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Technical Note N- 1081

DEEP-OCEAN BIODETERIORATION OF MATERIALS -  
SIX MONTHS AT 6,000 FEET

By

JAMES S. MURAOKA

APRIL 1970

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James S. Muraoka

ABSTRACT

This note reports the data obtained after exposing metallic and nonmetallic specimens for 6.3 months on the floor of the Pacific Ocean at a depth of 6,000 feet (Test Site I). The test specimens were attached to a Submersible Test Unit (STU) that was emplaced August 7, 1968 and retrieved on February 12, 1969. Preliminary examination of the specimens was made aboard ship, and the final examination, tests, and analyses were performed at the Naval Civil Engineering Laboratory.

Typical fouling organisms such as barnacles, bryozoa, and mussels were not found on test panels exposed at 6,000 feet, but the surfaces of plastics, metals and ropes were coated with a thin film of microbial slime. Untreated wood and ropes made of natural fibers (cotton and manila) were severely damaged by microorganisms and molluscan borers. Plastic panels which were in direct contact with wood were also affected by the wood borers. Strangely, extensive borer damage to wood panels was restricted to a narrow area extending from the mud-line to a distance of one or two feet above it. Certain chemically treated wood, certain plastics, rubber, and glass were resistant to biodeterioration. Ropes made of polyethylene and polypropylene increased in tensile strength after exposure at 6,000 feet. A limited study on the corrosion of carbon steel and aluminum alloy helped to confirm a long held suspicion that microorganisms might play a role in the corrosion of metals in the ocean.

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## INTRODUCTION

The Naval Civil Engineering Laboratory (NCEL) is conducting a research program to determine the effects of the deep-ocean environment on materials. The results of the finding will be of great value in establishing the best materials to be used in deep ocean construction in the Navy's conquest of "inner space". Various metallic as well as nonmetallic materials have been placed on a Submersible Test Unit (STU) which was designed and fabricated at NCEL. The STU can be lowered to the ocean floor and left there for long periods of exposure. Previously, NCEL has emplaced and recovered six STUs off the ocean bottom (nominal depths of 2,500 and 6,000 feet) after the test panels were exposed to the deep ocean environment for varying periods ranging from 4 months to 3 years.<sup>1,2,3</sup>

This report deals with STU I-5, the seventh one in the series to be placed on the deep ocean floor. It was emplaced on the sea floor on August 7, 1968 and recovered on February 12, 1969 for a period of 6.3 months at a depth of 6,000 feet at Test Site I. The exposure site is located about 80 nautical miles southwest of Port Hueneme, California (Figure 1). The test site was chosen because of the following reasons: (1) the area is exposed to the open ocean currents and not to restricted current circulation normally found in basins and (2) the ocean floor in this area is reasonably flat with firm bottom sediment for supporting the STU structure. STU I-5 was loaded with numerous varieties of non-metallic test specimens to study the effects of marine organisms on materials exposed on the sea floor at great depth. Numerous O-ring seal test jigs to study the effects of the deep ocean environment on O-ring materials and sealing systems and metallic test panels for the study of corrosion by other investigators were also placed on the STU.

This report describes and lists the test materials, the effects of marine organisms on materials, and the results of laboratory tests conducted on certain test specimens recovered from the deep sea.

## RESEARCH METHODS AND MATERIALS

### Oceanographic Information.

Concurrently with the STU test program, numerous cruises have been made to the STU test sites to collect oceanographic and biological data. Information has been gathered about the environmental parameters such as salinity, temperature, dissolved oxygen concentration, and biological activity. Such information is essential in evaluating changes in the materials exposed on the ocean floor, especially the corrosion of metals.

The environmental parameters found at Test Site I (6,000-foot depth) where STU I-5 was emplaced on the sea floor are presented in Table 1.

#### TEST MATERIALS

Over 150 individual test specimens were placed on the STU for evaluating the effects of deep ocean environment and marine animals on various engineering materials. A total of sixteen 2-foot-long plastic rods, tubes and pipes, and a rubber vacuum hose were assembled on a test rack and attached to the side of the STU (Figure 2). Two large pieces of untreated 2 x 4 x 30 inch fir were fitted around one end of each specimen to attract and lead molluscan borers into direct contact with each plastic specimen. One small section of each plastic specimen was wrapped with a pressure sensitive plastic electrical tape while a polycarbonate rod was wrapped with a 6-inch wide strip of burlap. The wrappings were to provide a favorable foothold for the attachment and growth of deep sea organisms. Five different kinds of rope, made of synthetic plastic fiber (nylon, polypropylene and polyethylene) and of natural fiber (cotton and manila), were tied to the plastic rods, tubes and pipes. Several ten-foot long coiled electrical cables (No. 16 tin coated copper wire) covered with 0.015 inch thick rubber and plastic insulation was also exposed on this test rack. The test racks were attached to the STU structure so that the upper portions would be exposed to seawater and the lower portions of the test specimens would be exposed near the bottom sediment where bacteria are ordinarily most active.

Smaller test specimens such as  $\frac{1}{2}$  x 2 x 4 inch wood panels, 10-inch long electrical cables, and glass plates were secured with  $\frac{1}{4}$  inch diameter nylon nuts and bolts to  $\frac{1}{4}$  x 6 x 12 inch plastic panels. These were then assembled in several exposure racks as shown in Figure 3. The plastic panels were held in place by four grooved polyethylene insulators which separated the test panels by about 1 inch.

The center divider and ends of the exposure racks were made of titanium alloy 75-A. The rods, threaded at both ends, passed through the insulators were nickel-copper alloy 400 fastened with nuts and washers of the same composition. Polyvinyl chloride (PVC) washers were used between the metal washer and the end plates. The two longer rods (those on the sides) were used to fasten the exposure rack onto the STU structure. Some specimens were exposed as high as 6 feet above the sediment whereas others were embedded 3 to 6 inches deep in the bottom sediment.

Saran and polytetrafluoroethylene (TFE) plastic films with a pressure sensitive adhesive backing were used to cover several  $1/8$  x 6 x 12 inch plastic and metal test specimens (Figure 4). This was to see if such a covering would provide protection from fouling organisms and corrosion at great depths. Information on the characteristics and cost of the plastic films is given in Table 2. These plastic films have been tested at the surface of the sea and the results of the findings have been published.<sup>4</sup>

The 1/8 x 6 x 12 inch plastic panels such as nylon, polycarbonate, polyethylene, polypropylene and acetal were placed in the exposure rack. Hardness and moisture absorption tests were to be conducted on these panels when recovered.

For the first time, wood panels treated with various toxic chemicals were exposed in the deep ocean for test and evaluation against molluscan wood borers. The panels were placed about 6 feet from the bottom of the STU structure. The preservatives used and the retention of the preservatives in wood panels are presented in Table 3. The methods used in the treatment of these panels are described in Reference 5.

To determine the effects of biological growth on corrosion rates at great depth, carbon steel (1010) and aluminum alloy (7178-T6) panels were selected for this study. The test panels (1/8 x 1 x 3 inch and 1/8 x 1 x 6 inch) were exposed in the sea as follows: (1) "Exposed" panels. So that the panels might be exposed to the total seawater environment including biological attachment, the steel and aluminum panels were secured to 1/4 x 6 x 12 inch acrylic sheets with nylon nuts and bolts. A plastic washer was placed between the test panels and acrylic sheet to expose as much metal surface area as possible to the seawater environment, and (2) "Control" panels. In order to keep the test panels free of biological growth the panels were first sterilized with alcohol and then placed inside a specially designed presterilized acrylic cylindrical test chamber sealed at both ends with 0.45 micron porosity membrane filters (Figure 5). To prevent the rupture of the membrane filters during descent to the sea floor the test chamber was filled with sterile sea water by submerging it in a plastic container filled with clean, filtered sea water aboard ship prior to exposure in the sea.

## RESULTS

### Marine Growth on STU Rigging Complex.

In general, there was very little fouling growth on various recovered materials. Hydroids and slime films were found on the surface of recovered components such as buoys, shackles, polypropylene rope, and pinger casing placed above the STU structure and at midwater depths. Typical fouling organisms such as barnacles, sea squirts, and bryozoans usually found on submerged objects in harbors and shallow water were not found attached to any of the recovered materials.

### Effects of Marine Organisms on Materials.

The STU structure with test specimens recovered from the sea after 6.3 months of exposure on the sea floor in 6,000 feet of water is shown in Figure 6. The results obtained from exposing materials in the deep ocean environment are summarized in Tables 3, 4, 5, 6, 7 and 8. The effects of deep sea organisms on various materials are discussed in the following pages.

Plastic Rods and Tubes. The 2-ft-long plastic rods and tubes were free of any fouling attachment when recovered from the sea as shown in Figure 7. There was, however, some slime growth over the test specimens. Closer examination of the materials showed that certain areas of the plastic specimens were damaged by deep ocean molluscan wood borers (Xylophaga washingtona).<sup>6</sup> The damaged areas include: (1) the surface of an acrylic plastic rod which was in direct contact with wood, and (2) the surface areas of polystyrene and polycarbonate rods, and vinyl tubes which were exposed immediately above the sediment layer. The borers were able to bore into the surfaces of these plastic specimens directly from the sea water environment without the aid of wood. These same plastics, on the other hand, were not affected by borers over the areas which were located about 12 inches above the sediment-sea water interface. One vinyl tube (Number 2807) was not affected by the wood borers; however, the entire surface area of this tubing was covered with a heavy slime growth. A plasticizer used in the formulation of this particular plastic tubing may have served as a source of food for the growth of these microorganisms. Other vinyl tubings were not covered with such a heavy slime growth when recovered from the sea. As shown in Figures 8 and 9, the surface of acrylic and polycarbonate plastic panels onto which wood panels were secured were also damaged by borers.

Plastic Films. The plastic films with pressure sensitive adhesive backing which were used to cover plastic and metal test specimens were in excellent condition. The films were attached to the surface of the test panels and protected the test specimens from corrosion and fouling growth. A 6061-T6 aluminum alloy covered with a saran film was protected from pitting corrosion while the surface of an identical panel which was not protected with such a covering was pitted (Figure 10). A 302 stainless steel panel covered with a TFE glass-fiber coated film was also protected from corroding and fouling (slime growth) at great depth. No control panel was available for test.

The plastic film covering was easily stripped off the 6 x 12 inch panels. The entire stripping process took three to five minutes per panel. The glass-fiber coated TFE film was slightly stronger and tougher than the skived TFE or the saran film. The pressure sensitive adhesive material on the saran film seemed to adhere more tenaciously to various clean test surfaces than the adhesive material on the TFE film.

Hardness and moisture absorption tests were conducted on the various 1/8 x 6 x 12 inch plastic panels (Figure 11). The results of these tests are presented in Table 5.

Electrical Cable Insulations. The recovered electrical cable insulations were examined under a stereoscopic microscope for signs of any biodeterioration and for physical effects of the deep ocean environment. The majority of the insulating materials buried in the

sediment and also those which were exposed in sea water above the sediment layer were in excellent condition (Figure 12). A silicone rubber insulated cable exposed at the seawater-sediment interface was slightly damaged by wood borers. Replicate insulating material exposed about 6 feet above the sediment was not affected. A silicone rubber caulking compound used as sealant was not affected in any way even at the seawater-sediment interface. A section of a polyvinyl chloride (PVC) covered insulation which had been buried in the bottom sediment had turned black (Figure 13). Spectrographic analysis showed that tin was present in the PVC electrical insulating material. Hydrogen sulfide produced by sulfate-reducing bacteria in bottom sediment could have combined with the tin to form tin sulfide which is black.

