The image shows four vertical metal plates of varying materials and degrees of corrosion, partially submerged in seawater. The plates are arranged in a row on a sandy beach. The water is shallow, with gentle waves lapping at the base of the plates. The plates show different levels of rust, pitting, and biological fouling, illustrating the effects of seawater on different metals.

THE INTERRELATION OF CORROSION AND FOULING OF METALS IN SEA WATER

INTRODUCTION

One of the unique and troublesome aspects of ocean engineering systems and materials in sea water is the occurrence of marine fouling, which can affect the operation and maintenance of structures in a number of ways. These organisms can greatly alter corrosion processes that are occurring on structural members and component parts. In addition, they can cause plugging problems in condensers, pipe lines and valves. They can have a significant effect on friction coefficient and pumping efficiencies for sea water handling systems. For these reasons, studies of the fouling properties of metals in sea water are of considerable importance to the ocean engineering community.

One of the best and most easily understood outlines of fouling in sea water, organism types and effects on corrosion is given by Clapp.¹ A fairly extensive study on corrosion and fouling of copper-base alloys in sea water was reported by Bulow² and for the copper-nickel system by LaQue and Clapp.³ In both of these investigations, particularly in the LaQue and Clapp paper, conclusions were drawn as to a maximum corrosion rate which the copper alloy must be undergoing in order to remain antifouling. This was based on short-term tests where the corrosion rates

of the alloys were varying considerably. The lower corrosion rate passive materials were observed to foul readily, while the higher corrosion rate nonpassive materials retained their fouling resistance. It has also been suggested that the sloughing off of solid corrosion products could be a factor determining the fouling resistance of the metals and alloys just as the toxicity of the corrosion product.^{1,3}

This paper brings together a number of different investigations conducted at the Francis L. LaQue Corrosion Laboratory of The International Nickel Company, Inc. in order to present a unified scientific picture of the fouling characteristics of metals and alloys. Particular emphasis is placed on the fouling resistant materials, the causes of their fouling resistance and their applications in ocean engineering systems.

For convenience and ease of understanding, the metals and alloys are divided into three classes: I. highly corrodible metals, II. passive metals and III. toxic film-forming metals. Each class is distinct in the form of corrosion product occurring on the metal, its effect on the succession of fouling and the effect of fouling on subsequent corrosion processes.

EXPERIMENTAL PROCEDURE

The laboratory site is at Wrightsville Beach, N. C. which lies in a temperate climate. Fouling in this area is classified as moderate to heavy as shown in Figure 1.⁴ The laboratory itself is located in a channel protected from wave action of the Atlantic Ocean by an intervening island, with a tidal flow of approximately one fps and a normal tidal range of four feet. Thus, the effect of sea water velocity in removing fouling by either excessive tidal action or wave action is obviated.

The seasons of attachment for the various organisms at the laboratory location are shown in Figure 2. Evaluations of the seasons of attachment for fouling organisms are made using non-toxic slate panels of both long term (6-month) and short term (1 month) exposures. Evaluations of these short term exposures determine the seasons for fouling attachment of the various organisms, while the long term panels provide a means of monitoring fouling succession.

Sea water analyses and temperatures are routinely determined and recorded. The general sea water chemistry for the laboratory location is given in Table I. Thus the sea water itself and fouling progression at the laboratory are continually monitored to fully characterize normal sea water conditions.

This bulletin is based on a paper by K. D. Elford
presented at NACE Corrosion/75, Toronto, Ontario, Canada, April 1975.

TABLE I
Chemistry of Sea Water at the Francis L. LaQue
Corrosion Laboratory
Wrightsville Beach, N. C.

	Major Characterization		
	Max	Min	Avg
pH	8.1	7.8	8.0
T, C	29	6	18
Cl, g/l	19.8	18.1	19.0
O ₂ , mg/l	9.3	5.0	6.4
Average Analysis, mg/l			
Cations		Anions	
Na	10,006	Cl	19,000
Ca	398	SO ₄	2510
Mg	1204	HCO ₃	133
K	369	NO ₃	1.2
Cu	.015	PO ₄	.01
Fe	.001	F	1.5
Zn	.012	Br	61
		I	0.16
Hardness CaCO ₃	5970 mg/l		

Figure 1. Coastal biological fouling chart of the Atlantic United States.⁴ The Francis L. LaQue Corrosion Laboratory is located at Wrightsville Beach, N.C. (circled).

