-day inspection.

It was thought that the differences in corrosion characteristics might be caused by differences in the zinc-coating thicknesses. This was not so, however, since the coating thicknesses of the two galvanized-steel wire ropes were similar (Table 1). The differences observed in the corrosion behavior cannot be fully explained but were believed to have been caused in part by the source 1 material having a fiber-strand core, whereas the source 2 material had an independent wire-rope core. The difference in the initial individual-wire diameters (Table 1) could also have contributed to the differences observed in the corrosion behavior of the source 1 and source 2 galvanized-steel wire ropes.

When the specimens were not cathodically protected by a zinc anode, both the source 1 and source 2 galvanized-steel wire ropes were quite severely corroded after 790 days in sea water, as shown in Fig. 2. The hemp-fiber-strand core of the source 1 galvanized-steel wire rope was severely deteriorated when this specimen was cathodically protected. The degree and extent of corrosion and the effectiveness of cathodic protection have been shown in Figs. 17 through 23.

The electrochemical potential of the galvanized-steel specimens have been plotted in Figs. 8 and 9. There was evidence that corrosion of the galvanized steel could be detected by the change in the electrochemical potential with time. The source 1 unprotected specimens had rusted considerably by the 183-day inspection, and the potential (Fig. 8) showed a change from approximately —1.0 volt to —0.7 volt during the first 90 days of the experiment.

The potential of the cathodically protected specimen remained more electronegative than approximately —1 volt for the entire 790-day exposure period. These observations correlated with the generally accepted cathodic protection rule-of-thumb guideline that steel corrodes in sea water unless the potential is —0.8 volt or more electronegative. On bare steel, an electronegative protective potential of this magnitude can only be achieved in sea water by cathodic protection.

The potential of the source 2 galvanized-steel wire rope (Fig. 9) also showed a change with time, but the change was not at the same rate as observed for the source 1 material. Only the potential of the partially immersed specimen of the source 2 material became more electropositive than —0.8 volt by the 183rd day, and heavy rust was observed on this specimen. The potential of the unprotected, totally immersed specimen was slightly more electronegative than —0.8 volt at 325-day inspection, and no corrosion was observed. The potential of this specimen continued to change and reached —0.7 volt at 486 days. The potential remained at approximately this value for the remainder of the experiment, and as indicated in Fig. 2 the corrosion was moderate to severe after 790 days in sea water.

The cathodically protected source 2 specimen had an initial potential of —1.04 volts and remained at approximately —1.0 volt for the duration of the experiment. This specimen was essentially uncorroded after 790 days in sea water.

Zinc in the form of galvanizing up to approximately 0.6 mil thick protected the steel in the wire rope for slightly more than one year on the totally immersed specimen which had an independent wire-rope core. Less than six months protection from the galvanizing was obtained either when the wire rope had a fiber-strand core or when the specimen was partially immersed.

Cathodic protection from a zinc anode extended the life of the galvanized wire rope to longer than two years, but severely deteriorated the hemp-fiber-strand core in the source 1 galvanized wire rope.

Aluminized Steel

In the totally immersed condition in sea water, the aluminized-steel wire rope was one of the most inherently corrosion-resistant materials studied. The degree of corrosion observed in the various exposure conditions after 790 days exposure has been plotted in Fig. 3.

Details on the extent and degree of corrosion and the effects of cathodic protection have been shown in Table 3 and Figs. 24 through 32.

Similar to the galvanized-steel wire ropes, the aluminized-steel wire rope with the hemp-fiber-strand core (source 1 material) did not have the inherent corrosion resistance of the material with the independent wire-rope center (source 2 material). This was especially evident in the tidal and splash zones (Figs. 3, 25, and 29) where severe to very severe corrosion was observed on the aluminized steel with the fiber-strand core. Only slight to moderate corrosion was observed on the totally immersed, unprotected specimens after 790 days in sea water (Fig. 3).

When the aluminized-steel wire ropes were cathodically protected with a zinc anode, much of the aluminum was still present on the individual wires, and the specimens were essentially corrosion free (Figs. 3, 26, 31, and 32) at the end of the experiment. The hemp-fiber-strand core was, however, severely deteriorated by the cathodic protection (Fig. 27). On the partially immersed specimen the fiber-strand core was also severely deteriorated but only in the tidal-zone area.

The difference in the corrosion behavior between the source 1 and source 2 aluminized-steel wire ropes, as in the galvanized steel, could not be attributed to coating thickness, because the coating thicknesses on the two materials were quite similar (Table 1). As in the galvanized steel, the hemp-fiber-strand core was believed to be the major cause for the differences in corrosion characteristics between the source 1 and source 2 materials. The differences in initial individual-wire diameters could also have been a contributing factor.

Because macroscopic examination of the aluminized-steel wire ropes was not sufficient to detect the relatively severe corrosion and the deterioration of the hemp-fiber-strand core observed on the source 1 material, it was necessary to separate and microscopically study the wire-rope strands. If metallographic cross-section studies could not have been performed, it would also have been necessary to separate the wire rope into individual wires before the microscopic examination.

The electrochemical potentials of the aluminized-steel wire ropes have been plotted in Figs. 8 and 9. The initial potential of unprotected specimens ranged from —0.76 to —0.81 volt. For the source 1 aluminized steel the potential ranged between —0.74 and —0.84 volt for the first 346 days, remained fairly constant at —0.76 volt from 347 to 600 days, and was more electronegative than —0.72 volt for the rest of the experiment. The cathodically protected specimens had an initial potential of —1.03 volts and remained more electronegative than —1.0 volt during the experiments. For the source 2 material the potential ranged from —0.74 to —0.79 volt for the first 600 days and remained more electronegative than —0.70 volt during the rest of the experiment. The cathodically protected specimen had an initial potential of —1.04 volts and remained more electronegative than —1.0 volt during the experiment.

It can be concluded from these relatively positive potential data and the relatively small amount of corrosion observed on the unprotected immersed specimens that the mechanism of protection for the aluminized-steel wire rope specimens was one of essentially barrier protection rather than cathodic protection.

With the barrier protection and the fact that the potential of the aluminized steel was generally more electropositive than —0.8 volt (the potential normally considered to be

required for cathodic protection of steel in sea water), one must not extrapolate the successful use of immersed and non-cathodically-protected aluminized-steel wire rope for time periods much in excess of the 790 days of this experiment. Longer term use of aluminized-steel wire rope can undoubtedly be realized in conjunction with an adequate cathodic-protection system.

Titanium 13V-11Cr-3Al Alloys

Table 1 shows that the individual wires in the titanium-alloy wire rope initially were approximately half the diameter of the smallest wires in the other materials and that the overall titanium-alloy wire-rope diameter was 1/8 in.

As noted in Table 3, this titanium-alloy wire rope had the greatest inherent corrosion resistance of any of the materials studied. The extent of corrosion on the unprotected specimens was that of occasional microscopic pitting and etching. The cathodically protected specimen was bright and corrosion free. Because of the excellent corrosion resistance of the titanium alloy, a plot of degree of corrosion as a function of the various exposure conditions would have resulted in a straight vertical line at approximately the "none" location on the abscissa. This type of plot has therefore been omitted from this report for the titanium-alloy wire rope.

The electrochemical potential data for the titanium alloy has been plotted in Fig. 10. The initial potential for the partially immersed specimen was —0.29 volt and by the 12th day had changed to +0.09 volt. The potential remained electropositive between +0.07 and +0.27 volt for the rest of the experiment, except for an occasional change to electronegative values. The initial potential of the unprotected, totally immersed specimen was —0.25 volt and remained between —0.2 and —0.25 volt for the first 90 days of the experiment. After this time period the potential changed in the electropositive direction and reached zero volt after 160 days. The potential remained in the electropositive potential range for the rest of the experiment, except for infrequent changes to electronegative values. After 655 days the potential remained fairly stable at approximately +0.22 volt.

The fluctuation in potential with time for the titanium specimens indicated that there may be a film breakdown and repair process in action which was responsible for the titanium alloy's excellent corrosion resistance. When the film on the titanium broke down, one would expect a more electronegative potential, due to the titanium metal being in contact with the sea water. When the film was self-repaired, the potential would be expected to shift in the electropositive direction. The fluctuation of potential with time and the absence of such fluctuations on other metals will be discussed in subsequent sections of this report.

The initial potential of the cathodically protected titanium-alloy specimen was —1.03 volts and remained more electronegative than —1.0 volt for the duration of the experiment. Corrosion was also nonexistent on this specimen of wire rope.

Although not a part of this study, it has been evident from experiences with titanium wire ropes that working over sheaves may cause rapid deterioration; therefore one could expect difficulty in an application of this type, although the inherent corrosion resistance could be expected to be excellent.

Nickel-Base Alloy

The material described in this report as the nickel-base alloy had the following nominal percent chemical composition: Ni — 62; Cr — 22; Mo — 9; Fe — 2; Cb and Ta — 3.75.

The degree of corrosion observed at the various exposure locations and under various conditions has been plotted in Fig. 4, which showed that the nickel-base alloy was relatively corrosion resistant even without cathodic protection. The only corrosion observed on this alloy occurred at the taped areas on the lower end of the specimens. The corrosion observed as being slight to moderate in quantity was additionally observed as being localized.

The cathodically protected specimen was free of corrosion. Details on the degree of corrosion observed on the nickel-base alloy have been shown in Table 3 and Figs. 33 through 35.

The electrochemical-potential-vs-time data for the nickel-base alloy have been plotted in Fig. 10. The initial potential of the partially immersed specimen was —0.06 volt and remained electronegative for the first 100 days of the experiment. The potential then changed to positive values (at one point reaching to +0.6 volt) and remained in the electropositive potential range up to 360 days, except for an occasional shift to electronegative values. After 360 days the potential remained electronegative (to —0.16 volt) and was fairly constant at zero volt for the last 95 days of the experiment.

The initial potential of the totally immersed and unprotected nickel-base-alloy specimen was —0.09 volt and after twelve days had reached zero volt. The potential remained electropositive up to 660 days exposure, except for an occasional and sometimes rather extended period when it was electronegative. A range of potential from —0.25 to +0.35 volt was observed on this specimen, although during the final 95 days of the experiment the potential was rather constant at approximately zero volt.

The initial potential of the cathodically protected, totally immersed, nickel-base-alloy specimen was —1.03 volts and remained more electronegative than —1.0 volt for the entire duration of the experiment. Corrosion was not observed on this specimen.

The discussion concerning the fluctuation in potential with time and film breakdown and repair in the section on the titanium-alloy wire-rope specimens is also applicable to the nickel-base alloy. Here again, there was evidence that the fluctuation in potential with time was indicative of a more corrosion-resistant metal.

Although not a part of this particular study on the corrosion resistance and the response to cathodic protection of wire rope, it has been observed that the nickel-base alloy studied may become embrittled on cooling if the temperature of the metal is raised approximately 200 degrees above room temperature. Caution should be exercised in socketing this nickel-base alloy with zinc since it may cause embrittlement.

Copper-Nickel Clad Stainless Steel (Types 304L and 205)
and Unclad Type 304L Stainless Steel

The 90/10 copper-nickel clad stainless steels and unclad Type 304L stainless steel were among the least corrosion resistant of the materials studied. Details on the type and degree

of corrosion observed on these stainless-steel materials in the various exposure conditions have been shown in Table 3 and Figs. 5, 6, 7, and 36 through 54.

Corrosion in the form of rust was evident on all the unprotected specimens after 183 days. The greatest quantity of rust was observed on the copper-nickel clad Type 205 stainless steel. At the 325-day inspection, more rust was evident on all unprotected specimens, and the Type 205 clad stainless steel had multiple broken wires in the splash-zone area.

The types of corrosion observed on both the clad and unclad stainless-steel wires ropes after 790 days in sea water were tunneling and crevice corrosion, which sometimes resulted in broken wires. Probing of the wire ropes with a needle during the final examination showed how misleading an external-only examination could have been. Figure 37 has shown the needle probe emerging from a wire that has been tunneled by corrosion. Note the excellent condition of the external surfaces of all the wires of this specimen. Figure 38 showed the relatively good condition of the external wire surfaces, but the needle point readily punctured the wire surface and showed that only a hollow shell or tube remained. The internal area of the wire had completely corroded.