Rope Specimens. A heavy slime growth was present over the surface of recovered cotton and manila ropes while light slime growth was present over the surface of nylon, polypropylene, and polyethylene ropes. The fibers of  $\frac{1}{2}$ -inch diameter cotton ropes were decayed considerably by bacterial activity but the cotton ropes were not damaged by wood borers. On the other hand, the  $\frac{1}{2}$ -inch diameter manila ropes were deteriorated by both microorganisms and borers (Figure 14). Borers ranging in size from  $\frac{1}{32}$  to  $\frac{1}{16}$  inch in diameter had completely infested the entire length of the 5-foot-long rope specimens. The rope fibers were severed by deep penetration.

Examination of the nylon, polypropylene and polyethylene rope under a stereoscopic microscope showed that the fibers of these ropes were not damaged by microorganisms nor by borers. Table 6 compares the breaking strength of these rope specimens in a dry condition before and after deep sea exposure. Tests revealed that the cotton and manila rope specimens had lost 47% and 46% of its original strength but, on the other hand, polypropylene and polyethylene rope specimens had increased their breaking strength after exposure in the deep sea environment. The nylon rope had decreased its strength (Table 6). In order to confirm this data, a test was conducted on additional plastic ropes in the laboratory by subjecting these to 10,000 psi hydrostatic pressure in a pressure vessel.

Each of the three plastic ropes for the pressure vessel test were cut from a roll of continuous length of rope. The 2-ft-long specimens with an eye spliced at both ends of the rope were randomly selected from a group of six test specimens. Three of these were placed in a pressure vessel (in seawater) and 10,000 psi pressure was applied for 6.5 continuous hours. As shown in Table 7, the results of the tensile strength test show that the polypropylene and polyethylene ropes had indeed increased their tensile strength as compared to non-pressure treated ropes. The reason for this is not known. The nylon rope, on the other hand, had decreased in strength similarly to those specimens exposed in the deep ocean.

Untreated Wood Panels. All of the untreated wood panels such as pine, fir, ash, maple, cedar, oak, balsa, and redwood were damaged by

molluscan wood borers (Xylophaga washingtona). The severity of the damage to wood panels depended upon where the test panels were exposed in relation to the sea floor (Table 3). The heaviest borer attack occurred on wood panels which were exposed at the sediment-seawater interface (700 borers per square inch of surface) as shown in Figures 15 and 16. The lightest borer attack occurred on panels which were exposed several feet above the bottom sediment (three borers per square inch of surface). The sections of the wood panel which were buried completely in the soft sediment were free of any borer attack. However, the surface layers (wood cells) of these panels were severely destroyed by marine bacteria and but slightly affected by fungi which causes "soft rot".<sup>7</sup>

The diameter of the shells of the majority of these borers found in the wood measured about 1/16 inch to 1/8 inch. Some had penetrated about 1/2 inch into the panels from the edge (Figure 17). The 2 x 4 x 30 inch untreated fir panels which were fitted around the 2-foot-long circular plastic rods and tubes to attract and lead the borers into direct contact with these plastic specimens were also damaged by borers.

Tropical Wood. Greenheart, a tropical wood noted for its resistance to marine borer attack was exposed at the sediment-seawater interface. Examination of the 1/2 x 1 x 6 inch specimen showed that it was damaged by about 500 borers per square inch of surface. Some had penetrated as much as 1/16 inch deep into the wood.

Treated Wood Panels. Douglas fir and Southern Yellow pine panels (1/2 x 1 x 6 inch) treated with various toxic chemicals were exposed about six feet above the sediment (Figure 18). In general the wood panels treated with creosote and coal tar creosote were damaged slightly by the wood borers after six months exposure. There were from six to 20 shallow (1/32 inch deep) borer holes per panel. On the other hand, panels treated with tri-butyltin oxide and copper arsenic salts were not affected by borers (Table 3). For comparison, the control or untreated wood panels exposed at the same height as the treated panels had about 50 borer holes per panel (4 per square inch). The borers had penetrated about 1/8 inch deep into the wood.

A 1 x 2 x 3 inch fir "wood plastic composite" (treated with methyl methacrylate monomer and then irradiated with cobalt 60)<sup>8</sup> was exposed in the sea about two feet above the sediment. There were about 60 borers per square inch on the surface of the block. Untreated fir panels exposed at about the same height had about 150 borers per square inch of surface.

Steel and Aluminum Panels. As soon as the STU structure was recovered from the sea and placed on the deck of the ship, two cylindrical test chambers containing "control" steel and aluminum panels for the study of biological corrosion were removed from the STU.

Seawater samples were aseptically collected from inside the chambers for conducting bacteriological analyses. Seawater contained inside the two test chambers was carefully collected and analyzed for dissolved oxygen concentration, salinity, and pH. The results of these tests are presented in Table 8. The results of seawater analyses conducted on water samples collected at the surface of the sea and from 6,000-ft depth are also presented in Table 8.

When the "exposed" steel and aluminum panels were examined immediately after recovery aboard ship, the test panels were found to be free of any fouling organisms; however, they were covered with slime growth. The steel panels were covered with a moderately thick layer of red rust (Figure 19). When a small section of this red rust was removed, a bright metal surface was found underneath the layer. The aluminum panels, especially along the edges and ends, were covered with a large mass of white aluminum oxide corrosion product (Figure 20). The steel and aluminum "control" panels which were protected inside the cylindrical test chambers were relatively free of any formation of corrosion products (Figure 21).

Examination of the "exposed" aluminum panels after chemical cleaning revealed that the edges and ends of these panels were severely corroded (Figure 22). Crevice corrosion was found around the bolt holes underneath the nylon nuts and bolts. Only a trace of pitting corrosion had occurred over the surface area of the aluminum panels. The "exposed" steel panels corroded uniformly without the formation of any pits or crevice corrosion on their surfaces. The "control" aluminum panels were free of pitting corrosion around the bolt holes, however, there were traces of very light corrosion along the edges and ends of these panels. The "control" steel panels corroded uniformly (Figure 23).

The differences in the corrosion rates between "exposed" and "control" 1010 carbon steel and 7178-T6 aluminum alloy panels exposed on the sea floor in 6,000 feet of water for a period of 6.3 months are presented in Table 8. The data shows that marine slime growth and their metabolic products may have played some part in initiating corrosion on the deep ocean floor.

Identical test panels of carbon steel and aluminum alloy have been exposed in the sea off Point Mugu pier to determine the effects of marine organisms on corrosion rates at the surface. A report is currently being prepared which compares the corrosion rate experienced at the surface and at 6,000 feet depth.

## FINDINGS

1. Marine fouling organisms such as barnacles, tunicates, mussels, bryozoa, etc. normally found on submerged objects in shallow waters were not found on test specimens exposed at a depth of 6,000 feet of water for a period of 6.3 months. However, the surfaces of the test specimens were covered with slime growth when recovered.

2. On the deep-ocean floor, molluscan wood borers identified as Xylophaga washingtona and marine microorganisms were responsible for extensive damage to certain test specimens. The materials damaged by borers include wood panels, various plastic panels in contact with wood and manila rope. The heaviest damage occurred to test panels which were exposed at the seawater-sediment interface. Wood treated with creosote and coal-tar creosote were slightly damaged by borers but panels treated with tri-butyltin oxide and copper arsenic salts were not affected by the borers. Greenheart, a tropical wood, and "wood composite" panels were attacked by borers. Marine microorganisms were able to decompose the fibers of cotton and manila ropes and also the outer layers of wood cells.

3. Ropes made of synthetic fibers were not affected by marine organisms. On the contrary, the polyethylene and polypropylene ropes had increased in tensile strength while nylon ropes had decreased in tensile strength.

4. Information from a limited study on the effects of marine organisms on corrosion rates showed that marine slime growth and their metabolic products formed over the surface of test panels may have played some part in the extent of corrosion on the deep ocean floor.

#### CONCLUSIONS

1. There are marine organisms living in the deep ocean which can inflict severe damage to man-made objects submerged in the sea. Materials which are susceptible to total biological destruction within a relatively short time include: untreated wood, including tropical wood, and cotton and manila rope made of natural fibers. Treated wood seems to be fairly resistant to borer attack after 6.3 months.

2. The plastic rods and tubings which were damaged by borers in the area underneath the wood bait piece can probably be used in the deep ocean if they are not placed in direct contact with untreated wood. Plastics for deep ocean use should be selected with caution because some will absorb considerably more moisture than others. This will change the hardness of the plastic material, and plastic like nylon sheet will become warped. On the other hand, exposure of polyethylene and polypropylene ropes in the deep ocean environment seem to have had some beneficial effect because their tensile strength had increased.

3. The following materials placed on STU I-5 and exposed at this particular test site were not affected by marine organisms: un-plasticized PVC pipe; butyl rubber, neoprene rubber, natural rubber, GR-S rubber, nylon, TFE, and polyethylene electrical cable insulations; rubber vacuum hose; nylon nuts and bolts; polypropylene, polyethylene, and nylon ropes; ethyl cellulose cable clamps; and glass.

#### CURRENT AND FUTURE PLANS

Studies on marine fouling and biodeterioration of materials in the deep ocean environment are continuing. Currently, test specimens are exposed on the sea floor in depths of:

- (1) 120 feet off the coast of Port Hueneme
- (2) 1,500 feet off the coast of San Clemente Island. This is a cooperative study program with Naval Undersea Research and Development Center, Pasadena.
- (3) 6,000 feet off the coast of Port Hueneme at Test Site I. The test specimens are placed on a STU which is designated as STU I-6.

Reports on the findings will be published as the test specimens are recovered from the deep water test sites.

Table 1. Environment at STU-5 Test Site (Average Values)

Environmental Factors	Surface Water	Test Site
Depth, ft.	Surface	6,000
Water temperature, °C	14.0	2.5
Dissolved Oxygen Content, ml/l	5.8	1.28
Salinity, o/oo (ppt)	33.6	34.56
pH	7.9-8.0	7.44
Hydrostatic pressure, psi	--	2,640
Currents, knots	Variable	0.03
Sediment	--	Green mud containing glauconite, foraminifera shells, fine silt, sand, etc.
Biological activity in the sediment	--	Numerous variety of benthic organisms including microorganisms.

Table 2. Characteristics of Plastic Films

Plastic Film	Basic Material	Pressure Sensitive Adhesive Backing	Thickness With Adhesive Backing (in.)	Width of Material (in.)	Cost Per Square Foot* (dollars)
Skived TFE Film, No. "T"***	polytetrafluoroethylene resin	silicone polymer	0.006	12	2.75
Glass-fiber coated with TFE, No. "A2005"***	polytetrafluoroethylene resin	silicone polymer	0.005	12	2.50
Saran***	vinylidene chloride resin	blend of crude and synthetic rubber with a modified wood resin tackifier	0.003	6	0.25

\*Price for small quantities.

\*\* Comes in rolls with paper backing strip.

\*\*\*Comes in rolls without paper backing strip.