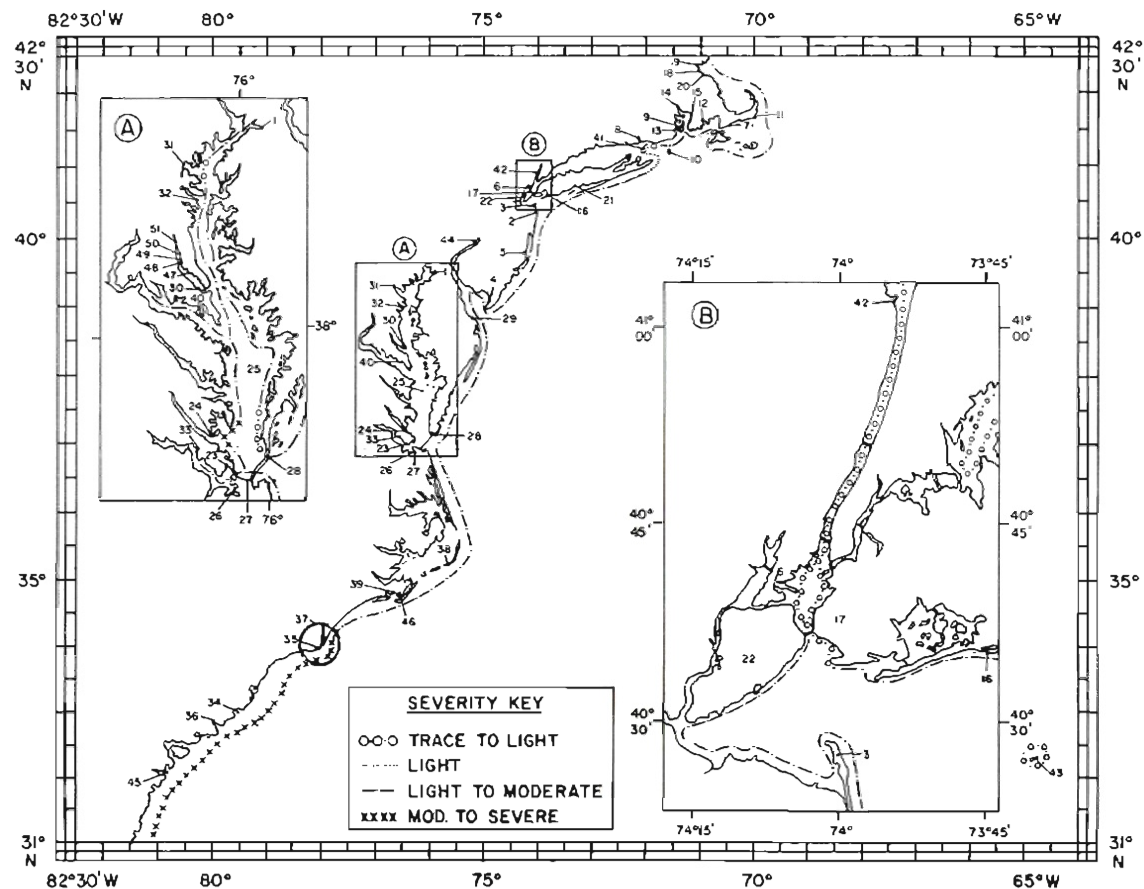


Figure 2. Seasons for the attachment of marine fouling organisms at Wrightsville Beach, N.C.

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Limnoria	•	•	•	•	•	•	•	•	•	•	•	•
Algae		•	•	•	•							
Teredinidae						•	•	•	•	•	•	
Sponges					•	•	•	•	•	•		
Hydroids				•	•	•			•	•	•	
Serpula						•	•	•	•	•	•	
Barnacles			•	•	•	•	•	•	•	•	•	
Encrusting Bryozoa					•	•		•	•	•	•	
Filamentous Bryozoa				•	•	•	•	•	•	•	•	
Anomia						•	•	•	•	•		
Mussels			•		•	•	•			•		
Tunicates	•	•	•	•	•	•	•	•	•	•	•	•

Experiment 1

Representative metals for the three classes were as follows:

- I. The corrodible metals—steel
- II. The passive metals—5086-0 aluminum
- III. The toxic film formers—copper, 90-10 Cu-Ni, and 70-30 Cu-Ni.