The corrosion data developed in this study have shown that the copper-nickel clad stainless steels were essentially no more resistant to corrosion in quiescent sea water than the unclad Type 304L stainless steel, which also had very poor inherent corrosion resistance.

The effectiveness of cathodic protection from a zinc anode on the clad and unclad stainless-steel wire ropes has also been shown in Table 3 and Figs. 5, 6, 7, 40, 46, 47, and 54. These data showed that even with cathodic protection, only the copper-nickel clad Type 304L stainless steel was essentially free from corrosion (Fig. 40) after 790 days in sea water.

The electrochemical potentials of the clad and unclad stainless-steel wire ropes have been plotted in Fig. 11. The potentials of the copper-nickel clad stainless steels were less than 0.2 volt more electronegative than the potential of the unclad Type 304L stainless steel. This small difference in potential was insufficient for the copper-nickel cladding to cathodically protect the stainless steel. The corrosion data also showed that the copper-nickel cladding was not effective as a barrier coating to prevent the corrosion of the stainless steels.

The maximum change in the long-term potential for any of the unprotected specimens was 0.1 volt. There was no correlation between potential changes and the corrosion observed after 183 and 325 days. The relatively constant potential data with time for these stainless steels (Fig. 11) which corroded severely were in contrast to the changing potential data observed for the titanium and nickel-base alloys (Fig. 10) that had good inherent corrosion resistance. Although it would require many more experiments and the correlating of much more data to confirm, it appeared from these potential data and corrosion characteristics that a material with a relatively stable electrochemical potential corroded severely in quiescent sea water and that a material whose potential fluctuated often had better inherent corrosion resistance.

Outer Strand vs Center Strand Corrosion

Table 4 showed that, except for fiber-strand-core wire ropes where only the outer strands were metallic, there was no pattern which indicated either the outer or inner strands were more severely corroded under all the exposure conditions. Only in the clad and unclad stainless steels was there somewhat of a consistent pattern, i.e., in the unprotected, totally immersed condition the most severe corrosion occurred in the center strand. This again points out how misleading the appraisal of the condition of a stainless-steel wire rope could have been if only the exterior surfaces of the wire rope were inspected.

FOULING CHARACTERISTICS

A qualitative summary of the degree of marine fouling observed on the various materials after 531 days in sea water has been shown in Table 5. None of the materials was completely free of fouling, but as would be expected the materials containing copper were most resistant to marine fouling.

SUMMARY

A summary of the corrosion characteristics and response to cathodic protection of nonworking wire ropes in sea water has been shown in Table 6. This summary showed that only three materials — the aluminized steel, the titanium alloy, and the nickel-base alloy — were judged suitable for use in sea water for approximately two years service even without cathodic protection. When aluminized steel was partially immersed, however, the hemp center deteriorated in the tidal-zone area. The precautions indicated in the remarks column of Table 6 should be considered when deciding on a particular wire-rope material for use in sea water. The 90/10 copper-nickel clad Type 205 stainless steel could not be considered a satisfactory material for use in sea water even with cathodic protection from zinc anodes.

Cathodic protection was effective, however, in reducing the corrosion of all materials studied but did not completely eliminate the pitting on the unclad Type 304L stainless steel and caused severe deterioration of the fiber-strand cores in the phosphor bronze, the galvanized-steel, and the aluminized-steel wire ropes.

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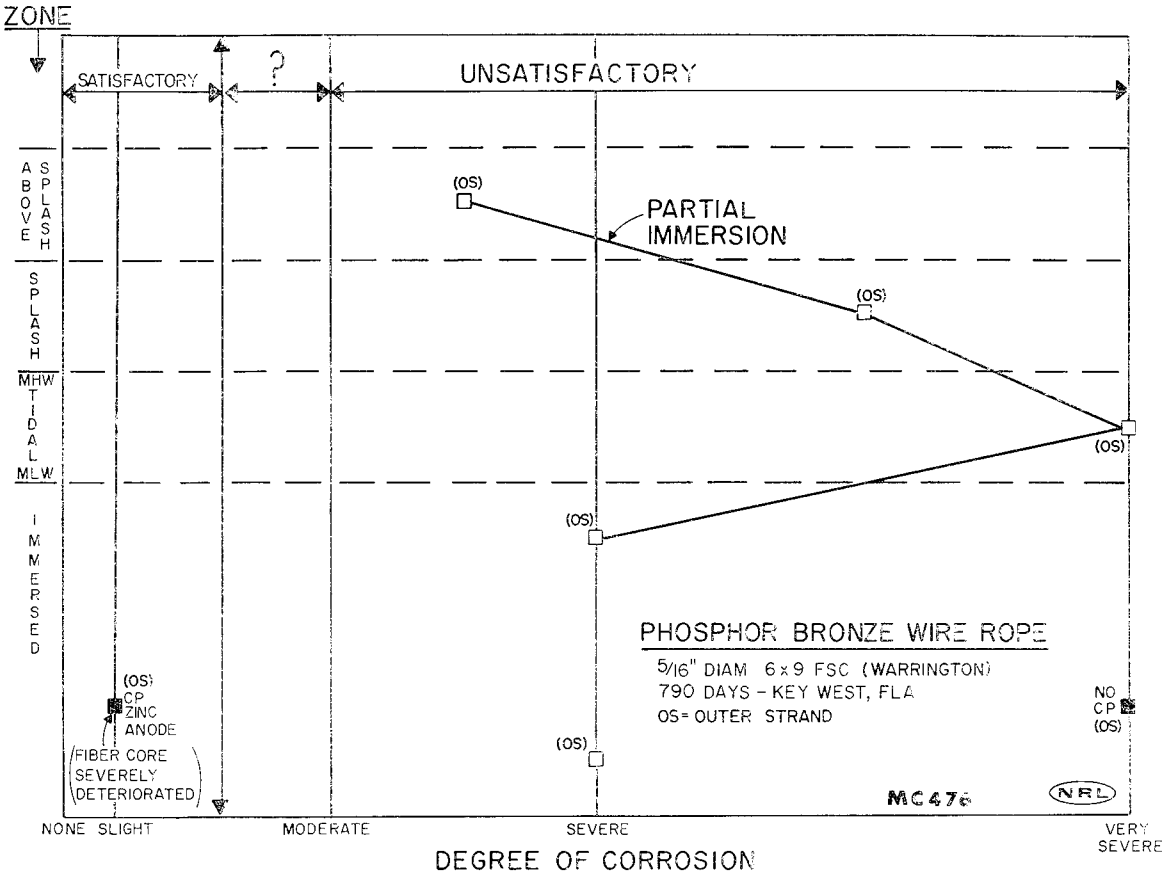


Fig. 1 — Degree of corrosion and cathodic-protection response for phosphor bronze wire rope

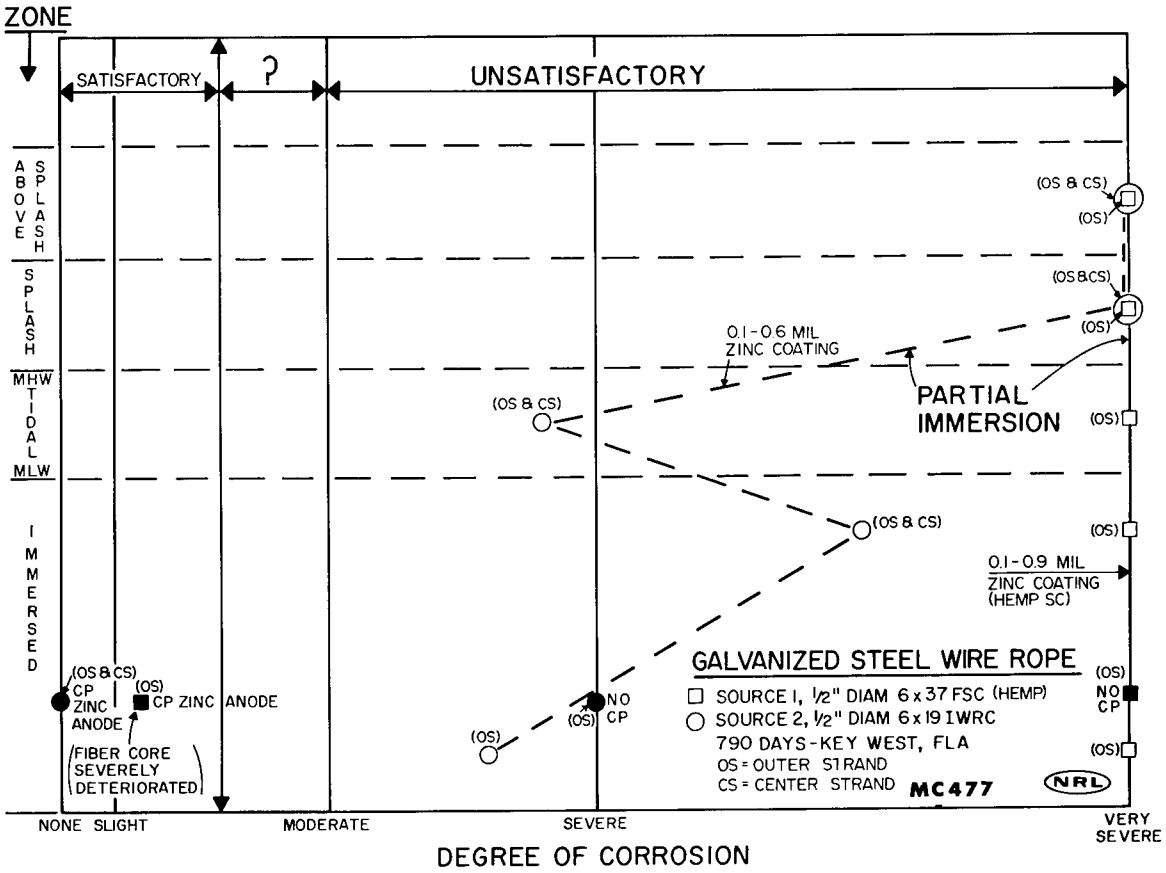


Fig. 2 — Degree of corrosion and cathodic-protection response for galvanized-steel wire rope

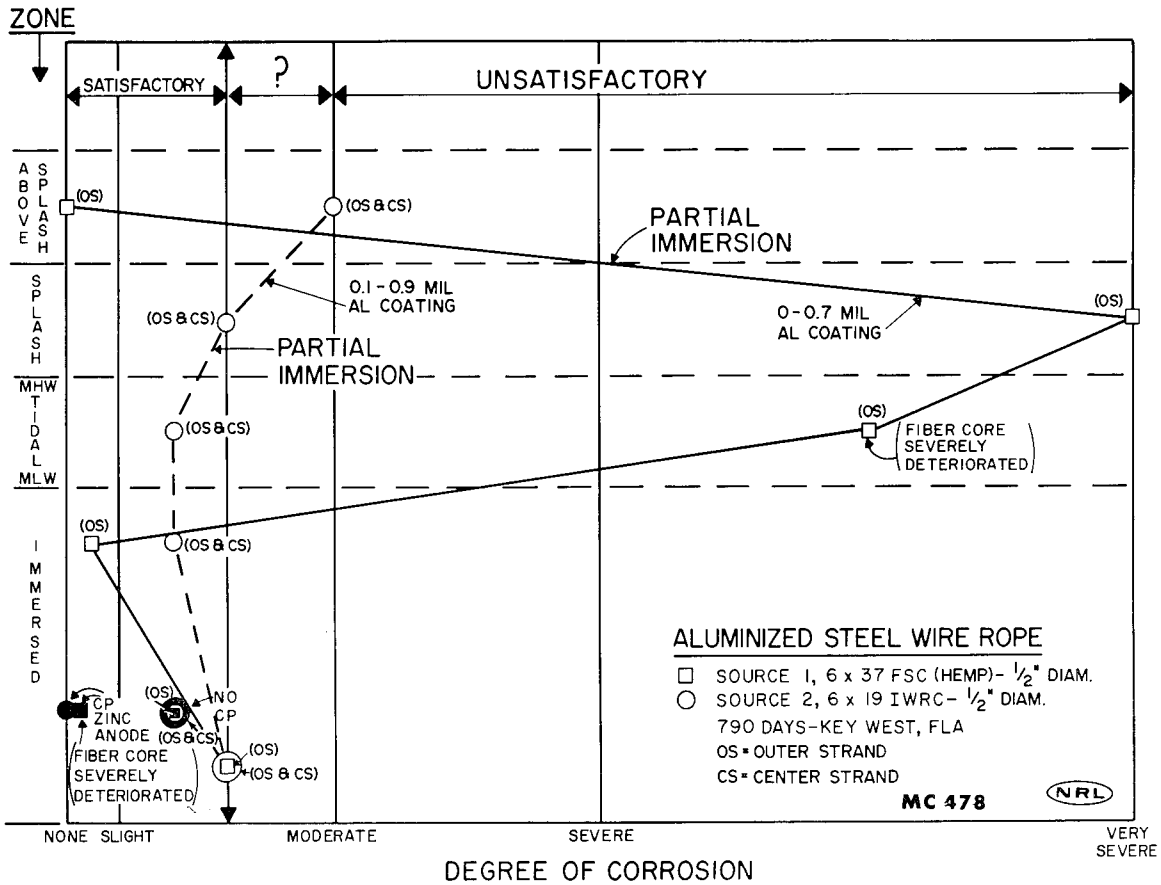


Fig. 3 — Degree of corrosion and cathodic-protection response for aluminized steel wire rope