Table 3. Effects of Borers on Untreated Wood Panels

Wood Panels	Treatment	Retention of Preservative, (lb/cu ft.)	Location	Number of Borers per sq. in. of surface	Remarks
	<u>Untreated Panels</u>				
Fir	Untreated		Buried in sediment	0	$\frac{1}{2}$ x 2 x 6 inch panels. Surface of panel deteriorated by microorganisms.
Pine	Untreated		Sediment-seawater interface	700	
Maple	Untreated		Same as above	420	
Ash	Untreated		Exposed a few inches above the sediment	425	The shells of these borers ranged in size between 1/16 and 1/8 inch in diameter. Some had penetrated about 1/2 inch into the wood.
Cedar	Untreated		Same	420	
Oak	Untreated		Same	400	
Redwood	Untreated		Same	400	
Balsa	Untreated		Same	360	
Fir	Untreated		Same	350	

Table 3. (Cont'd)

Wood Panels	Treatment	Retention of Preservative, (lb/cu ft.)	Location	Number of Borers per sq. in. of surface	Remarks
Fir	Untreated		2 feet above sediment	150	
Oak	Untreated		Same	190	
Ash	Untreated		Same	120	
Oak, Ash, Pine, Cedar and Maple	Untreated		6 feet above sediment	3	
Fir	Untreated		6 feet above sediment	2	
Redwood	Untreated		Same	1	
Balsa	Untreated		Same	1	
	<u>Treated Panels</u>				
Fir (7471)	100% Creosote	24.3	6 feet above sediment	0	<p><math>\frac{1}{4}</math> x <math>1\frac{1}{2}</math> x 6-inch panels. Vacuum treated with toxic chemicals. Plastic washers were placed between the panels and plastic sheet so that both sides of the wood surfaces would be exposed to the seawater environment.</p>

Table 3. (Cont'd)

Wood Panels	Treatment	Retention of Preservative, (lb/cu ft.)	Location	Number of Borers per sq. in. of surface	Remarks
Fir (7471)	100% Creosote	24.5	6 feet above sediment	Less than 1 (6 borers on panel)	The molluscan borers had just started to bore into the wood.
Fir (7491)	70-30 Coal Tar Creosote	20.0	Same	Less than 1 (15 borers on panel)	Same
Fir (7492)	Same as above	17.5	Same	Less than 1 (20 borers on panel)	Same
Fir (5743)	0.5% tri-butyltin oxide	0.12	Same	No borers on panel	
Fir (5745)	Same	0.12	Same	No borers on panel	
Fir (5757)	1% tri-butyltin oxide	0.31	Same	No borers on panel	
Fir (5759)	Same	0.23	Same	No borers on panel	
Fir (6789)	1% tri-butyltin oxide and 50% creosote	0.33 16.4 (creosote)	6 feet above sediment	No borers on panel	

Table 3. (Cont'd)

Wood Panels	Treatment	Retention of Preservative, (lb/cu ft.)	Location	Number of Borers per sq. in. of surface	Remarks
Fir (2850)	Chromated copper arsenate (CCA, Type A)	0.52	6 feet above sediment	No borers on panel	
Fir (2854)	Same	0.53	Same	No borers on panel	
Fir (2858)	Chromated copper arsenate CCA, Type B	0.54	Same	No borers on panel	
Pine (2869)	Same	0.54	Same	No borers on panel	
Fir	Untreated (Control)		Same	4 (about 50 borers on panel	Exposed same height as treated panels. Some borers had bored about 1/8 inch deep into wood.
Fir	Untreated		2 feet above sediment	150	Two 2 x 4 x 30 inch wood bait piece over plastic rods.
Douglas Fir	"Wood composite." Wood treated with Methacrylate monomer and irradiated with cobalt 60.		Same	60	1 x 2 x 3 inch wood specimens. The entrance holes were about 1/64 inch in diameter.

Table 3. (Cont'd)

Wood Panels	Treatment	Retention of Preservative, (lb/cu ft.)	Location	Number of Borers per sq. in. of surface	Remarks
Tropical wood, Greenhart			sediment-seawater interface	500	1/4 x 1 x 6 inch wood specimens.

Table 4. Biological Effects on Materials

Materials	Size and Description	Results
Plastic rods	2-ft-long specimens. Commercially available through catalogs	
Cast acrylic	1 inch diam.	6 small borer holes under wood bait piece.
Extruded acrylic	1 inch diam.	5 small borer holes under wood bait piece.
Cellulose acetate	1 inch diam.	Not affected.
Polyethylene	1 inch diam.	Not affected.
Polystyrene	1 inch diam.	2 small borer holes at the bottom near the sediment. The borers had started to bore directly into the plastic without the aid of wood.
Phenolic laminate	3/4 inch diam., No. 911	Not affected.
Nylon	3/4 inch diam., Type 1	Not affected.
Polycarbonate	1 inch diam. Surface of plastic etched	About 30 borer holes per square inch over the bottom section of the rod exposed immediately over the sediment. The area exposed about 1 foot above the sediment was not affected.
Acetal resin	3/4 inch diam., yellow	Not affected.
Polytetrafluoroethylene	3/4 inch diam.	Not affected.
Plastic pipe, Polyvinyl Chloride (PVC)	2-ft-long/5/16 in. OD.; grey, unplasticized	Not affected.

Table 4. (Cont'd)

Materials	Size and Description	Results
Plastic tubings	2-ft-long, 1 inch OD.; 1/8 inch thick wall; commercially available	Not affected by borers. However, the tube was covered with a film of slime growth.
Vinyl	Flexible, low-temperature tube, black, 2807	Approximately 10 small borer holes per square inch of surface area where the plastic was exposed immediately above the sediment. The borers had started to bore directly into the plastic without the aid of wood. There were a few small bore holes under the wood bait piece.
Vinyl	Semirigid, general utility chemical hose, black, 2400	Same as 2400 above.
Vinyl	Flexible, fuel and lubri- cating tube, yellow, 4000	Same as 2400 above.
Vinyl	Flexible, general utility chemical hose, black, 3400	The wrapping was covered with slime growth. The fibers could be ripped apart very easily with ones' fingers.
Burlap wrappings over plastic rods	Jute fibers	Not affected. In good condition when recovered.
Plastic tape, electrical	Pressure sensitive adhesive backing. 0.010 inch thick, 3/4 inch wide black tape	2 specimens of each were exposed. One was exposed on the sediment while the second specimen was exposed about 6 feet above the sediment.
Electrical cable insula- tion	10 in. long, single and multiconductor cables	Not affected. In excellent condition.
Butyl rubber	0.508 inch OD., black	

Table 4. (Cont'd)

Materials	Size and Description	Results
Neoprene rubber	0.431 inch OD., black	Not affected. In excellent condition.
Natural rubber	0.356 inch OD., black	Not affected. In excellent condition.
PVC	0.323 inch OD., black	Not affected. In excellent condition.
Silicone rubber	0.325 inch OD., blue	Approximately 15 borer holes (1/64 x 1/32 inch) per linear inch on cable exposed immediately above the sediment. The cable exposed 6 feet above the sediment was not affected by borers.
PVC	0.243 inch OD., black	Not affected. In excellent condition.
Polyethylene	0.199 inch OD., translucent low density	Not affected. In excellent condition.
Nylon	0.155 inch OD., white opaque	Not affected. In excellent condition.
Teflon	0.120 inch OD., clear	Not affected. In excellent condition.
Plastic cable clamps	1/16 x 3/8 inch clamps of various sizes, ethyl cellulose, yellow	Not affected. No visible deterioration. Probably could be reused.
Nylon nuts and bolts	3/4 x 1 inch black and some white	Not affected. No visible deterioration. Material was soft when wet but hardened when dry. Could be reused.
Glass panel	1/16 x 3.5 x 10 inch	Not affected.
Plastic film coverings		Plastic films with pressure adhesive backing.
Saran film	Protective covering over a 6061-T6 aluminum alloy (1/8 x 6 x 12 inch) panel	The saran wrapping over the test panel was in excellent condition. It protected the aluminum panel from pitting corrosion.

Table 4. (Cont'd)

Materials	Size and Description	Results
<p>Unprotected aluminum panel (control)</p> <p>Glass fiber coated TFE film (no. A2005)</p>	<p>1/8 x 6 x 12 inch 6061-T6 aluminum alloy panel</p> <p>Protective covering over a 1/8 x 6 x 12 inch 302 stainless steel panel</p>	<p>Pitting corrosion occurred over the surface of the panel.</p> <p>The TFE film was in excellent condition and was adhered to the surface of the panel. The underlying metal surface was shiny and bright, free of any corrosion.</p>
<p>Skived TFE film (no. "T")</p>	<p>Protective covering over a 1/8 x 6 x 12 inch polypropylene plastic panel</p>	<p>The TFE film was in excellent condition. The film was adhered to the surface of the panel protecting it from damage.</p>
<p>Saran film</p>	<p>Protective covering over a 1/8 x 6 x 12 inch polypropylene panel</p>	<p>The saran film was in excellent condition. The film was adhered to the surface of the panel protecting it from damage.</p>

Table 5. Deep-Ocean Environmental Effect

Materials	Size and Description	Hardness Test (Durometer, Type D)			Moisture (%)
		Before Exposure	After Exposure		Before Exposure
			Wet <sup>2/</sup>	Dry <sup>1/</sup>	
<u>Plastic Panels</u>	1/8 x 6 x 12-inch				
Polyethylene		45	45	45	135.32
Polycarbonate		84	84	84	179.06
Acetal resin		85	85	85	236.70
Polypropylene		74	74	74	136.50
Nylon		75	65	70	175.90
Acrylic	Clear, transparent	90	90	90	-
<u>Plastic Panels</u>	1/8 x 6 x 12-inch				
Polyethylene					
Polyethylene					
Polycarbonate					
Polypropylene					
Delrin					
Nylon					
Acrylic					

<sup>1/</sup> Kept in 20% RH room for 2 weeks.

<sup>2/</sup> Soaked in seawater for 2 weeks after recovery from the sea. The panels were returned to the Laboratory.

A

Mean Environmental Effects on Plastic Panels

Test Type D)		Moisture Absorption (grams)			Remarks
After Exposure		Before Exposure	After Exposure		
Wet <sup>2/</sup>	Dry <sup>1/</sup>		Wet <sup>2/</sup>	Dry <sup>1/</sup>	
					Exposed about 6 ft above seafloor.
45	45	135.32	135.32	135.03	Not affected
84	84	179.06	179.40	179.08	Not affected
85	85	236.70	237.53	236.65	Not affected
74	74	136.50	136.50	136.48	Not affected
65	70	175.90	188.20	180.65	Not affected by borers. Panel was warped (distorted) when wet and remained warped when dried.
90	90	-	-	-	Not affected
<p>Wood panels (½ x 2 x 6-inch) were attached to these plastic panels with nylon nuts and bolts and were exposed at the seawater-sediment interface.</p> <p>Surface area underneath wood panel was damaged by borers.</p> <p>Same as above</p> <p>Same as above</p> <p>Same as above</p> <p>Same as above. Panel was warped.</p> <p>Same as above</p>					

in the sea. The panels were exposed to the air during transportation to the

B

Table 6. Breaking Strength of Rope Specimens Before and After Deep Sea Exposure

Rope Materials	Diam. (in.)	Breaking Strength (lbs)		Remarks
		Unexposed Specimens	Exposed Specimens	
Cotton	½	1700	1000	Covered with a slime growth. Fibers decayed by microorganisms. 47% loss in strength.
	¾	1655	777	
	¾	1785	890	
		1713 (average)	889 (average)	
Manila	½	2300	1325	Covered with a slime growth. Fibers damaged by borers and microorganisms. 46% loss in strength.
	¾	2585	975	
	¾	2360	1375	
	¾	2415 (average)	1500	
		2415 (average)	1294 (average)	
Nylon	¾	1437	1137	Light slime growth found over nylon, polyethylene and polypropylene ropes. 29% loss in strength.
	¾	1652	1040	
	¾	1537	1100	
	¾	1550	1092 (average)	
		1544 (average)		
Polypropylene	¾	1225	1285	5.5% gain in strength.
	¾	1202	1337	
	¾	1213 (average)	1250	
	¾	1284	1284 (average)	
Polyethylene	¾	1127	1250	5% gain in strength.
	¾	1175	1262	
	¾	1151 (average)	1087	
	¾	1255	1214 (average)	
		1151 (average)		

Table 7. Breaking Strength of Rope Specimens Before and After Exposure to 10,000 psi Hydrostatic Pressure

Ropes	Diam. (in.)	Breaking Strength (lbs)		% Change
		Unexposed Specimens	Exposed <sup>1/</sup> Specimens	
Nylon	$\frac{1}{8}$ $\frac{1}{8}$ $\frac{1}{8}$	1457	1457	6.5% loss in strength
		1567	1400	
		1605	1450	
		<u>1543</u> (avg)	<u>1441</u> (avg)	
Polypropylene	$\frac{1}{8}$ $\frac{1}{8}$ $\frac{1}{8}$	1175	1300	8% gain in strength
		1175	1312	
		1175	1225	
		<u>1175</u> (avg)	<u>1150</u> (avg)	
Polyethylene	$\frac{1}{8}$ $\frac{1}{8}$ $\frac{1}{8}$	962	1100	11% gain in strength
		937	1170	
		1175	1180	
		<u>1025</u> (avg)	<u>1150</u> (avg)	

<sup>1/</sup> Exposed to 10,000 psi for 6.5 hours in a seawater medium at ambient temperature.