All of the alloys used were commercially produced materials with compositions as given in Table II. The samples were cleaned according to ASTM G-1 Recommended Practice standard methods which varied for the particular metal or alloy in question, degreased in acetone, rinsed in distilled water, air dried, and mounted on racks made from MONEL* nickel-copper alloy 400, using bolts produced from MONEL alloy 400 and TEFLON† insulators as support. The racks were then suspended on a floating dock which provided a constant depth of immersion at approximately 18 inches for all samples, with the panels facing in an east-west direction. This provided optimum conditions for fouling attachments and growth.

During the exposure period, inspections were carried out at intervals of 3, 9, 18, 36, 48 and 60 months, where the racks were pulled up, and photographs taken of the individual samples. This gave a sequential record of fouling for the various metals in sea water as a function of time and season of attachment. The test was terminated after 60 months' exposure, the samples cleaned using ASTM G-1 Recommended Practice methods, and weight losses and corrosion rates calculated.

* Trademark of The International Nickel Company, Inc.

† Trademark of E. I. DuPont de Nemours, Inc.

Experiment 2

This experiment was designed to study the effect of Cu alloy corrosion on fouling of adjacent non-toxic materials. Two 90-10 Cu-Ni samples (4" x 12") from sheet used in the previous experiment were cleaned and painted over one half of their length with white vinyl paint. The panels were mounted on MONEL nickel-copper alloy 400 racks and porcelain insulator supports with the painted half above the exposed Cu-Ni for one panel and below the Cu-Ni for the other panel. The exposure was made from the floating dock as before at a constant depth of 18 inches during the summer heavy fouling season. The Cu-Ni/vinyl paint interface was inspected and photographed after exposure times of 1, 3, 7, 10 and 24 weeks.

Experiment 3

This experiment was designed to study the effect of waterline exposure on the fouling of the toxic film forming metals. Panels of adequate size (4" x 18") were vertically exposed from a floating dock to maintain approximately 12" below water, facing in an east-west direction to provide optimum fouling conditions. The panels exposed were white vinyl coated steel, Cu₂O antifouling paint on steel, copper, 90-10 Cu-Ni and

70-30 Cu-Ni. Exposure was made at the beginning of the heavy fouling season at Wrightsville Beach (April) to obtain maximum fouling probability in the shortest time period.

RESULTS AND DISCUSSIONS

1. Fouling of the Highly Corrodible Metals in Sea Water

The highly corrodible metals are characterized by the formation of loose, voluminous corrosion product in sea water exposure and are represented as a class in this investigation by carbon steel. The fouling properties of this material are of importance because of the simple fact of the tonnage volume of steel used in sea water structures and ocean engineering systems. Most steels in sea water corrode at very similar rates and the fouling sequences discussed here are generally applicable to all steels, both carbon and low alloy.

The five-year sequence of fouling on carbon steel is shown in Figure 3. After three months' exposure, the panels show a rust film with attached filamentous bryozoa and small tunicates. However, at nine months, all fouling organisms have sloughed off and a voluminous red rust is evident on the panels. At 18 months, the rust film is being covered over by large tunicates, barnacles, and seaweed attachment. At 36 months' exposure, it is evident that a large amount of fouling is very close to the steel surface, having essentially replaced the voluminous red rust film. Filamentous bryozoa, tunicates, barnacles and some serpulids are evident, as well as seaweed and algae attachment. After an exposure period of 48 months, the panels have been completely covered by fouling organisms consisting of tunicates, filamentous bryozoa, some encrusting bryozoa and seaweed. At 60 months, much of the accumulated fouling has sloughed off and red rust is again apparent. A section of one sample is completely corroded away.