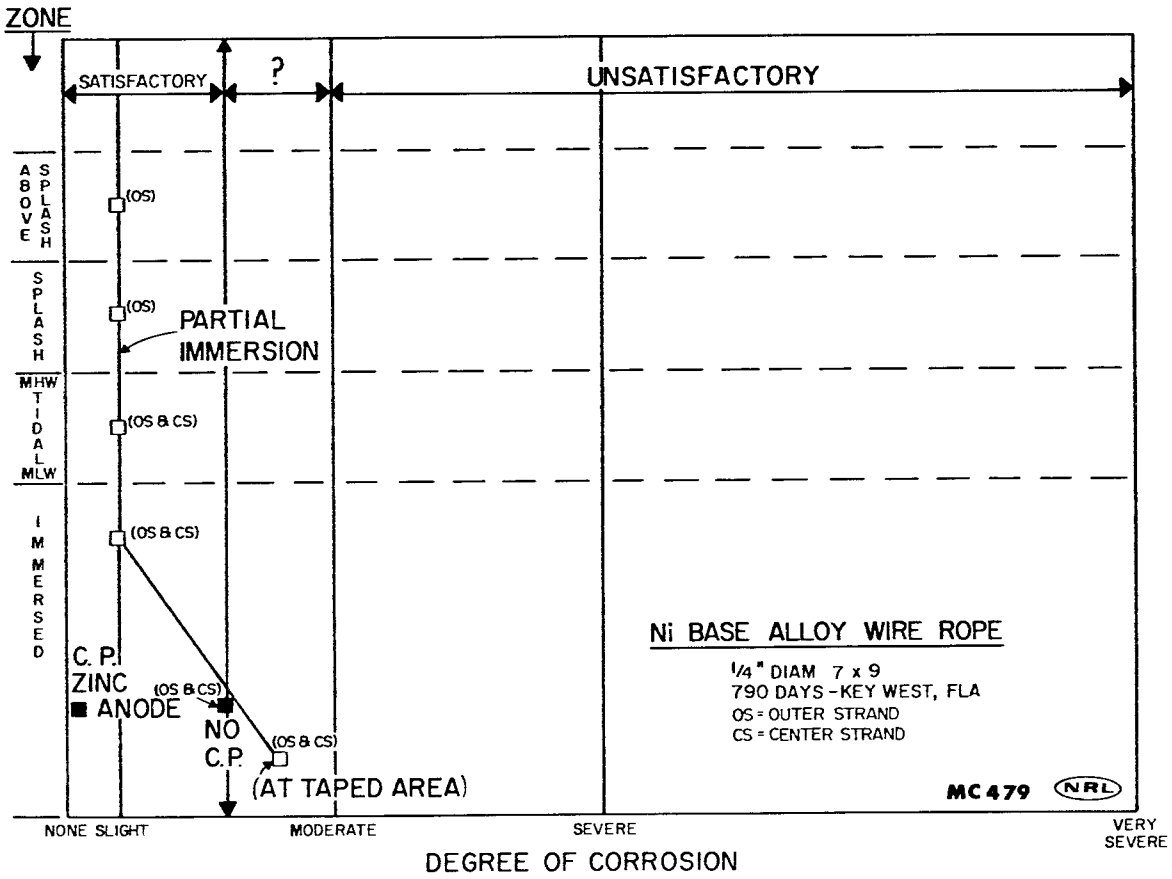


Fig. 4 — Degree of corrosion and cathodic-protection response for nickel-base-alloy wire rope

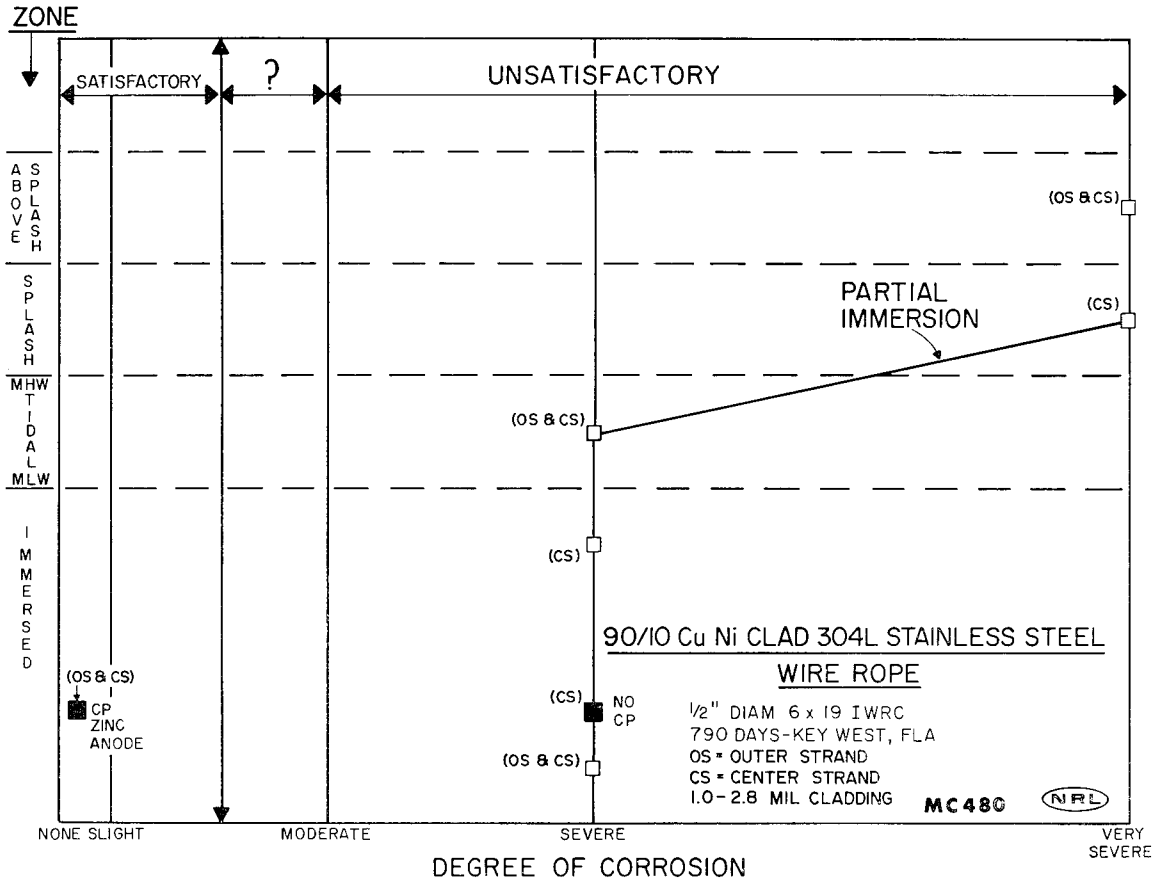


Fig. 5 — Degree of corrosion and cathodic-protection response for 90/10 copper-nickel clad Type 304L stainless steel wire rope

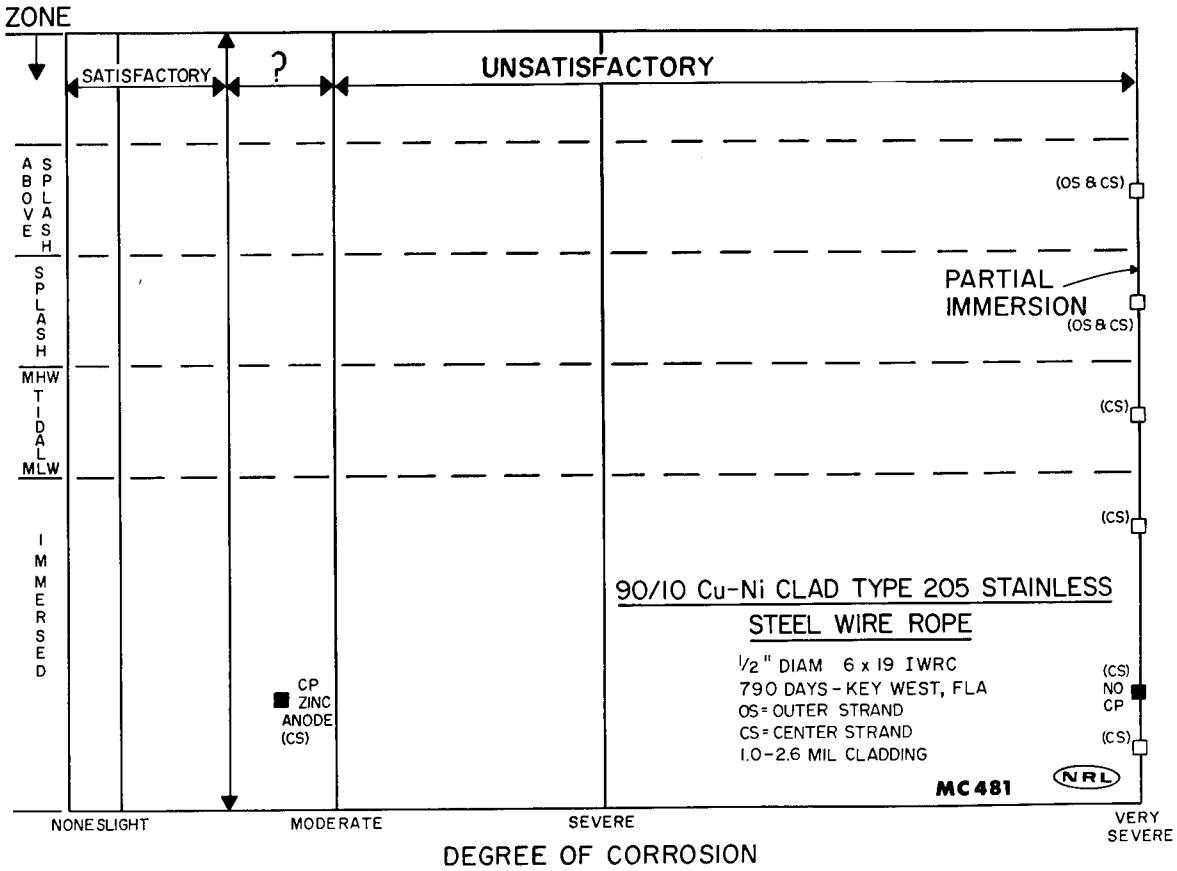


Fig. 6 — Degree of corrosion and cathodic-protection response for 90/10 copper-nickel clad Type 205 stainless steel wire rope