Table 8. Environmental Data and Corrosion Rates of T

Test Panels and Seawater Samples	Corrosion Rates			Environmental D		
	Wt loss per panel (gm)	MDD <sup>1/</sup>	MPY <sup>2/</sup>	Oxygen ml/l	pH	Salinity o/oo
Carbon Steel, 1010						
"Control"	0.2157 0.2155 0.2131	2.64	0.48	2.557	7.88	32.95
"Exposed"	1.2985 1.1331 1.2703	7.33	1.34	1.382	7.42	34.60
Aluminum Alloy, 7178-T6						
"Control"	0.0297 0.0280 0.0306	3.62	1.85	2.834	7.88	33.37
"Exposed"	1.2450 1.1460 1.1912	7.12	3.65	1.382	7.42	34.60
Surface Seawater Samples Collected Over STU Test Site				5.822	7.62	33.23

<sup>1/</sup> Milligram per square decimeter per day.

<sup>2/</sup> Mils penetration per year.

A

Corrosion Rates of Test Panels Exposed in the Deep Ocean

Environmental Data						Remarks
pH	Salinity o/oo	Temp °C	Pressure psi	Currents knots		
7.88	32.95	2.26	2,640	Nil	Test panels were placed inside a cylindrical test chamber sealed at both ends with membrane fitters. Seawater samples were collected from inside this test chamber for analyses. Some bacteria were found in the seawater sample.	
7.42	34.60	2.26	2,640	0.03	Test panels were free from large fouling organisms but were covered with slime growth and corrosion products. Environmental data is an average of 6 water samples taken near the sea floor in about 6000 feet of water at the STU test site.	
7.88	33.37	2.26	2,640	Nil	Same as above ("Control")	
7.42	34.60	2.26	2,640	0.03	Same as above ("Exposed")	
7.62	33.23	14°C		Vari- able	Seawater samples collected and analyzed during month of December (winter). Temperature range 14°C to 18°C.	

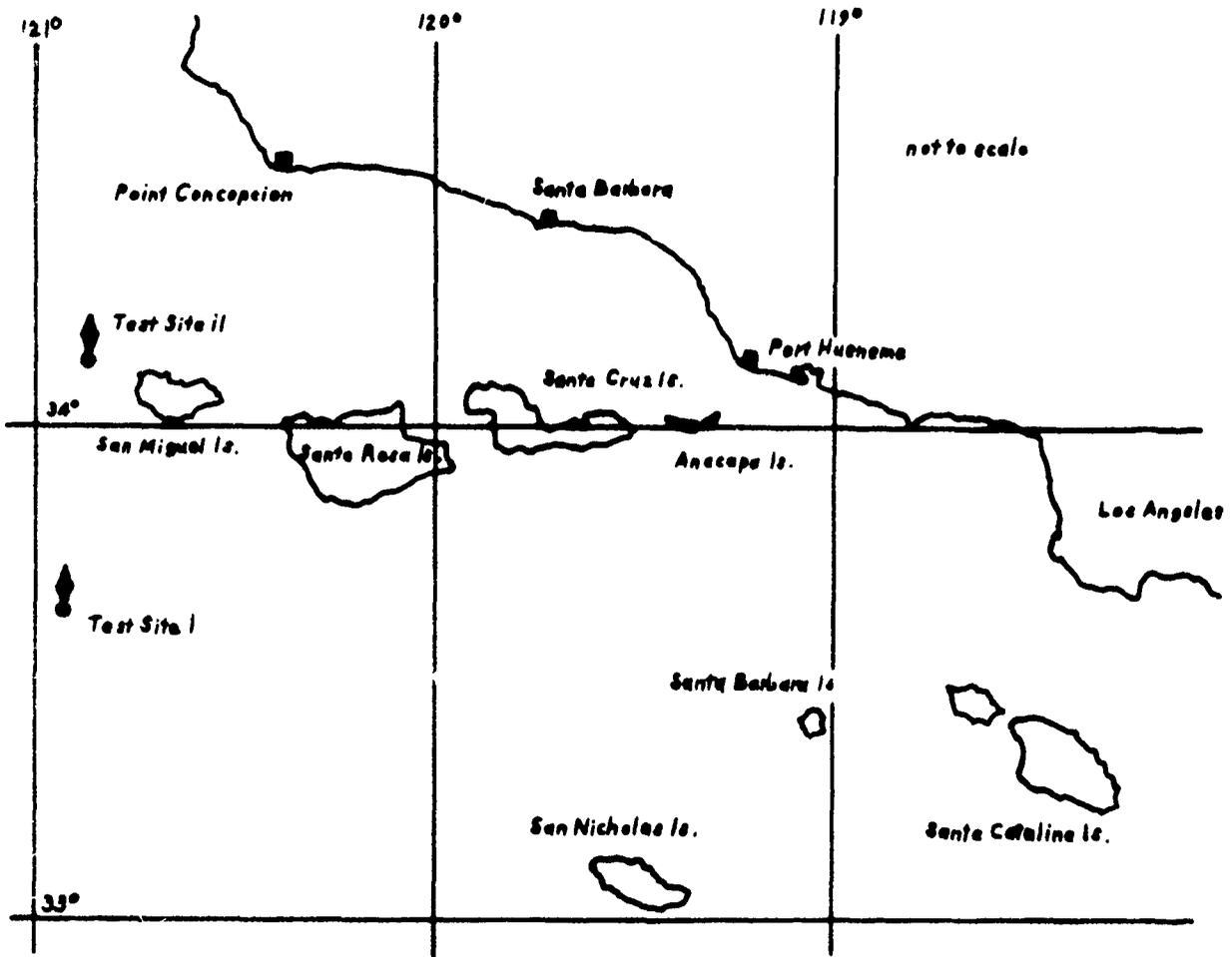


Figure 1. STU I-5 exposure site in relation to Port Hueneme and the Channel Islands (Test Site I).

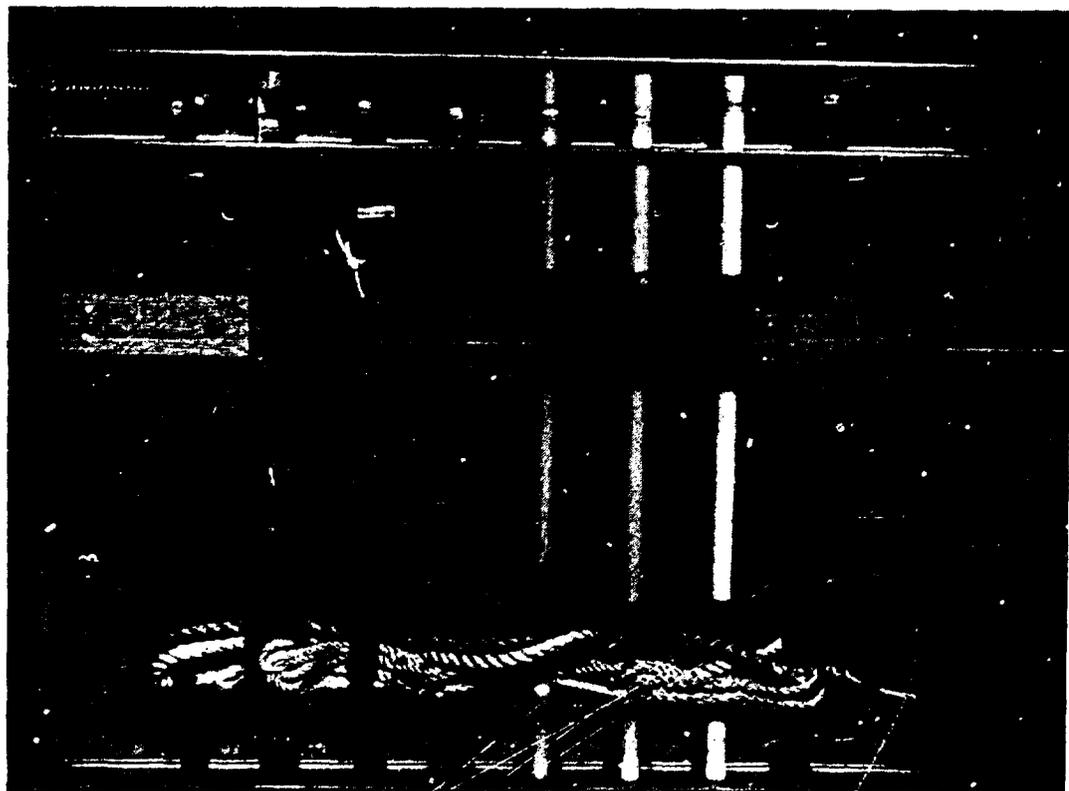
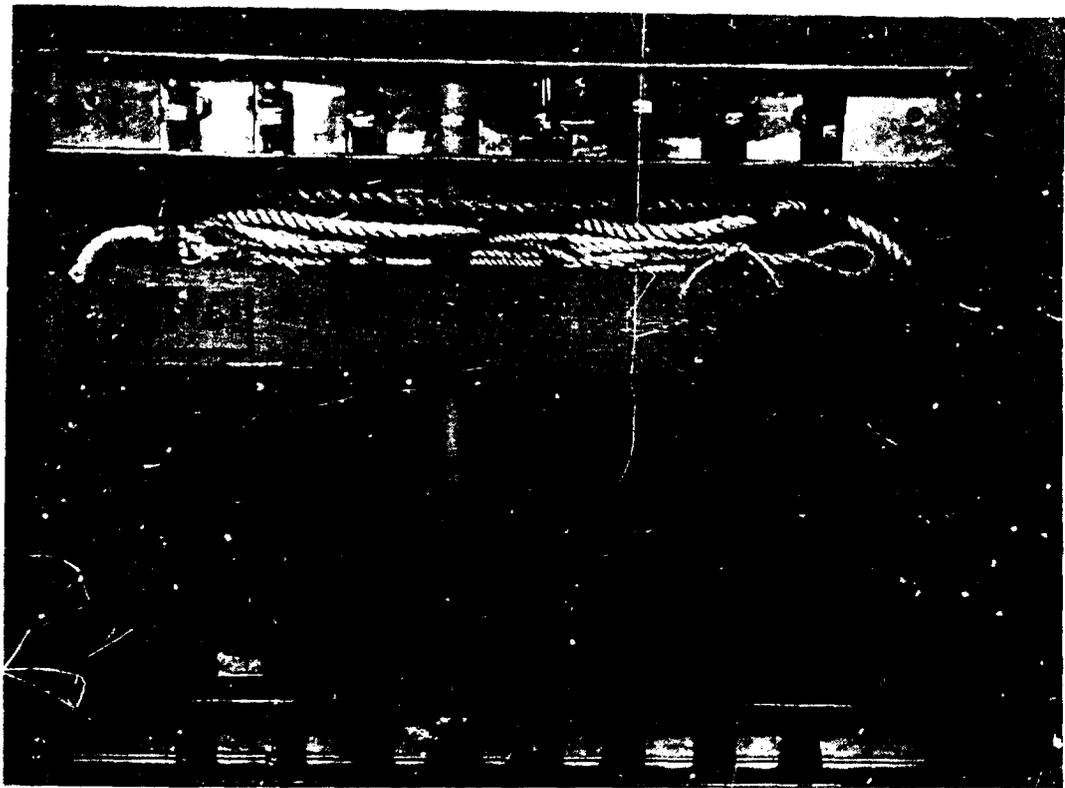


Figure 2. Test specimens assembled in racks.