TABLE II
Chemical Analysis of Materials Tested for Marine Fouling in Sea Water

Alloy	Class*	Composition, % wt
Carbon Steel	I	Bal Fe, .07 Ni, 0.41 Mn, .03 Cr, 0.15 C, .02 Si, <.01 Mo, .015 P, .032 S
5086-0 Aluminum	II	Bal Al, 3.95 Mg, 0.15 Cr, 0.30 Fe, 0.18 Si, .08 Cu, 0.28 Mn, 0.14 Zn, .02 Ti
ETP Copper (CA 110)	III	99.98 Cu, .017 P
90-10 Cu-Ni (CA 706)	III	Bal Cu, 9.74 Ni, 1.27 Fe, 0.72 Mn, 0.30 Zn, <.02 Pb, .010 P
70-30 Cu-Ni (CA 715)	III	Bal Cu, 30.38 Ni, 0.52 Fe, 0.41 Mn, 0.10 Zn, .005 Pb, .010 P

* Class I = corrodible metals

Class II = passive metals

Class III = toxic film forming metals

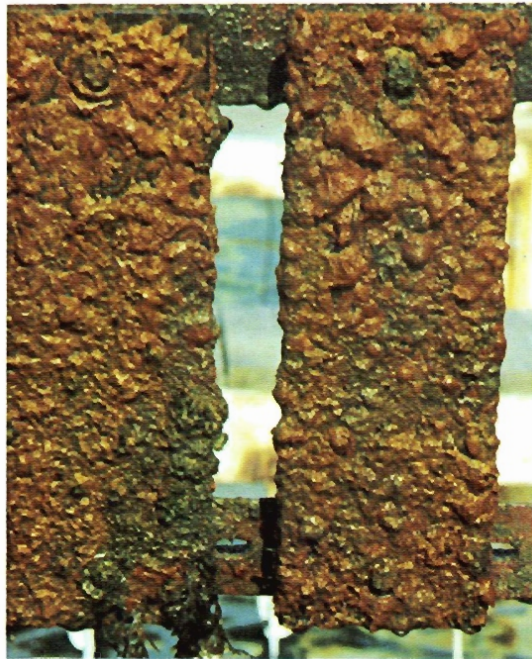


Figure 3. The five-year sequence of fouling on carbon steel in sea water. Exposure periods are (from left to right):
 Top—3 months, 9 months, 18 months.
 Bottom—36 months, 48 months, 60 months.

The accumulation of fouling organisms on steel structures immersed in sea water has detrimental effects including increased weight of the structure in air because of accumulated fouling organisms, and in the case of intake systems and pipe lines, the sloughing off of fouling organisms which are then carried into other parts of the system using sea water. In addition, there is a significant effect of attached fouling on friction coefficient and pumping efficiencies.

2. Fouling of the Passive Metals in Sea Water

The passive metals are characterized by the formation of a tightly adherent passivating film on exposure to sea water. These materials include the stainless steels, titanium, many nickel-base alloys (e.g. INCONEL* nickel-chromium alloy 625), and some aluminum alloys (5000 series). The alloy used in this experiment to investigate the fouling properties of passive metals was 5086-0 aluminum.

The sequence of fouling for the 5086-0 aluminum alloy panels is given in Figure 4. After 3 months' sea water exposure, the aluminum has become covered with filamentous bryozoan and small tunicate fouling. At 9

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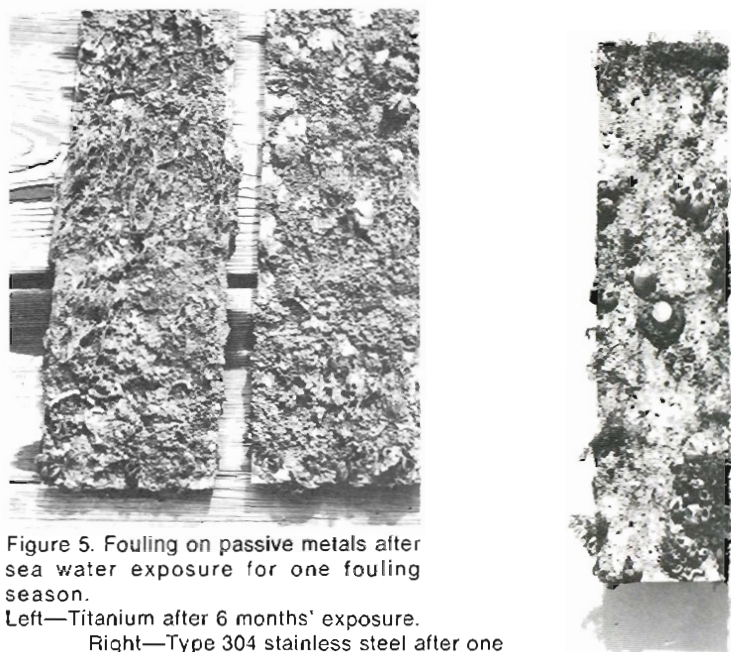


Figure 5. Fouling on passive metals after sea water exposure for one fouling season.