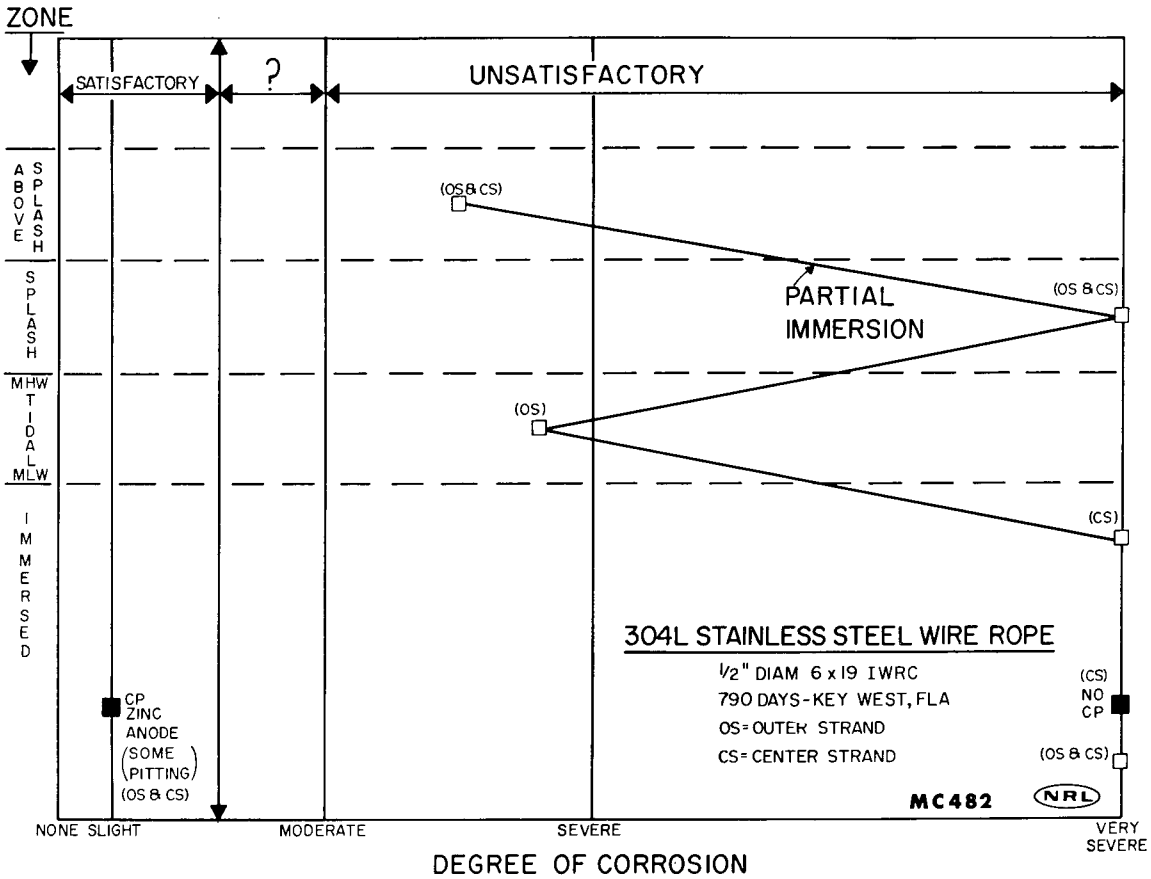


Fig. 7 — Degree of corrosion and cathodic-protection response for Type 304L unclad stainless steel wire rope

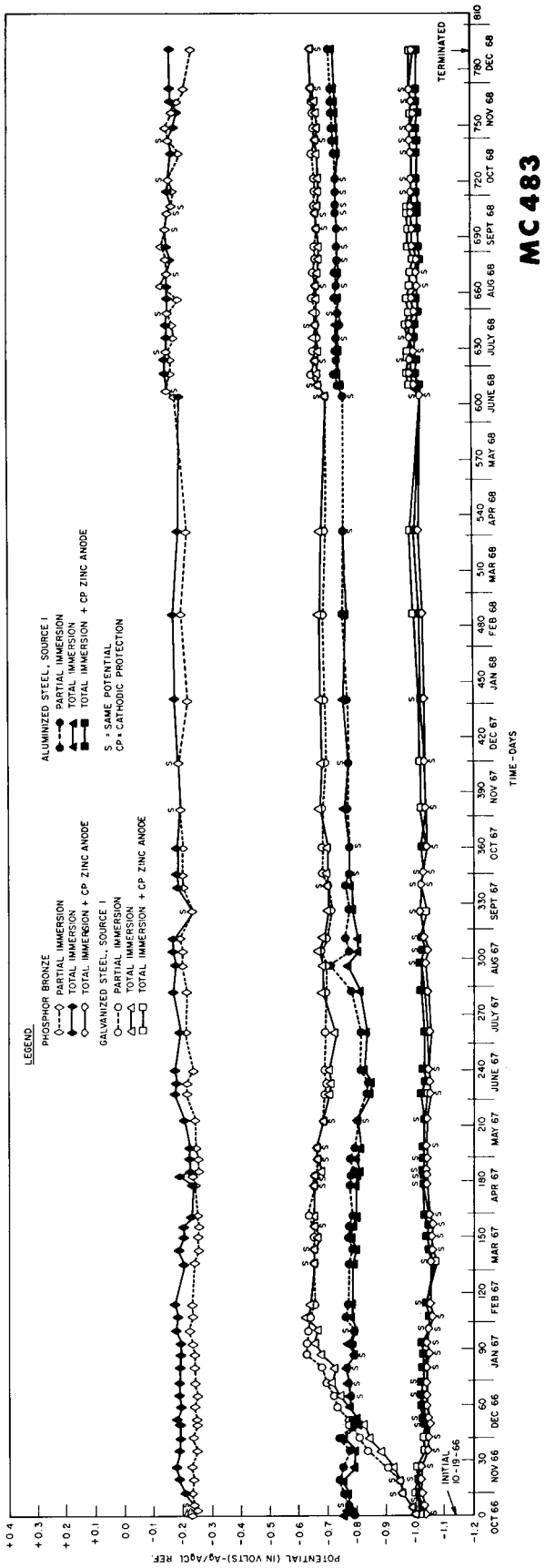


Fig. 8 — Potential vs time data for phosphor bronze, source 1 galvanized-steel, and source 1 aluminized-steel wire rope with and without cathodic protection — 790 days in sea water

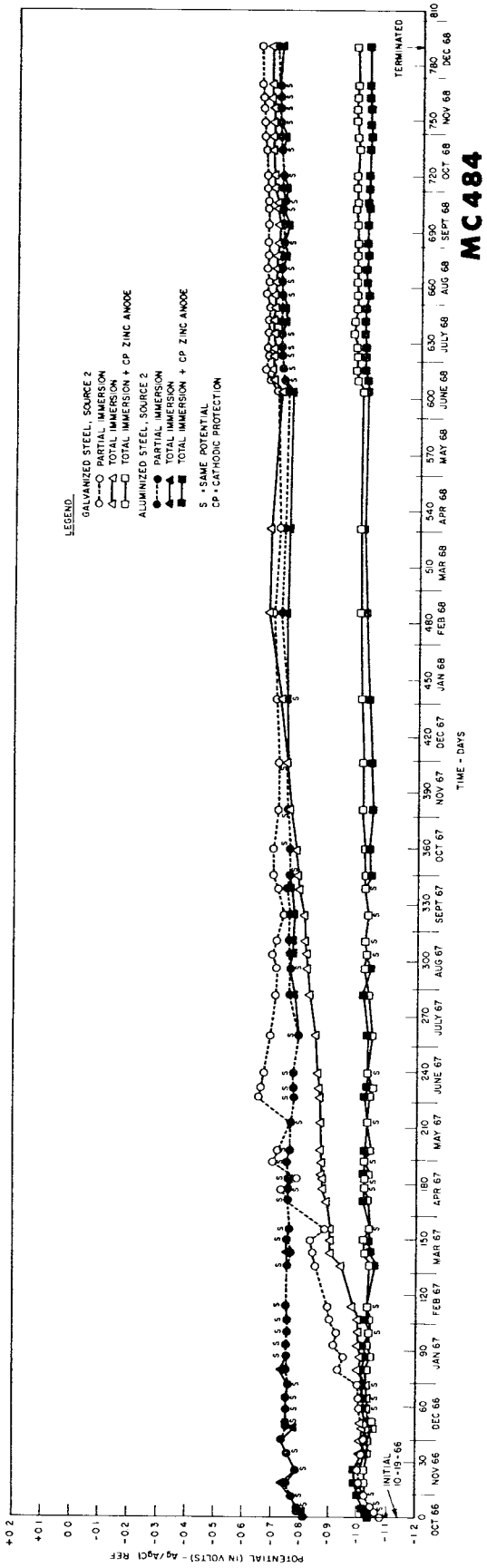


Fig. 9 — Potential vs time data for source 2 galvanized-steel and source 2 aluminized-steel wire rope with and without cathodic protection — 790 days in sea water

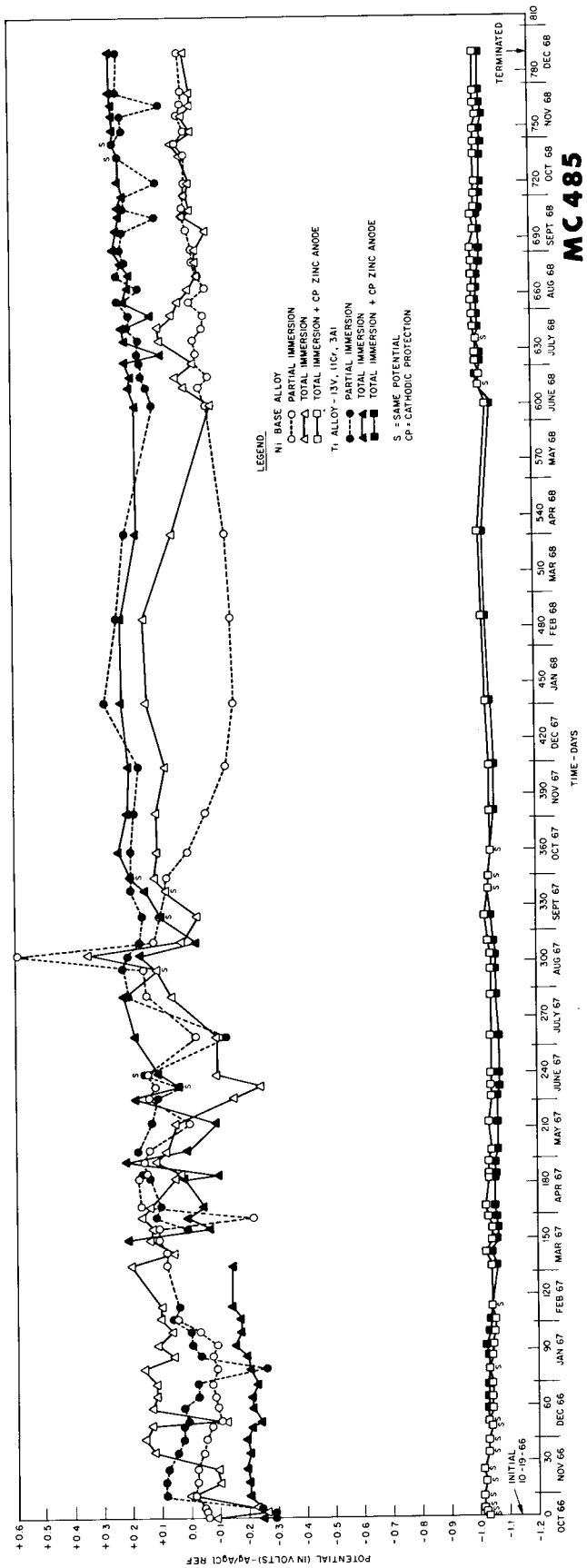


Fig. 10 — Potential vs time data for nickel-base-alloy and titanium 13V-11Cr-3Al alloy wire rope with and without cathodic protection — 790 days in sea water