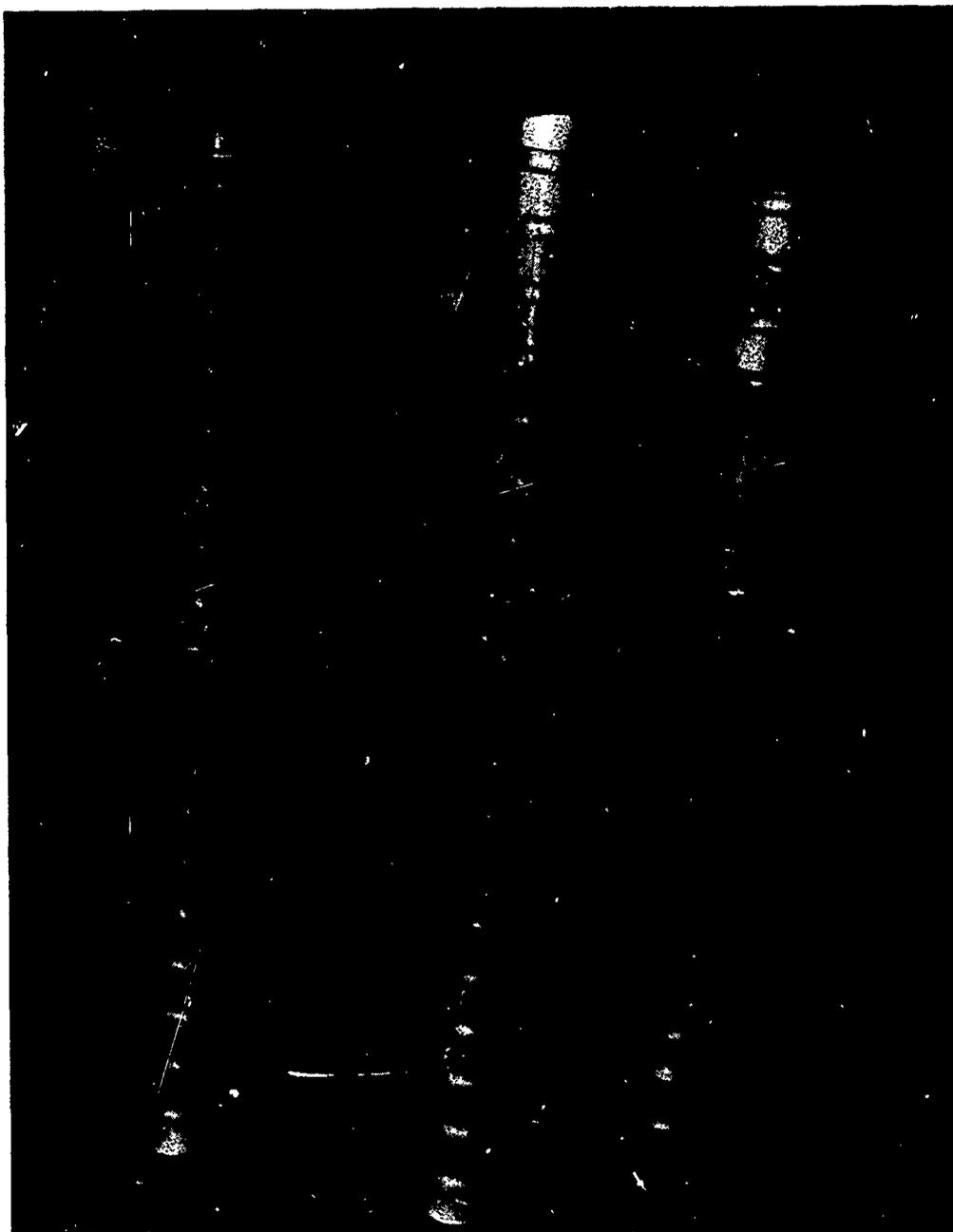


Figure 3. Smaller test specimens attached to plastic sheet and placed in exposure rack.

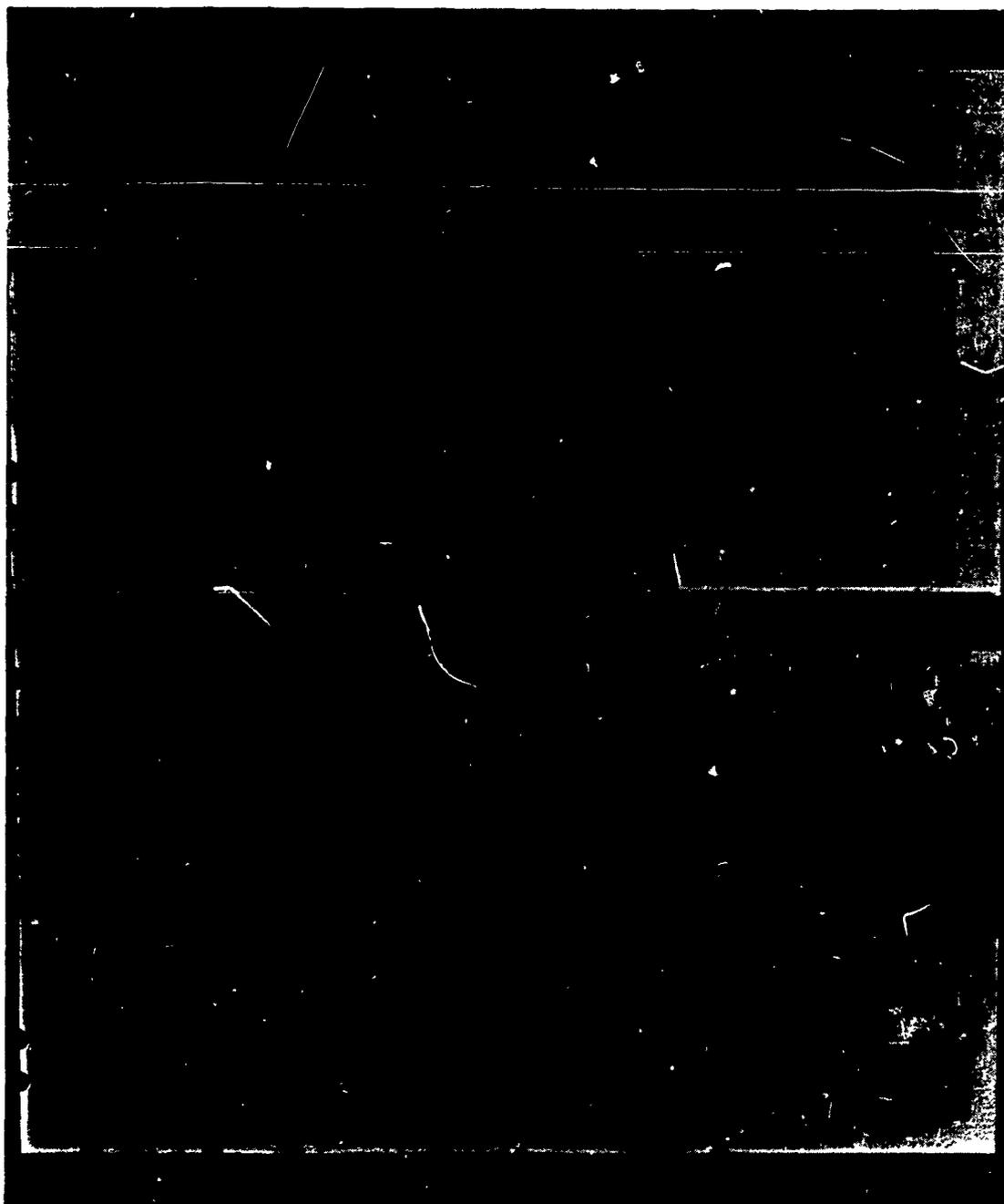


Figure 4. Aluminum alloy test panel on the right is protected with a covering of saran film. Panel on the left is unprotected.

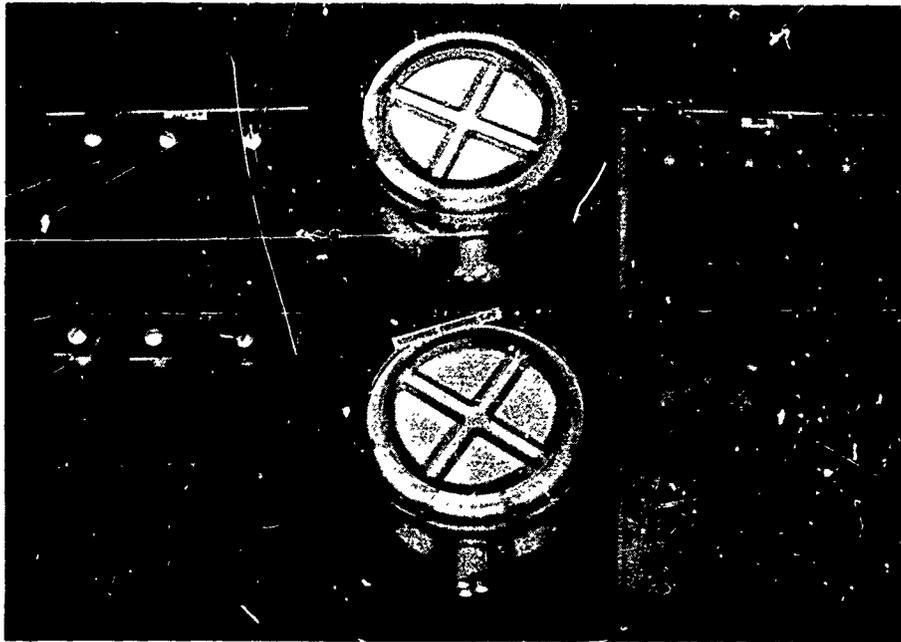


Figure 5. "Exposed" test panels assembled on plastic sheets and "control" panels placed inside cylindrical test chambers for the study of biological corrosion.