Left—Titanium after 6 months' exposure.

Right—Type 304 stainless steel after one year exposure.

months, this fouling has been replaced by a heavy slime film, barnacles, larger tunicates and encrusting bryozoa. After 18 months, barnacles and tunicates have grown to fairly large size and seaweed has attached to the panels. There is an overgrowth of barnacles and tunicates on the encrusting bryozoa, and subsequent overgrowth of bryozoa over the barnacles. At 36 months, much of this fouling has been replaced by filamentous bryozoa and seaweed fouling, however, numerous barnacles are still evident on the panel surface. At 48 months, tunicates are again replacing the filamentous bryozoa, however, bryozoan fouling is still quite heavy and there has been heavy seaweed attachment on the panel surface. After 60 months' exposure, sponges have added to the prolific fouling community previously attached to the alloy.

In general, the sequence of fouling that is observed on the passive metals is the same as would be observed on a non-toxic inorganic structure such as slate, and the normally observed sequence of fouling replacement and overgrowth is occurring. Figure 5 gives examples of fouling attachment on other passive metals such as titanium and stainless steel. Fouling attachment tends to restrict oxygen diffusion to the sample surface, and the occurrence of fouling can accelerate localized corrosion on alloys that are highly susceptible to oxygen concentration cells. An excellent example of this effect is the crevice corrosion of stainless steels under barnacles as shown in Figure 6.



Figure 6. Crevice corrosion beneath barnacles on Type 304 stainless steel after 2 years sea water exposure.

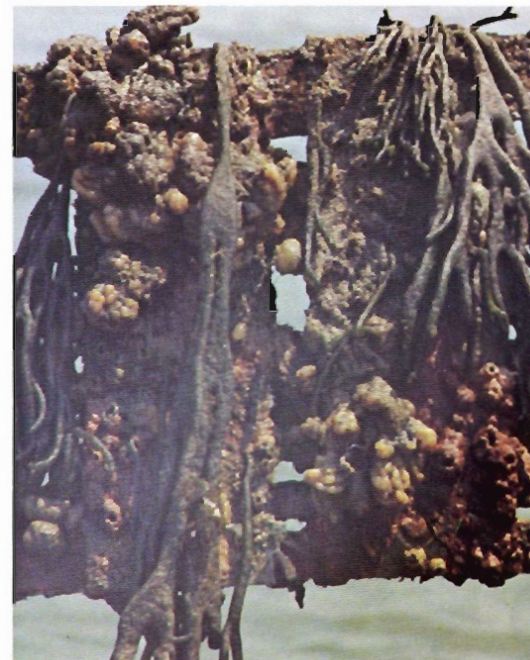


Figure 4. The five-year sequence of fouling on 5086-0 Aluminum in sea water. Exposure periods are (from left to right): Top—3 months, 9 months, 18 months. Bottom—36 months, 48 months, 60 months.

3. Fouling of the Toxic Film Forming Metals in Sea Water

The toxic film forming metals as a class are of interest for use in ocean engineering systems because of their possibility of inherent fouling resistance without the use of coatings or sea water treatments. The natural materials that one would expect to have a degree of fouling resistance because of the formation of a toxic film would be those whose metal ions are poisonous to animal life forms. This would include metals and alloys based on the elements beryllium, chromium, copper, zinc, silver, lead, mercury and tin.

This concept of fouling resistance is not always valid, however, since metals such as lead and beryllium will quite readily foul as shown in Figure 7. At this writing, the only metals that have been shown to possess inherent fouling resistance are those based on the elements zinc, silver and copper. In previous tests, zinc remained antifouling for two years at which time excessive fouling began, while silver retained its fouling resistance for a three-year exposure period. The copper-base alloys were emphasized in this investigation because of their commercial usefulness and ready availability.

Three copper alloys were used in order to look at the effects of copper dilution in the metal, and to include three commercially available copper-base alloys. There were ETP copper (CA 110), 90-10 Cu-Ni (CA 706) and 70-30 Cu-Ni (CA 715).