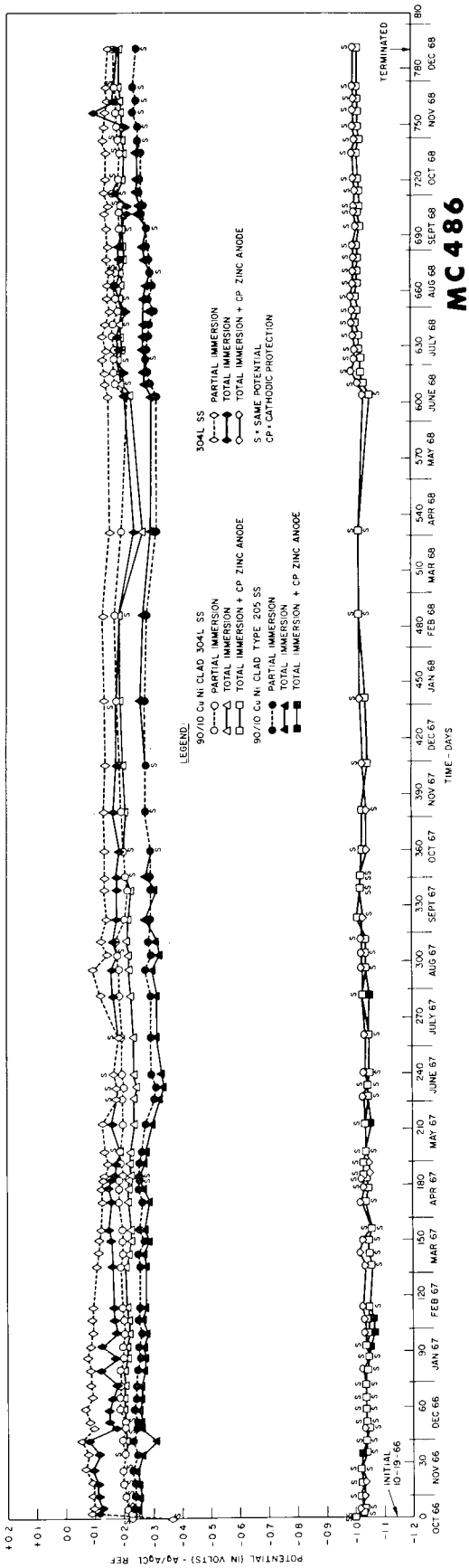
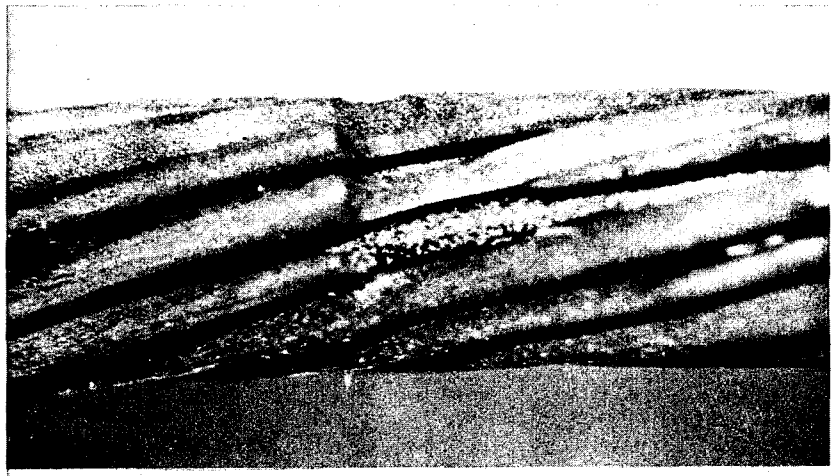


Fig. 11 — Potential vs time data for 90/10 copper-nickel clad Types 304L and 205 stainless steel and unclad Type 304L stainless steel wire rope with and without cathodic protection — 790 days in sea water

MC487

Fig. 12 — Phosphor bronze (entire wire rope) showing severe corrosion at the tidal zone; specimen partially immersed — 790 days in sea water; 9X magnification

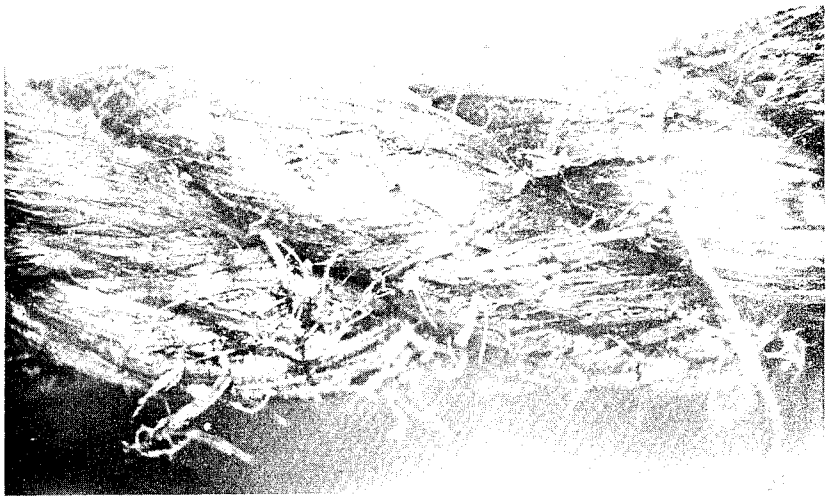


MC488

Fig. 13 — Phosphor bronze (outer strand) showing severe corrosion just outside the PVC-taped area in the immersed zone; specimen partially immersed — 790 days in sea water; 19X magnification

MC 489

Fig. 14 — Phosphor bronze (outer strand); top — without cathodic protection, showing very severe corrosion and broken wires; bottom — with cathodic protection, showing relatively good condition; just outside the PVC-taped area; specimens totally immersed — 790 days in sea water; 19× magnification



MC490

Fig. 15 — Fiber core of phosphor bronze wire rope without cathodic protection, showing the good condition of the fibers; specimen totally immersed — 790 days in sea water; 19× magnification

MC491

Fig. 16 — Fiber core of phosphor bronze wire rope with cathodic protection, showing the severe deterioration of the fibers; specimen totally immersed — 790 days in sea water; 19× magnification

MC492

Fig. 17 — Source 1 galvanized steel (entire wire rope) showing severe corrosion in the splash zone; specimen partially immersed — 790 days in sea water; 9× magnification

Fig. 18 — Source 1 galvanized steel (outer strand) showing severe corrosion and broken wires in the tidal zone; specimen partially immersed — 790 days in sea water; 25× magnification

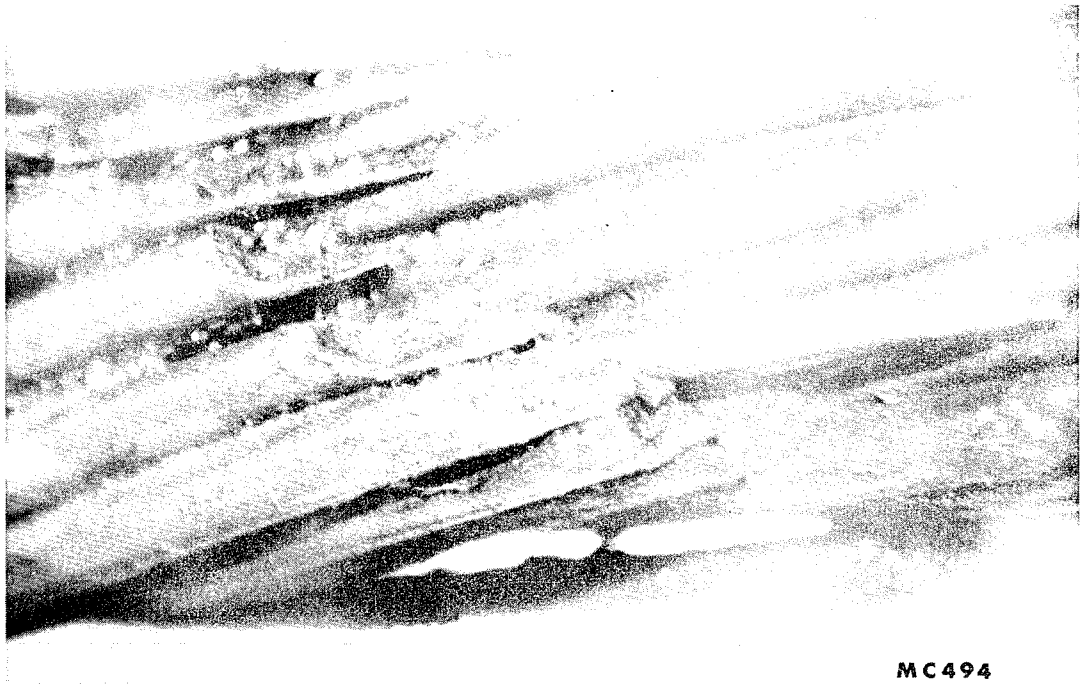
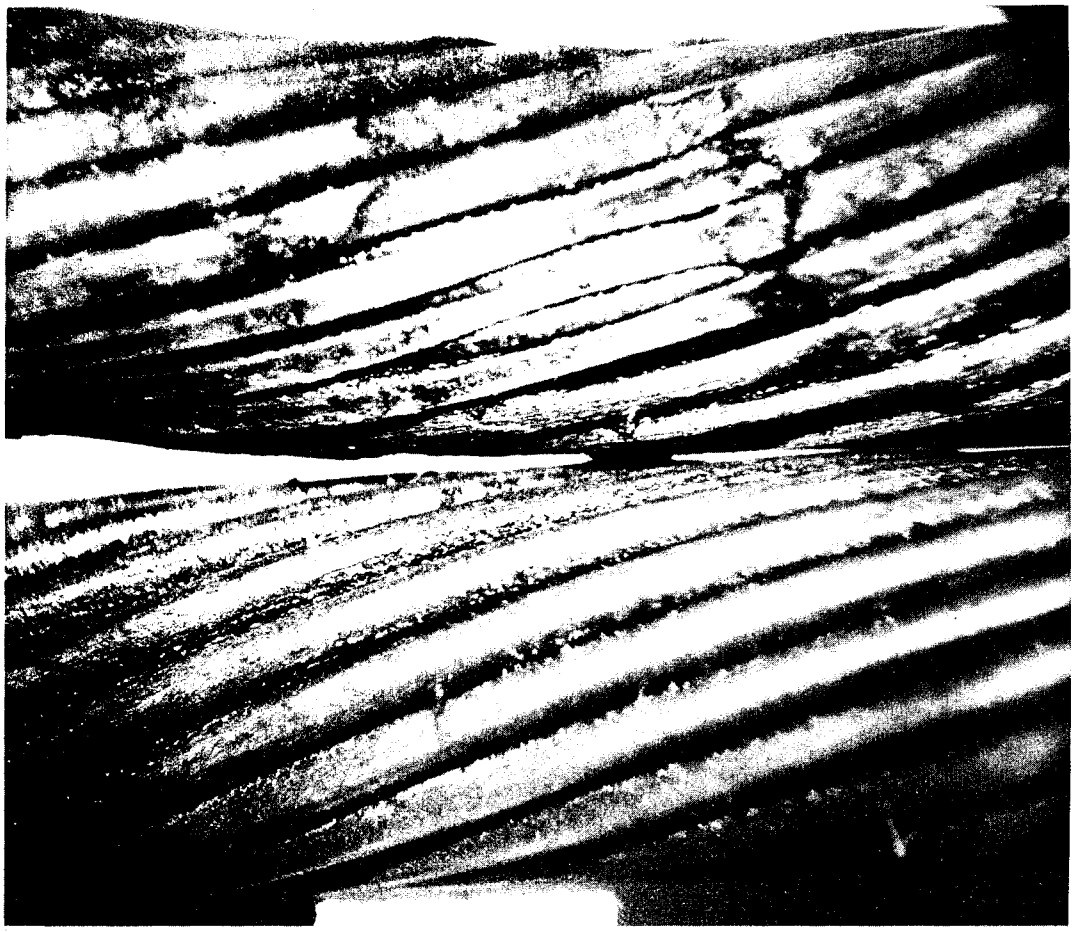


Fig. 19 — Source 1 galvanized steel (outer strand) showing severe corrosion in the immersed zone; specimen partially immersed — 790 days in sea water; 25× magnification



MC495

Fig. 20 — Source 1 galvanized steel (outer strands); top — without cathodic protection, showing severe thinning of the wires; bottom — with cathodic protection, showing slight roughened surfaces; specimens totally immersed — 790 days in sea water; 19X magnification