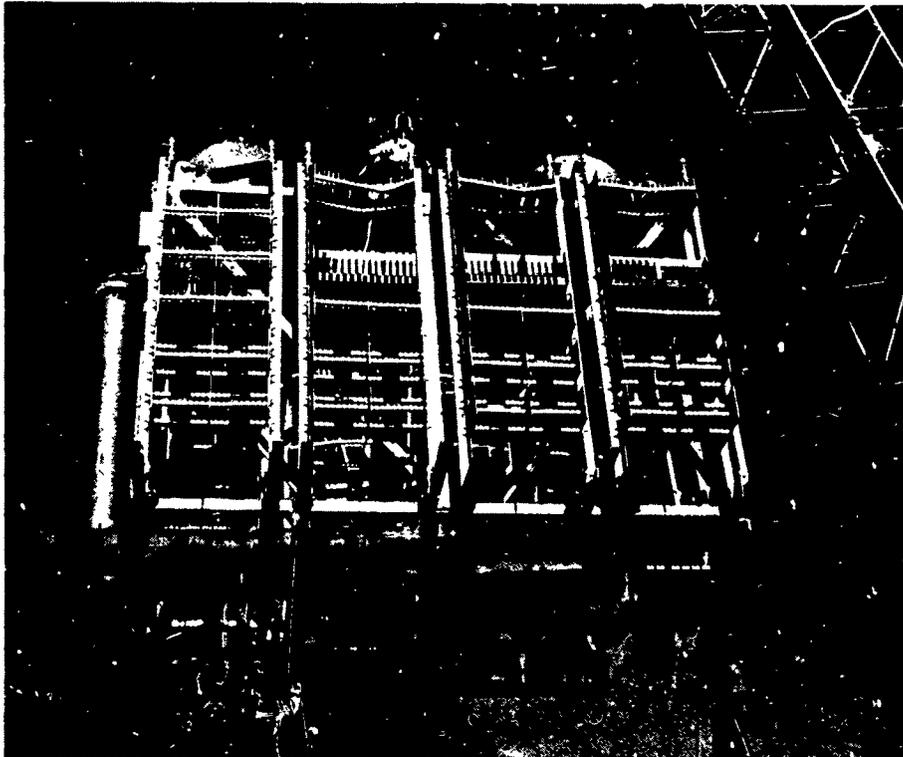


Figure 6. STU I-5 recovered from the sea.

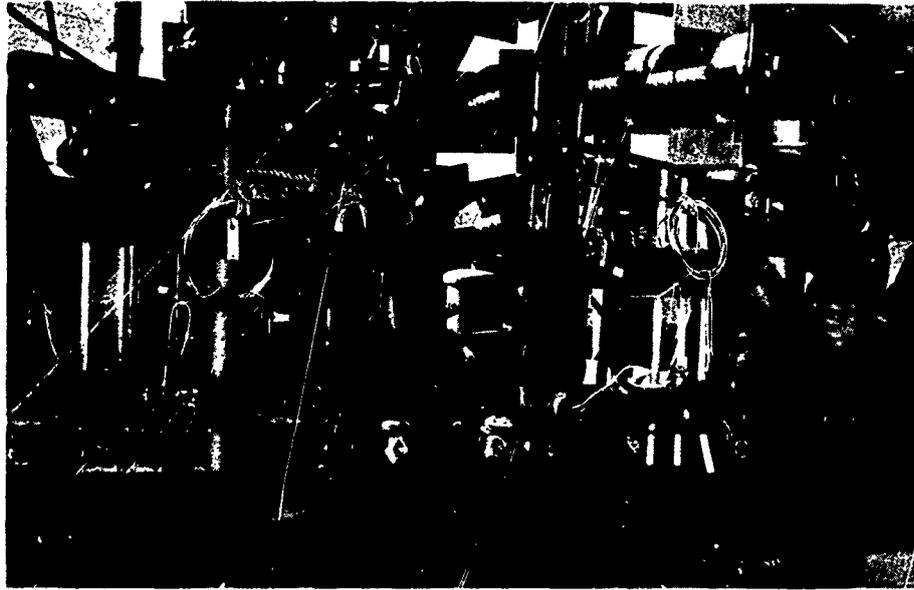


Figure 7. Test specimens immediately after recovery from the sea.

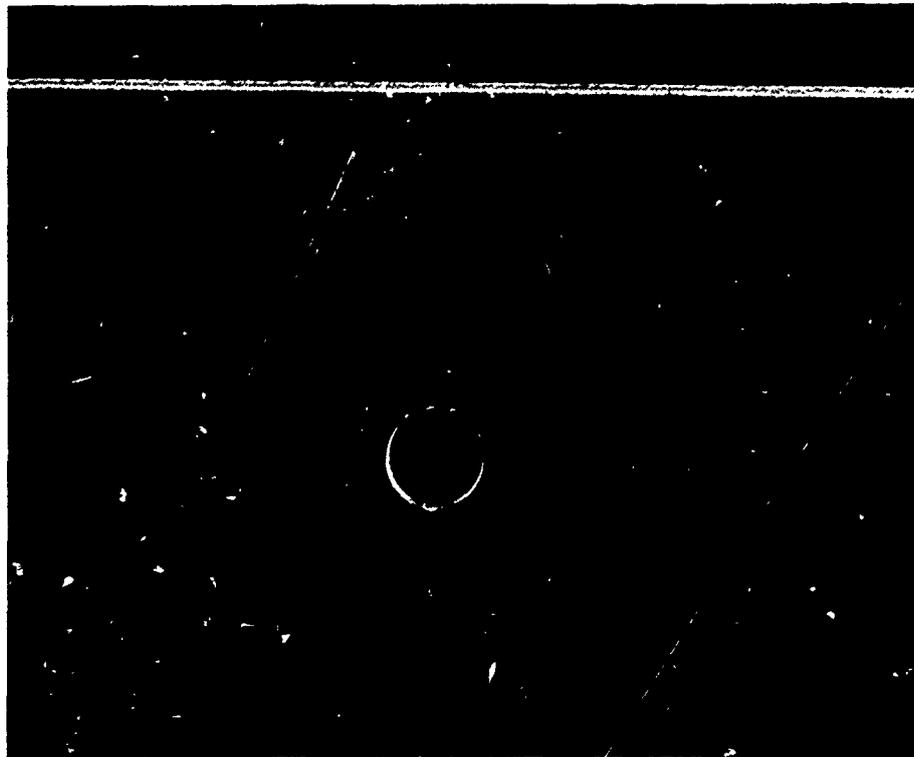


Figure 8. Surface of acrylic plastic panel damaged by borers. A wood panel was secured to the plastic over the damaged area.



Figure 9. Surface of polycarbonate plastic panel damaged by borers.  
A wood panel was secured to the plastic over the damaged area.

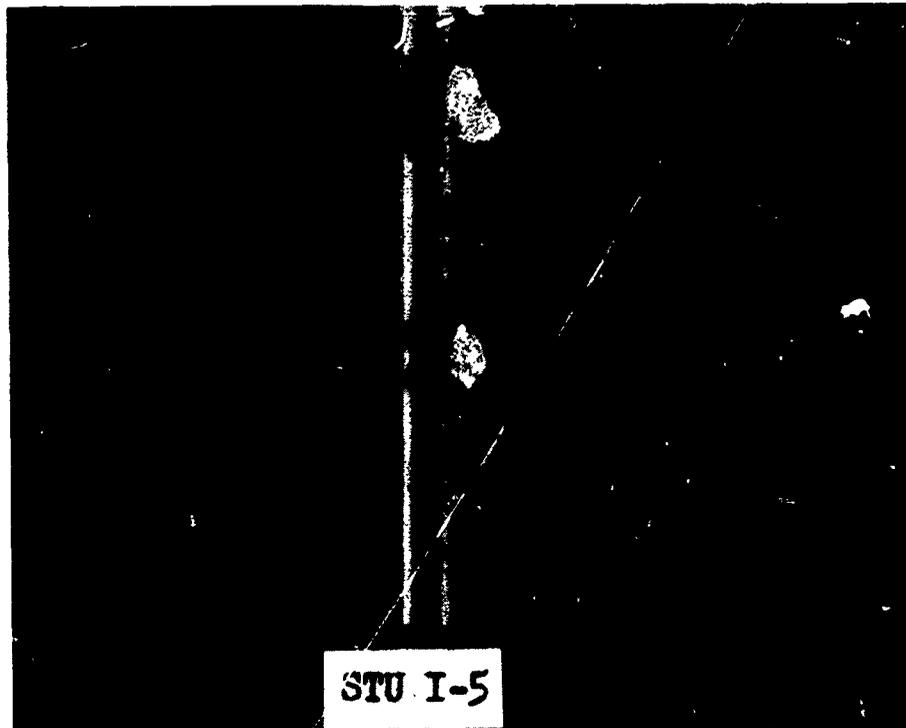


Figure 10. Close-up view of surface of aluminum panel which had been  
protected with saran film (left) and corroded surface of  
unprotected panel (right).

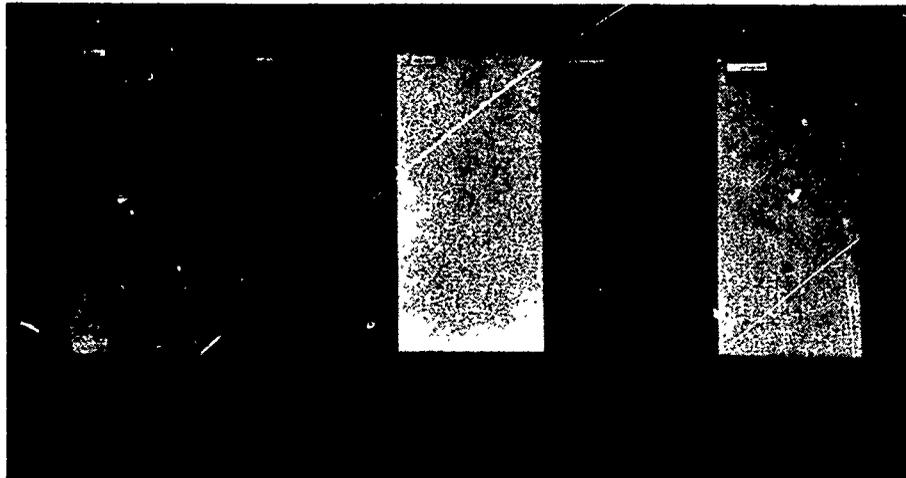


Figure 11. Nylon, polypropylene, delrin, polycarbonate, and polyethylene 1/8 x 6 x 12 inch test panels.

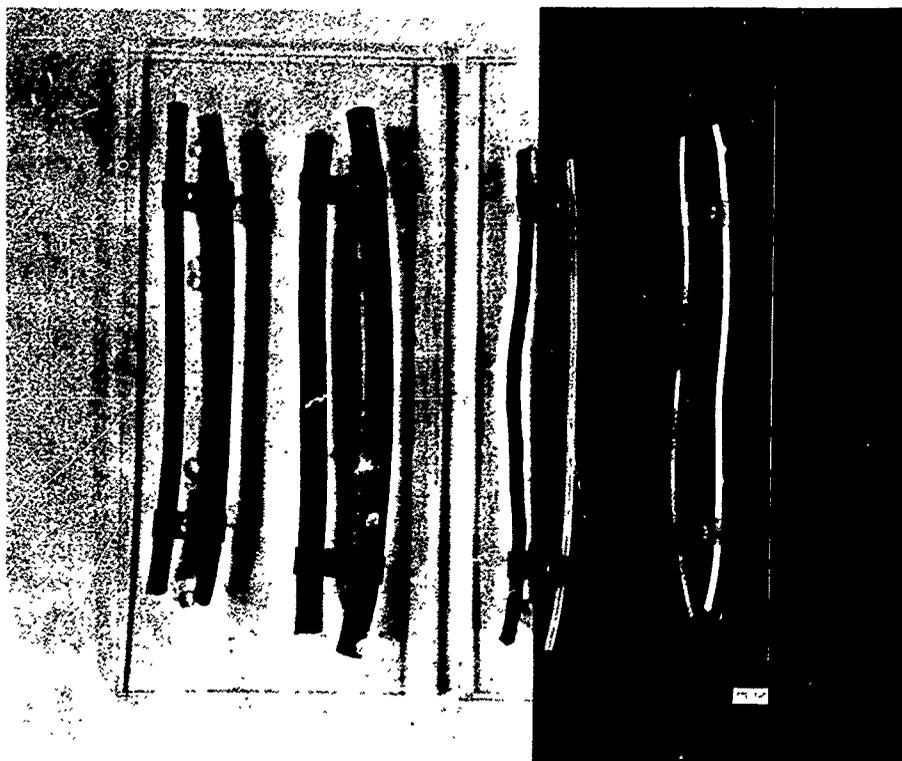


Figure 12. Plastic and rubber insulated electrical cable test specimens after recovery from the sea.