MC 496

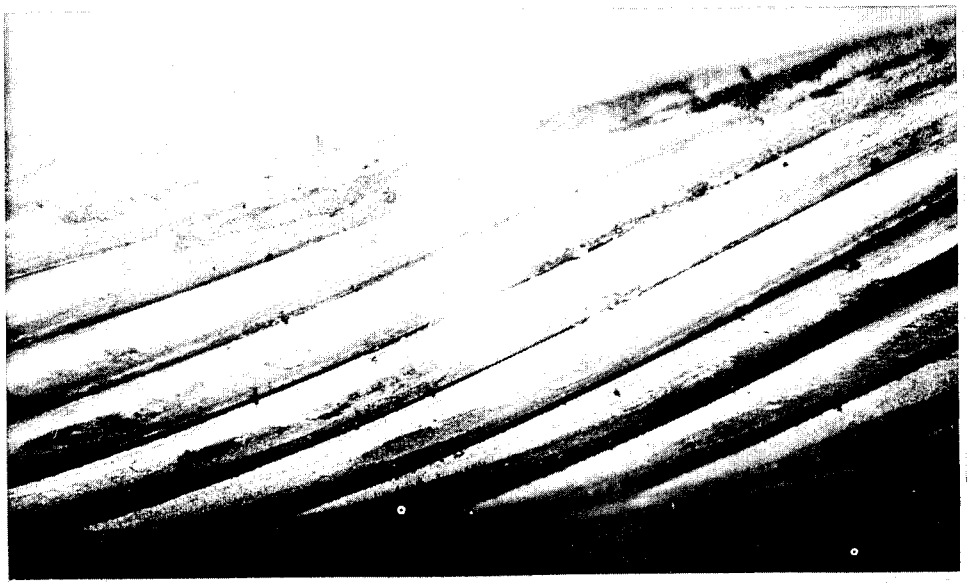
Fig. 21 — Source 2 galvanized steel (entire wire rope) showing severe corrosion in the splash zone; specimen partially immersed — 790 days in sea water; 11X magnification

MC497

Fig. 22 — Source 2 galvanized steel (outer strand) showing the general thinning of wires in the immersed zone; specimen partially immersed — 790 days in sea water; 25X magnification

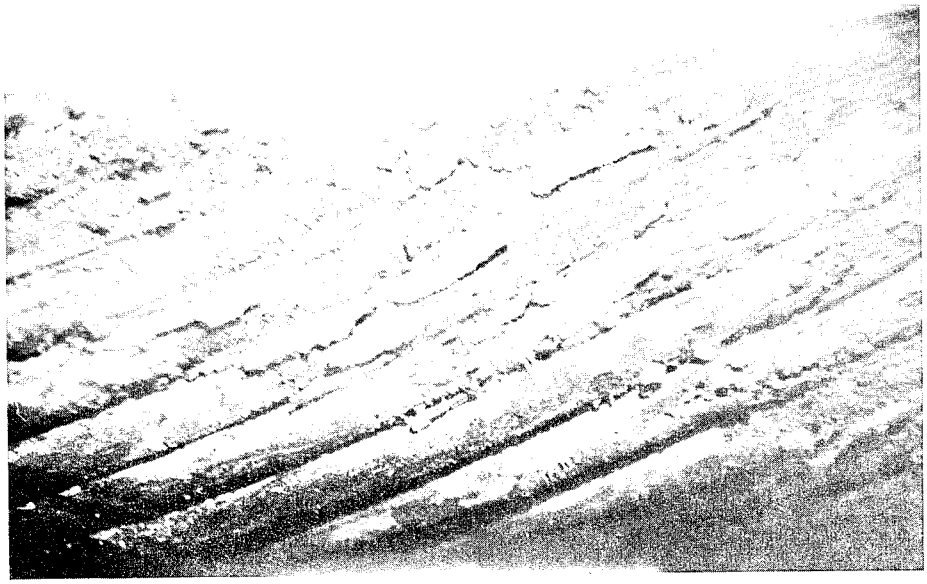
MC498

Fig. 23 — Source 2 galvanized steel (outer strands); top — without cathodic protection, showing slight to moderate corrosion; bottom — with cathodic protection, showing absence of corrosion; specimens totally immersed — 790 days in sea water; 13× magnification



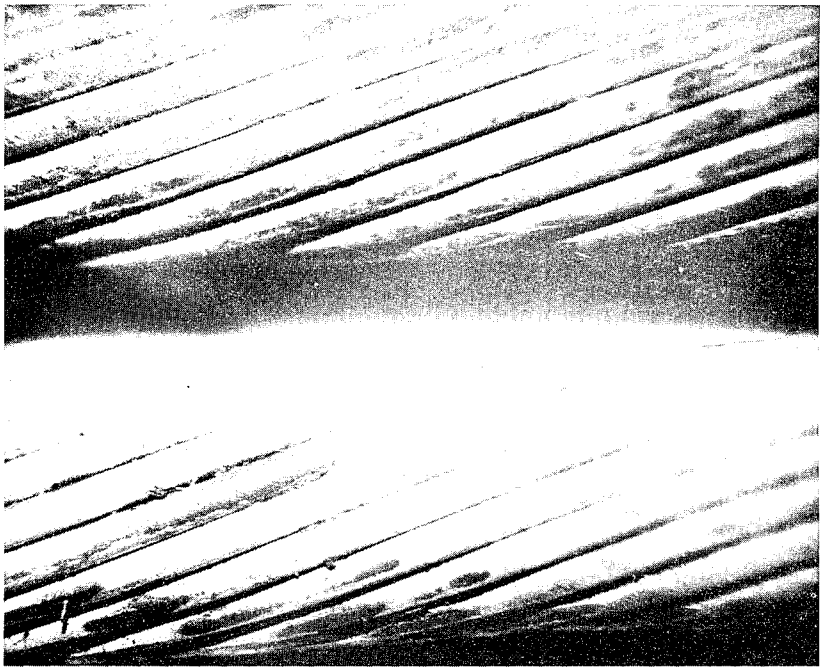
MC499

Fig. 24 — Source 1 aluminized steel (outer strand) showing the good condition of the wire rope, except for some mechanical deformation, at 3 ft above mean high water; specimen partially immersed — 790 days in sea water; 19× magnification



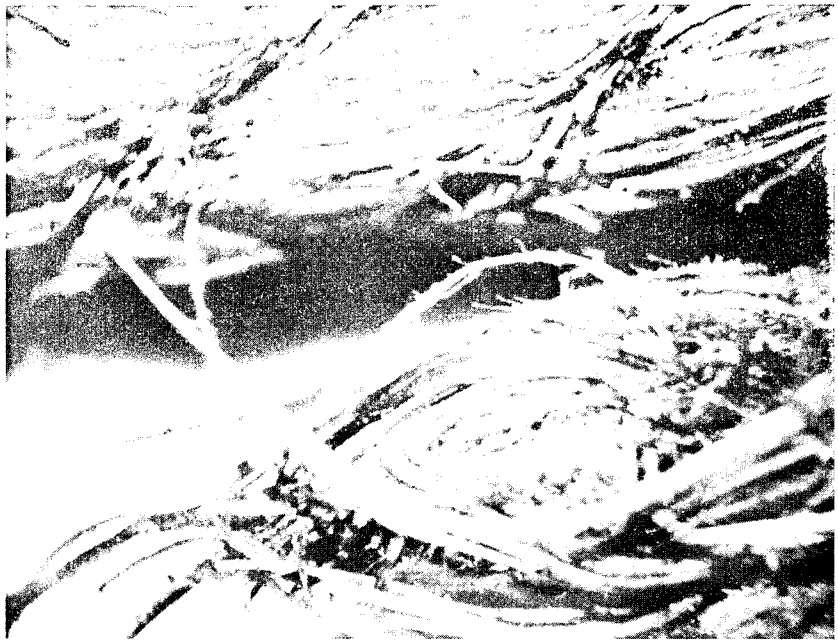
MC 500

Fig. 25 — Source 1 aluminized steel (outer strand) showing very severe corrosion and scaling at the splash zone; specimen partially immersed — 790 days in sea water; 19X magnification



MC 501

Fig. 26 — Source 1 aluminized steel (outer strands); top — without cathodic protection showing rust stain; bottom — with cathodic protection, showing a greater amount of aluminum remaining and slight superficial rust; specimens totally immersed — 790 days in sea water; 13X magnification



MC 502

Fig. 27 — Source 1 aluminized steel (hemp-fiber core); top — without cathodic protection, showing the good condition of the fibers; bottom — with cathodic protection, showing severe deterioration of the fibers; specimen totally immersed — 790 days in sea water; 13× magnification

MC503

Fig. 28 — Source 2 aluminized steel (IWRC) showing corrosion and flaking at 2 ft above mean high water; specimen partially immersed — 790 days in sea water; 19× magnification

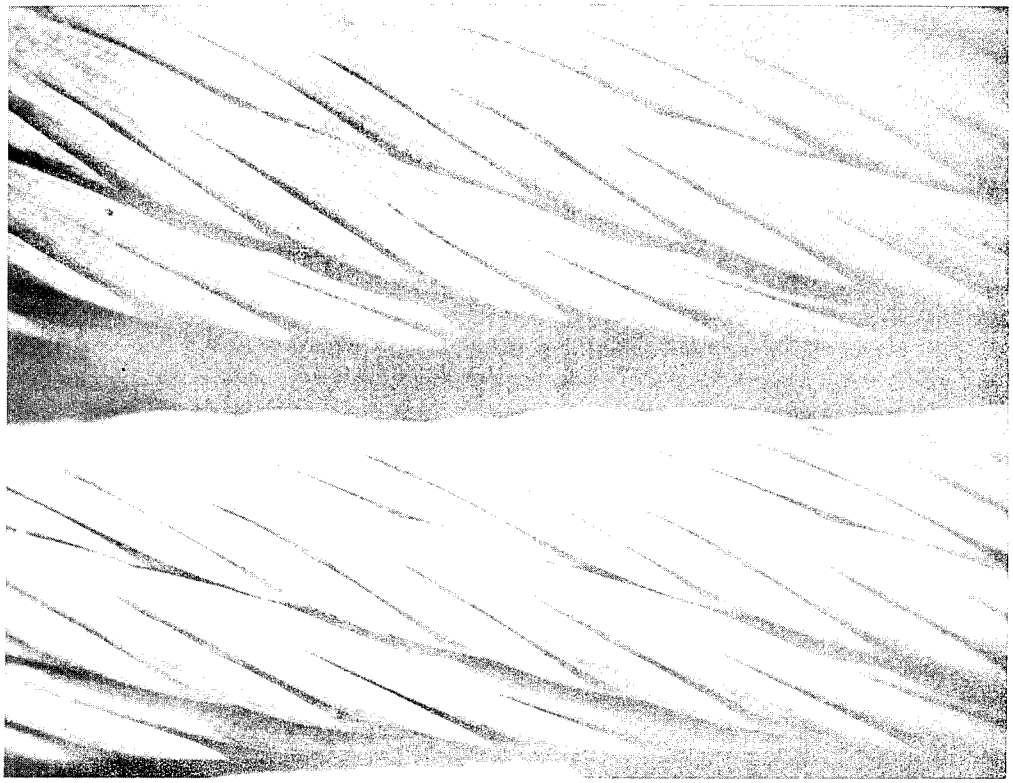
MC 504

Fig. 29 — Aluminized steel (outer strands) showing differences in corrosion characteristics; top — Source 1 with a fiber-core center; bottom — Source 2 with IWRC; at the splash zone; specimen partially immersed — 790 days in sea water; 13X magnification

MC 505

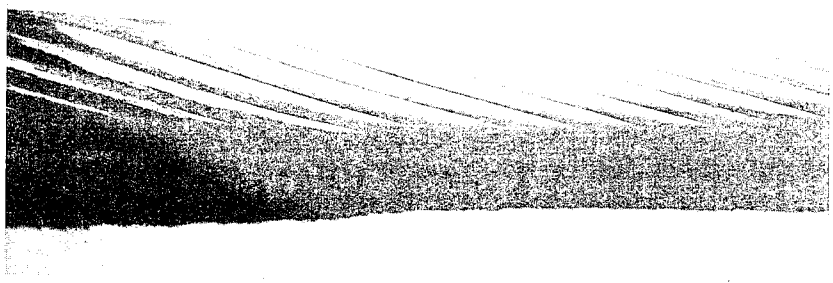
Fig. 30 — Source 2 aluminized steel (IWRC) showing flaking and corrosion just outside the PVC-taped area; at the immersed zone; specimen partially immersed — 790 days in sea water; 19X magnification

Fig. 31 — Source 2 aluminized steel (IWRC); top — without cathodic protection; bottom — with cathodic protection; showing relatively good condition under the PVC-taped area; specimens totally immersed — 790 days in sea water; 13× magnification



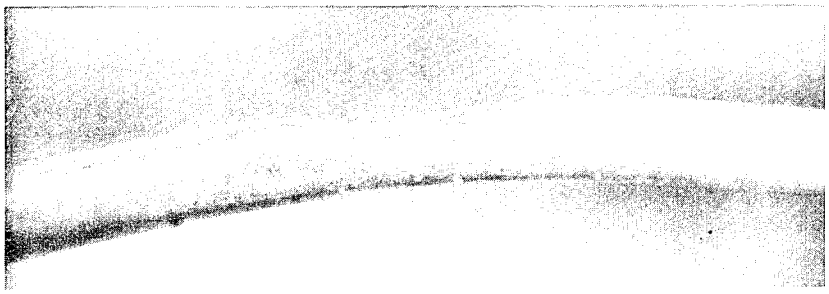
MC 507

Fig. 32 — Source 2 aluminized steel (IWRC); top — without cathodic protection; bottom — with cathodic protection; showing relatively good condition, especially of the cathodically protected specimen (area not under the PVC tape); specimans totally immersed — 790 days in sea water; 13× magnification



MC 508

Fig. 33 — Nickel-base alloy (IWRC) showing necked-down crevice corrosion under the tape at the immersed zone; specimen partially immersed — 790 days in sea water; 9× magnification



MC509

Fig. 34 — Nickel-base alloy (outer strand) without cathodic protection, showing crevice corrosion under the taped area; specimen totally immersed — 790 days in sea water; 38× magnification

MC510

Fig. 35 — Nickel-base alloy (outer strand) without cathodic protection, showing corrosion at the taped area; specimen totally immersed — 790 days in sea water; 25× magnification

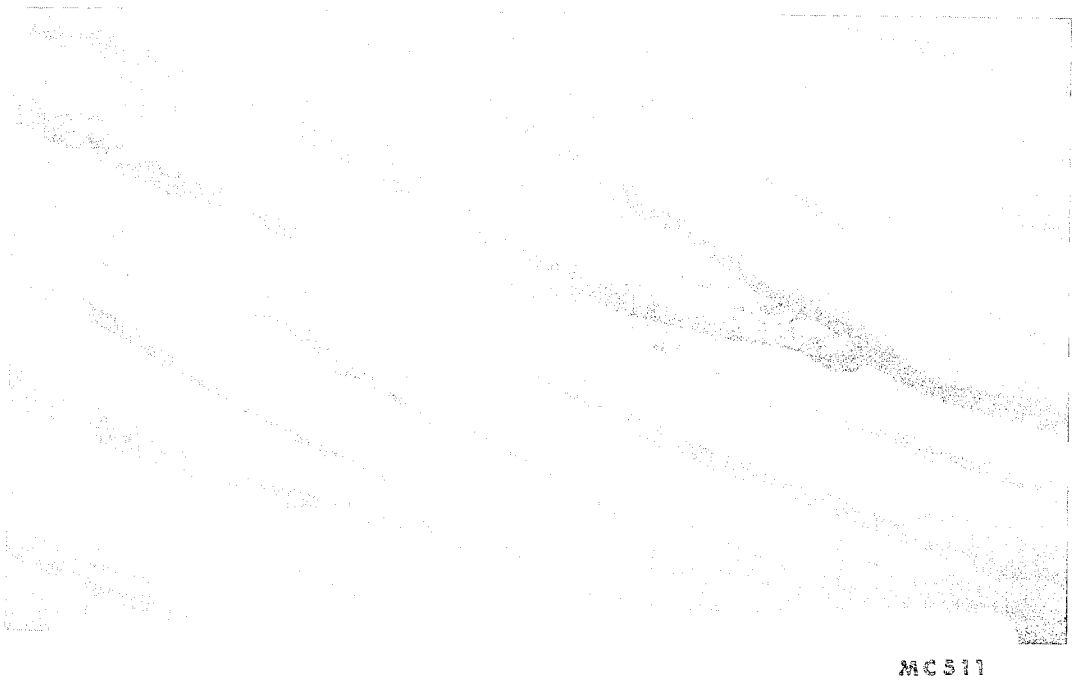
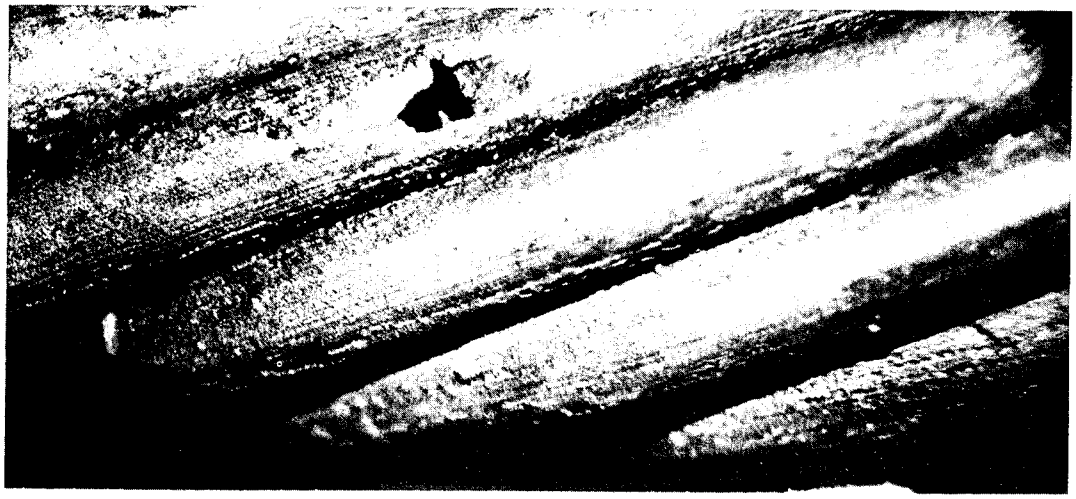


Fig. 36 — 90/10 copper-nickel clad Type 304L stainless steel (IWRC) showing very severe tunneling and crevice corrosion at 2 ft above mean high water; specimen partially immersed — 790 days in sea water; 25× magnification

Fig. 37 — 90/10 copper-nickel clad Type 304L stainless steel (outer strand) showing needle emerging from tunneled wire at the tidal zone; specimen partially immersed — 790 days in sea water; 25× magnification

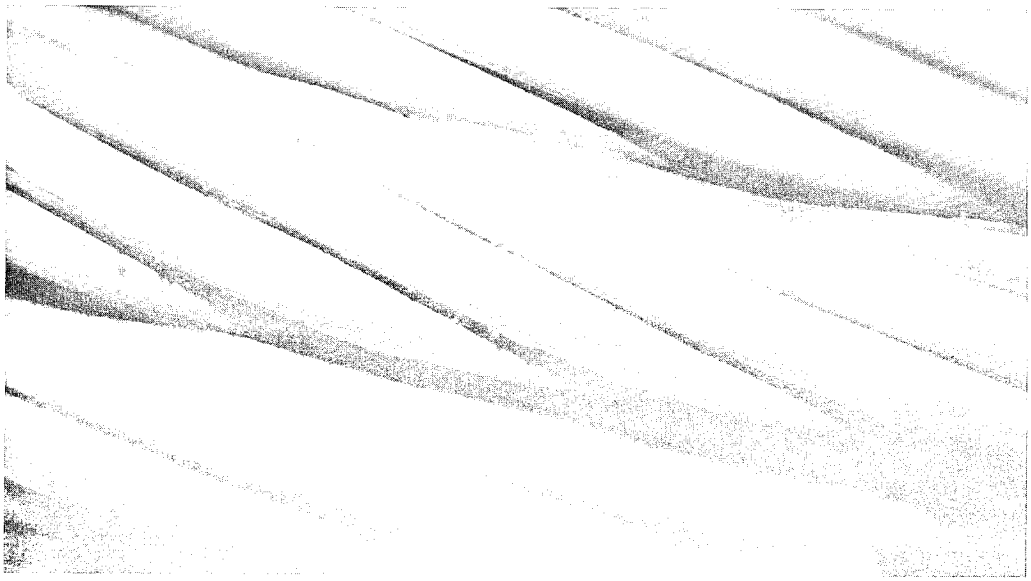


MC 513

Fig. 38 — 90/10 copper-nickel clad Type 304L stainless steel (outer strand) showing tunneling at the immersed zone; specimen partially immersed — 790 days in sea water; 25× magnification

MC 514

Fig. 39 — 90/10 copper-nickel clad Type 304L stainless steel (IWRC) without cathodic protection, showing crevice corrosion and tunneling (considerable Cu-Ni clad remaining); specimen totally immersed — 790 days in sea water; 25× magnification



MC 515

Fig. 40 — 90/10 copper-nickel clad Type 304L stainless steel (IWRC) with cathodic protection, showing deformed wires and essential absence of corrosion; specimen totally immersed — 790 days in sea water; 25× magnification

MC 516

Fig. 41 — 90/10 copper-nickel clad Type 205 stainless steel (IWRC) showing severe tunneling and broken wires at 2 ft above mean high water; specimen partially immersed — 790 days in sea water; 25× magnification

MC 517

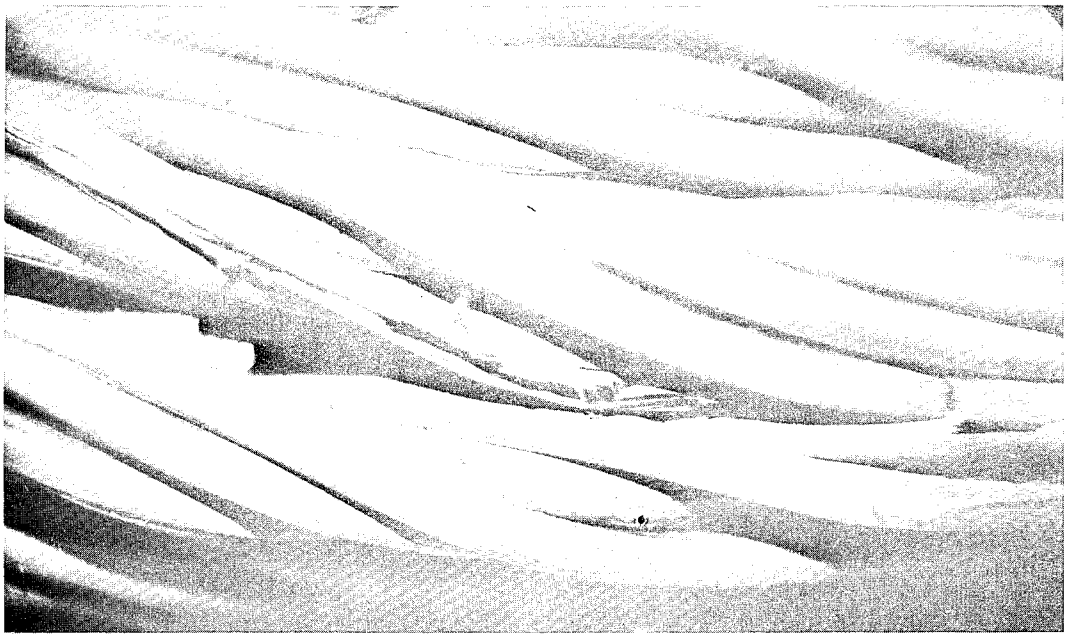
Fig. 42 — 90/10 copper-nickel clad Type 205 stainless steel (IWRC) showing severe tunneling at the splash zone; specimen partially immersed — 790 days in sea water; 25X magnification

MC 518

Fig. 43 — 90/10 copper-nickel clad Type 205 stainless steel (IWRC) showing severe tunneling at the tidal zone; specimen partially immersed — 790 days in sea water; 25X magnification