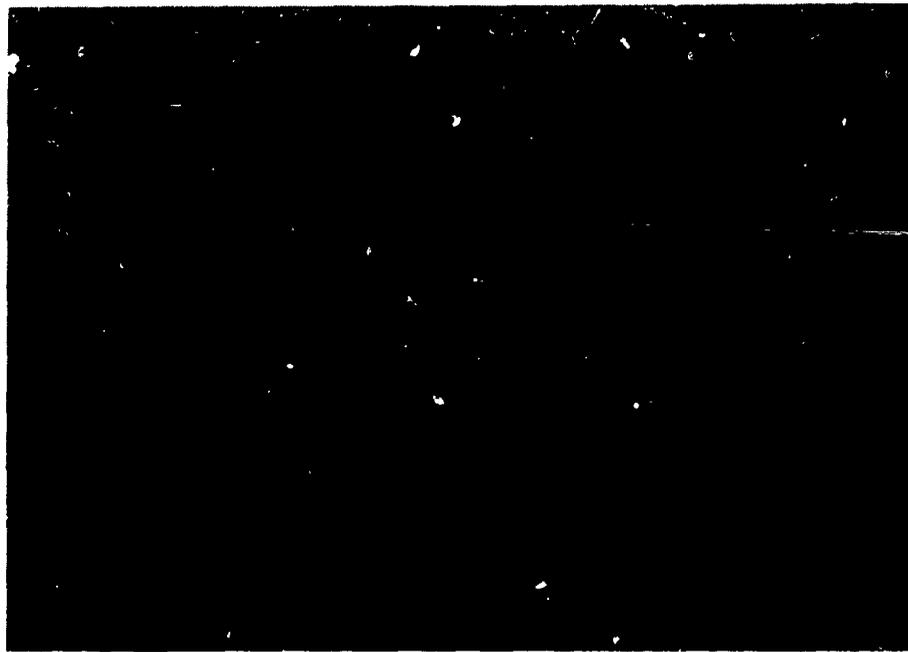


Figure 13. White polyvinyl chloride electrical cable insulation. The area which was buried in the bottom sediment had turned black.



Figure 14. Close-up view of fibers of manila rope showing damage caused by borers and microorganisms.

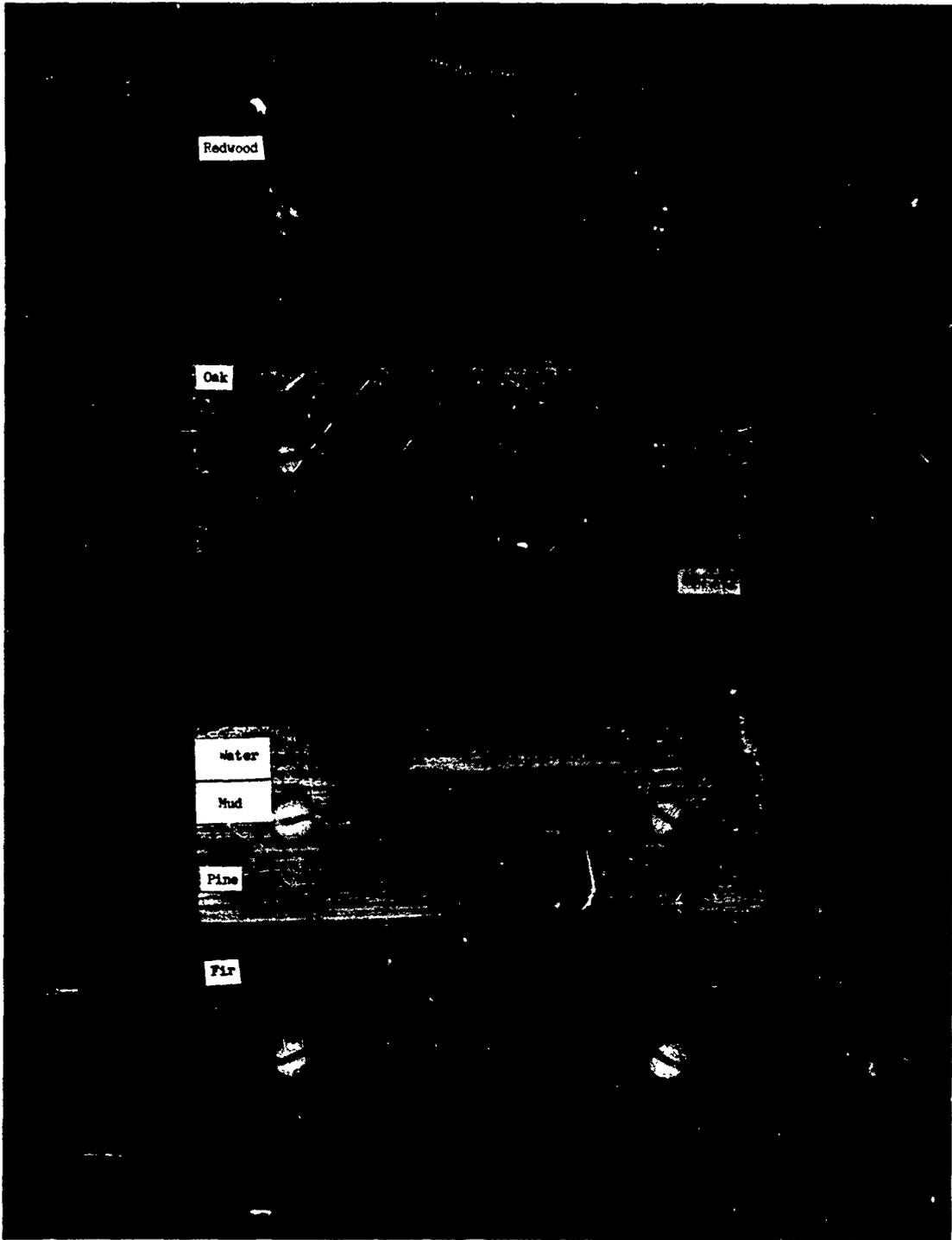


Figure 15. Wood panels buried in bottom sediment (fir), at sediment-sea water interface (pine) and in water above the sediment (redwood and oak).

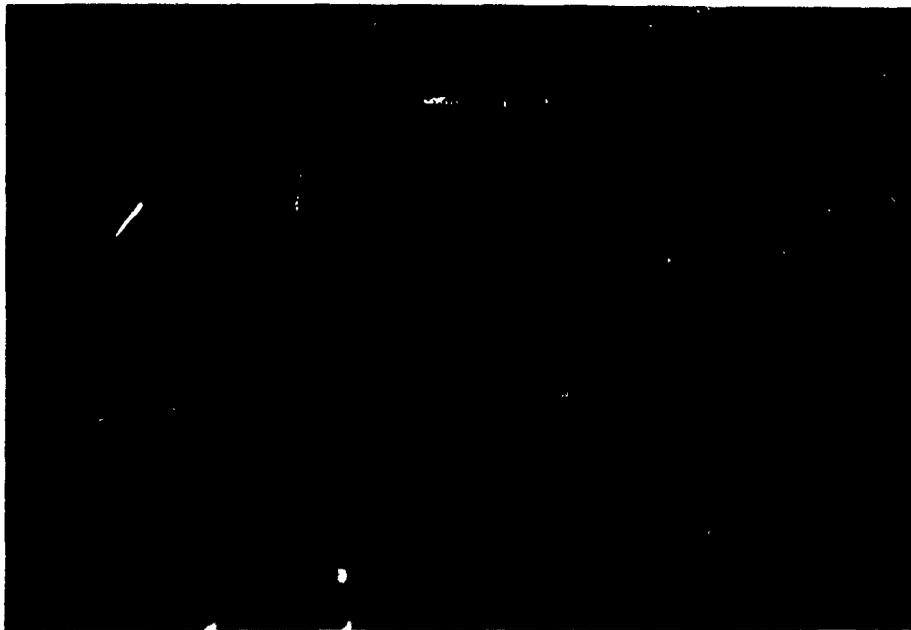


Figure 16. Close-up view of pine shown in Figure 15. Upper section exposed to seawater immediately above the sea water - sediment interface is severely damaged by borers. The bottom sediment is not damaged by borers.



Figure 17. Some borers had bored over  $\frac{1}{2}$  inch deep into a cedar test panel. The shells of these borers are visible in the wood.

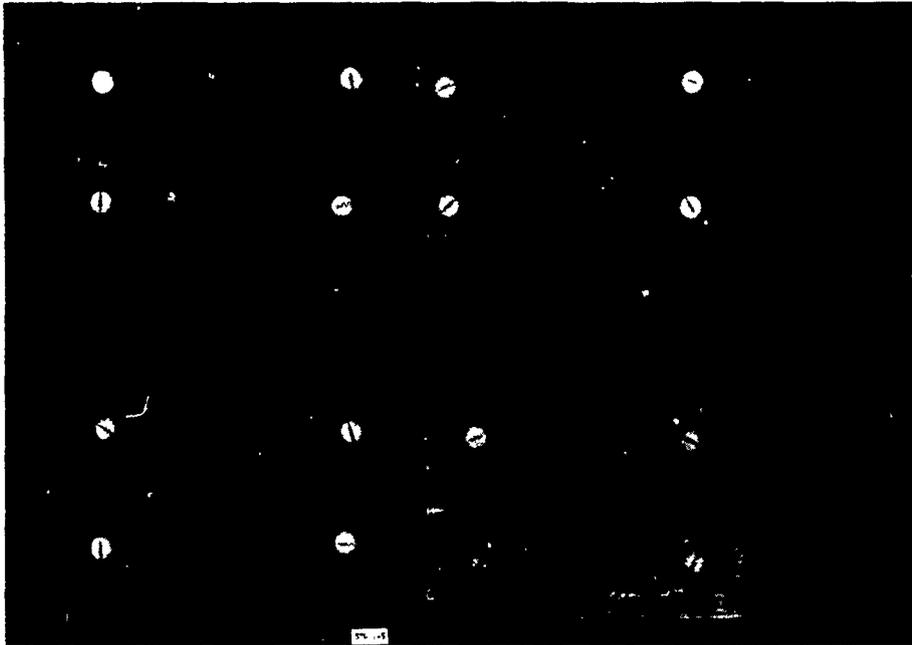


Figure 18. Treated and untreated wood panels attached to plastic sheets.