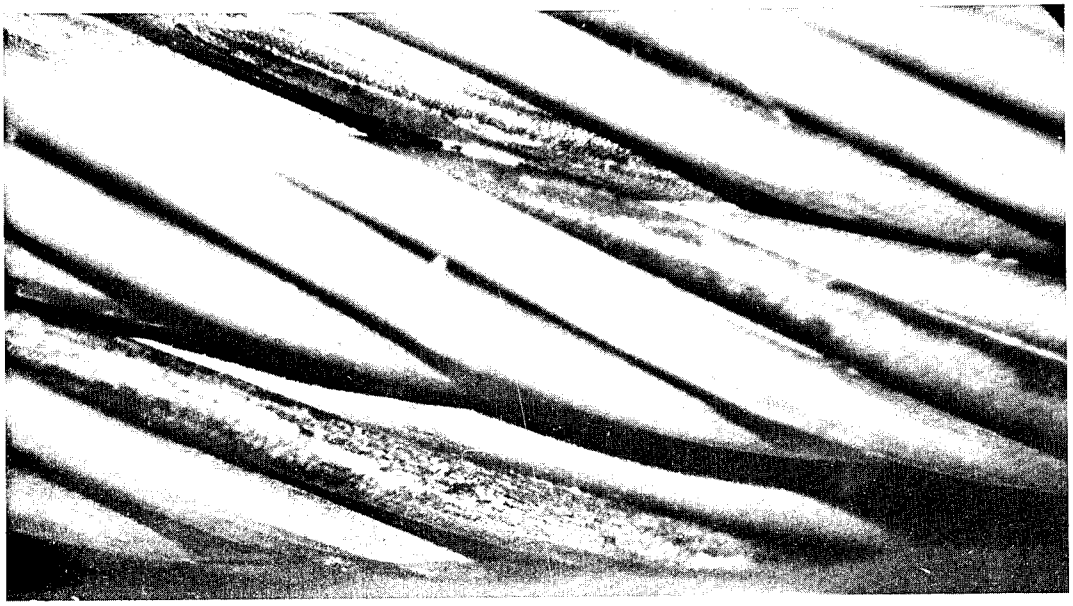
MC 519

Fig. 44 — 90/10 copper-nickel clad Type 205 stainless steel (IWRC) showing severe tunneling at 1 ft below mean low water; specimen partially immersed — 790 days in sea water; 25× magnification



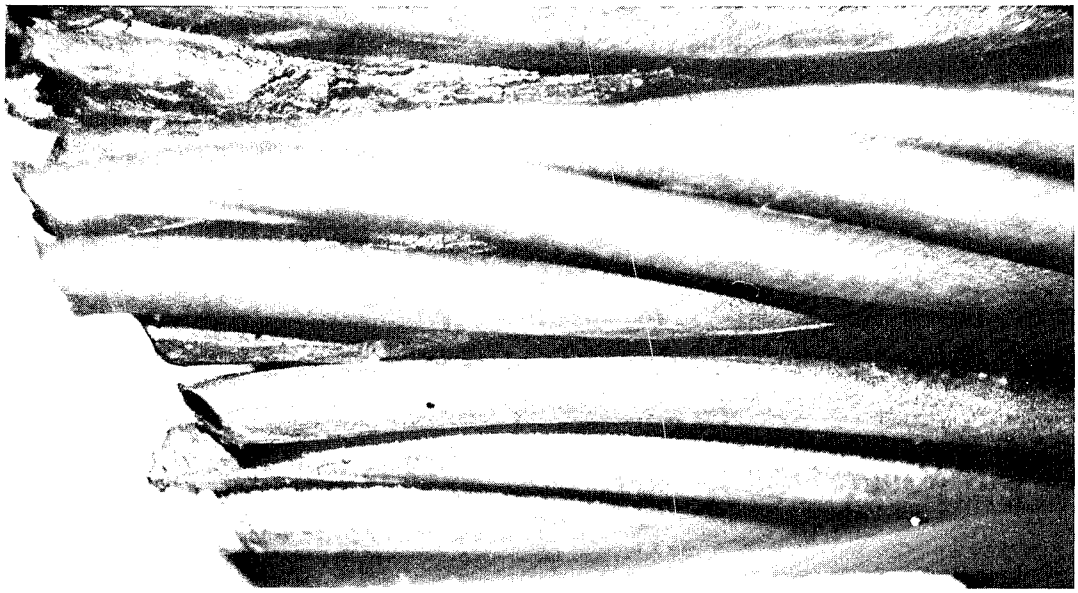
MC 520

Fig. 45 — 90/10 copper-nickel clad Type 205 stainless steel (IWRC) without cathodic protection, showing very severe tunneling; specimen totally immersed — 790 days in sea water; 19× magnification



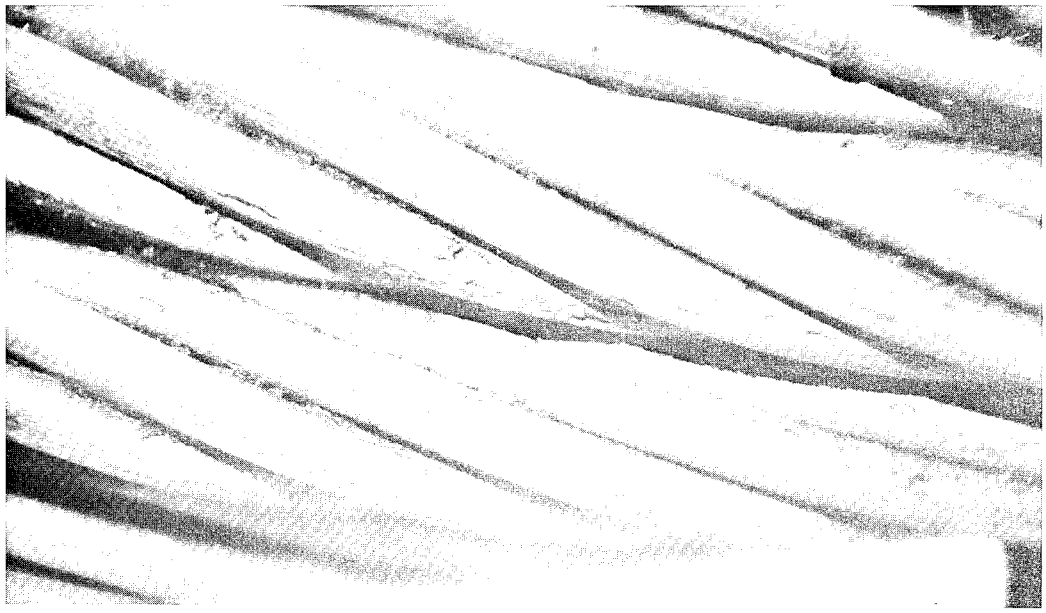
MC 521

Fig. 46 — 90/10 copper-nickel clad Type 205 stainless steel (IWRC) with cathodic protection, showing localized corrosion on some wires; specimen totally immersed — 790 days in sea water; 25X magnification



MC 522

Fig. 47 — 90/10 copper-nickel clad Type 205 stainless steel (IWRC) with cathodic protection, showing crevice corrosion under the taped area; specimen totally immersed — 790 days in sea water; 25X magnification



MC 523

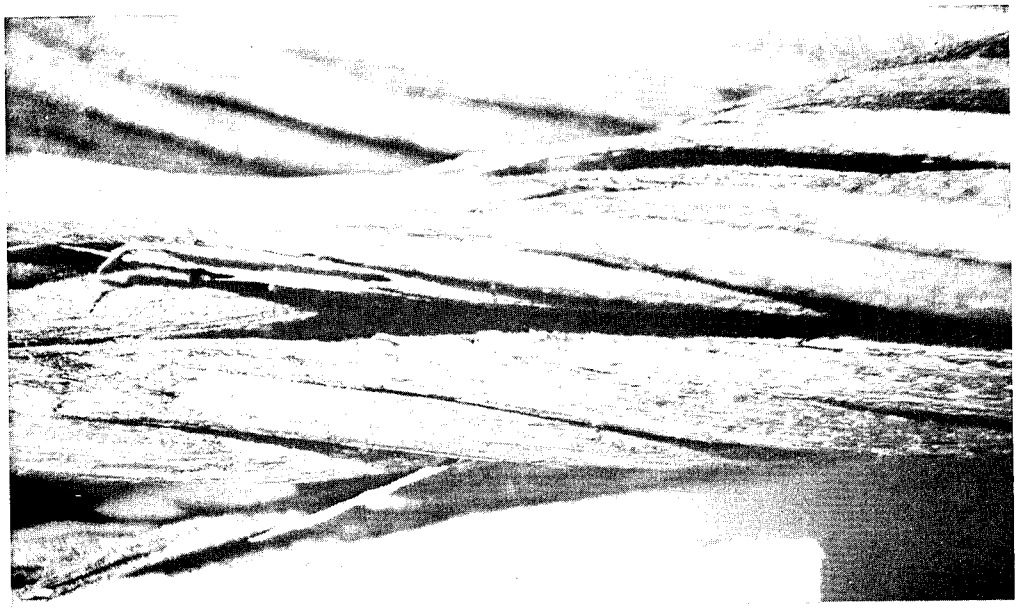
Fig. 48 — Unclad Type 304L stainless steel (IWRC) showing corrosion at 2 ft 6 in. above mean high water; specimen partially immersed — 790 days in sea water; 25× magnification

MC 524

Fig. 49 — Unclad Type 304L stainless steel (outer strand) showing localized corrosion in the tidal zone; specimen partially immersed — 790 days in sea water; 25× magnification

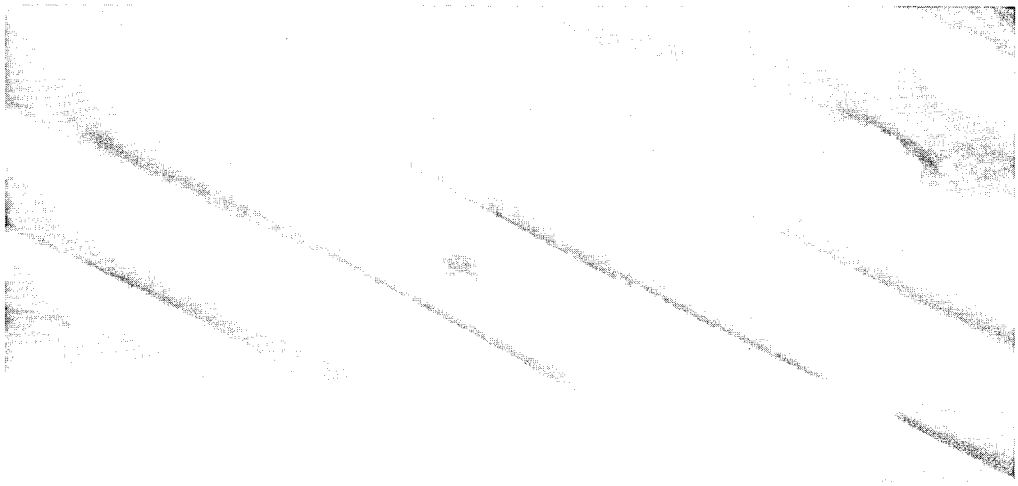
MC 525

Fig. 50 — Unclad Type 304L stainless steel (outer strand) showing very severe tunneling outside the taped area in the immersed zone; specimen partially immersed — 790 days in sea water; 25× magnification



MC 526

Fig. 51 — Unclad Type 304L stainless steel (IWRC) showing severe corrosion at the taped area in the immersed zone; specimen partially immersed — 790 days in sea water; 25× magnification



MC 527

Fig. 52 — Unclad Type 304L stainless steel (IWRC) without cathodic protection, showing severely tunneled wire punctured by the needle point; specimen totally immersed — 790 days in sea water; 38X magnification

MC 528

Fig. 53 — Unclad Type 304L stainless steel (IWRC) without cathodic protection, showing very severe tunneling and crevice corrosion under the taped area; specimen totally immersed — 790 days in sea water; 25X magnification

MC 529

Fig. 54 — Unclad Type 304L stainless steel (outer strand) with cathodic protection, showing the pitting that occurred; specimen totally immersed — 790 days in sea water; 19X magnification