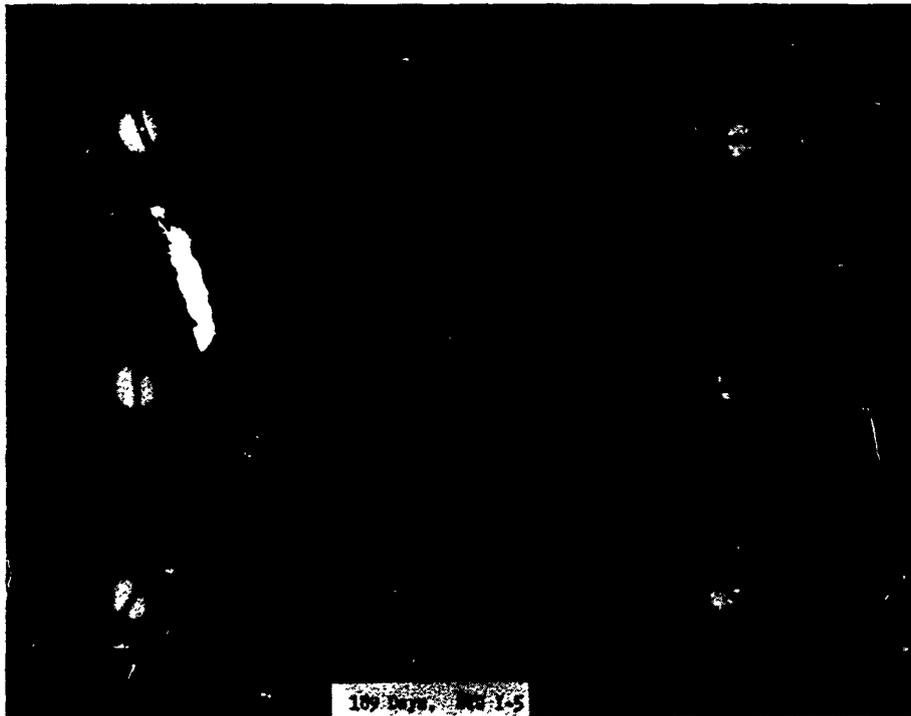


Figure 19. "Exposed" carbon steel panels with layers of red rust formed over the surface.

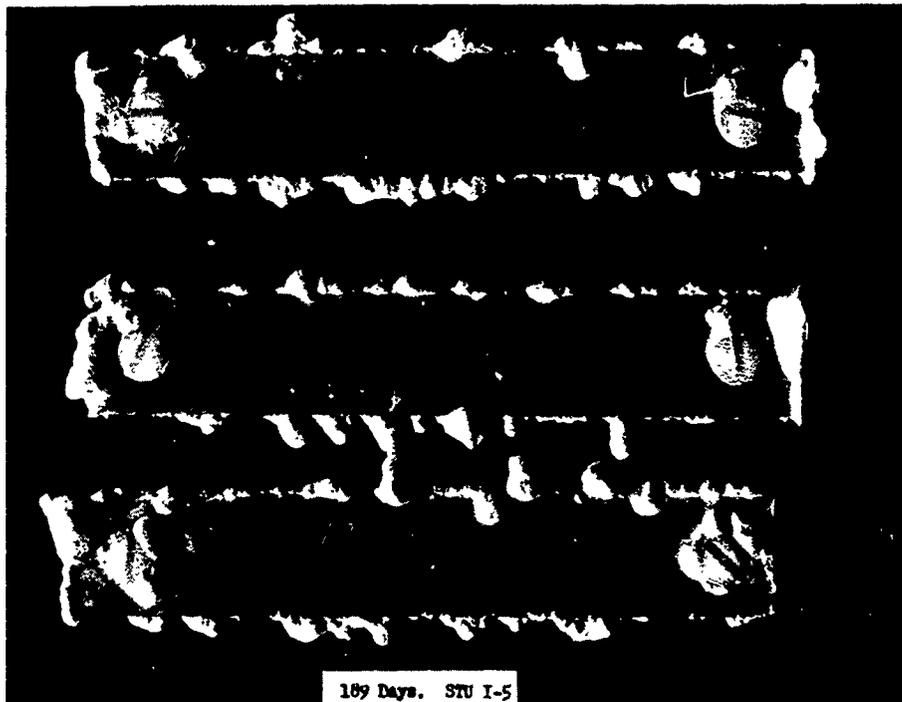


Figure 20. "Exposed" aluminum alloy test panels with corrosion products formed along the ends and edges.

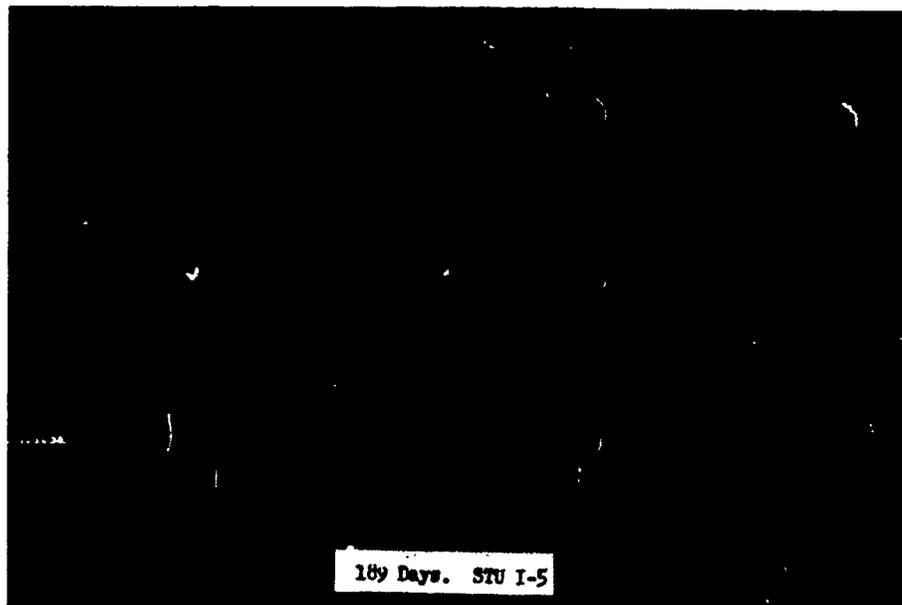


Figure 21. "Control" carbon steel and aluminum alloy panels. These were exposed inside the "sterile" cylindrical test chambers.



Figure 22. After the aluminum panels shown in Figures 20 and 21 were cleaned chemically, the edges and ends of "exposed" panels were found to be severely corroded (right) while the "control" panels were slightly affected (left).

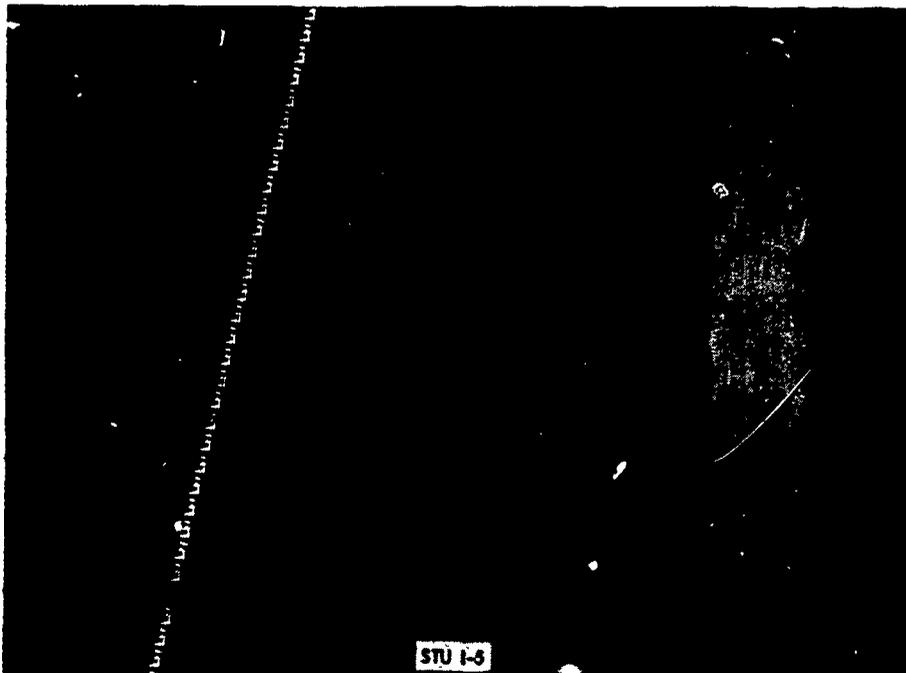


Figure 23. Surface condition of "control" (short) and "exposed" (long) carbon steel and aluminum panels after undergoing chemical cleaning.

#### REFERENCES

1. Naval Civil Engineering Laboratory. Technical Report R-525: Deep-ocean biodeterioration of materials - Part III. Six months at 6,000 feet, by J. S. Muraoka. Port Hueneme, California. May 1967.
2. \_\_\_\_\_. Technical Report R-504: Corrosion of materials in hydrospace, by F. M. Reinhart. Port Hueneme, California. December 1966.
3. \_\_\_\_\_. Technical Report R-369: Design, placement, and retrieval of submersible test units at deep-ocean sites, by R. E. Jones. Port Hueneme, California. May 1965.
4. \_\_\_\_\_. Technical Report R-612: Plastic film coatings for protection from marine fouling and corrosion, by J. S. Muraoka. Port Hueneme, California. February 1969.
5. \_\_\_\_\_. Technical Report R-027: Harbor Screening Test of Marine Borer Inhibitors - I, by H. Hochman and T. Roe, Jr.. Port Hueneme, California. July 1959.
6. R. D. Turner. "Implications of Recent Research in the Teredinidae" in Internationales Symposium Holtz und Organismen, Berlin-Dahlem, 1965, edited by G. Becker and W. Liese. Berlin, Buncker and Humblot, 1966, pp. 437-446.
7. Personal communication with Dr. Jan Kohlmeyer, University of North Carolina, Institute of Marine Sciences, who examined the wood panels for the presence of deep-sea fungi.
8. E. E. Halmos, Jr. "The Atomic Age's WPC Latest in Wood Preservation." Wood Preserving News. Vol. 43, No. 11. November 1965, pp 7-9, 12-13.
9. "Relationship between marine fouling and corrosion rate of carbon steel and aluminum alloy at the surface and at 6,000 feet depths" (In preparation).

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<p>This note reports the data obtained after exposing metallic and nonmetallic specimens for 6.3 months on the floor of the Pacific Ocean at a depth of 6,000 feet (Test Site I). The test specimens were attached to a Submersible Test Unit (STU) that was emplaced August 7, 1968 and retrieved on February 12, 1969. Preliminary examination of the specimens was made aboard ship, and the final examination, tests, and analyses were performed at the Naval Civil Engineering Laboratory.</p> <p>Typical fouling organisms such as barnacles, bryozoa, and mussels were not found on test panels exposed at 6,000 feet, but the surfaces of plastics, metals and ropes were coated with a thin film of microbial slime. Untreated wood and ropes made of natural fibers (cotton and manila) were severely damaged by microorganisms and molluscan borers. Plastic panels which were in direct contact with wood were also affected by the wood borers. Strangely, extensive borer damage to wood panels was restricted to a narrow area extending from the mud-line to a distance of one or two feet above it. Certain chemically treated wood, certain plastics, rubber, and glass were resistant to biodeterioration. Ropes made of polyethylene and polypropylene increased in tensile strength after exposure at 6,000 feet. A limited study on the corrosion of carbon steel and aluminum alloy helped to confirm a long held suspicion that microorganisms might play a role in the corrosion of metals in the ocean.</p>		

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Glass						
Carbon steels						
Aluminum alloys						
Rope						
Deep water						
Sea water						
Ocean bottom						
Aquatic microbiology						
Slime						
Submersible Test Unit						