The fouling sequence for a five-year exposure of copper is shown in Figure 8. After 3 and 9 months' exposure, the green copper hydroxy-chloride film is evident with no fouling attachment and only slight sliming. After 18 months' exposure, heavy sliming has occurred, but no fouling organisms have attached. After 36 months' exposure, some small serpulids have attached and filamentous bryozoa has begun growing on the serpulid attachments. At 48 months, additional serpulid attachment has occurred with filamentous bryozoa and some tunicate growth over the serpulids, and encrusting bryozoa has begun to cover some of the panel surface. After 60 months' exposure, tunicate, bryozoa and serpulid fouling has covered almost 60% of the sample surface.

The fouling sequence for the 90-10 Cu-Ni is shown in Figure 9. Here again, little other than the formation of corrosion product is noted after 3 and 9 months' exposure. The corrosion product in this case, however, is brown as opposed to the green copper corrosion product. At 18 months, a heavy slime film has formed on the panels. After 36 months' exposure, there has been slight serpulid growth with some filamentous bryozoa attachment to the serpulids. After 48 months, the serpulid attachment has spread, with filamentous bryozoa and tunicate attachment as

well as the growth of some encrusting bryozoa on the panel surface. At 60 months, fouling, consisting of tunicates, bryozoa and serpulids, has covered about 70% of the alloy surface.

The fouling sequence for 70-30 Cu-Ni is shown in Figure 10. As before, nothing other than brown general corrosion product forms until the 18-month inspection at which time a heavy slime film has covered the panel surface. At 36 months, there has been some serpulid growth on the 70-30 Cu-Ni, with filamentous bryozoa and small tunicate attachment to the serpulids. At 48 months, this serpulid growth has spread over more of the sample surface resulting in additional filamentous bryozoa and tunicate attachment. There is again some encrusting bryozoa covering the sample surface. After 60 months' exposure, serpulid, tunicate and bryozoa fouling has covered approximately 60% of the sample surface.

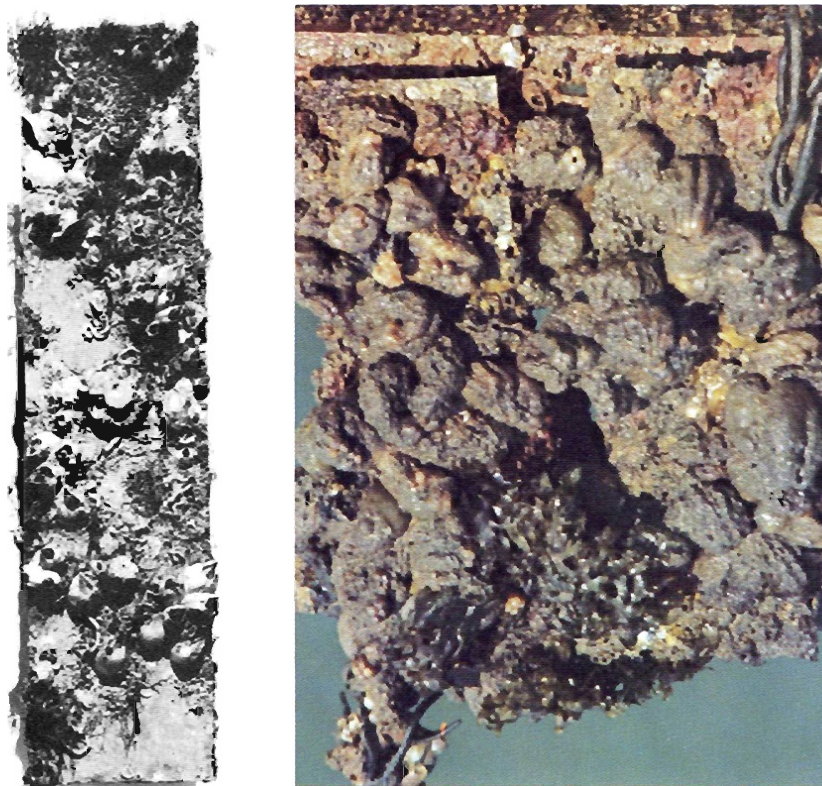


Figure 7. Marine fouling on beryllium (left) and lead (right) after one year exposure in sea water.

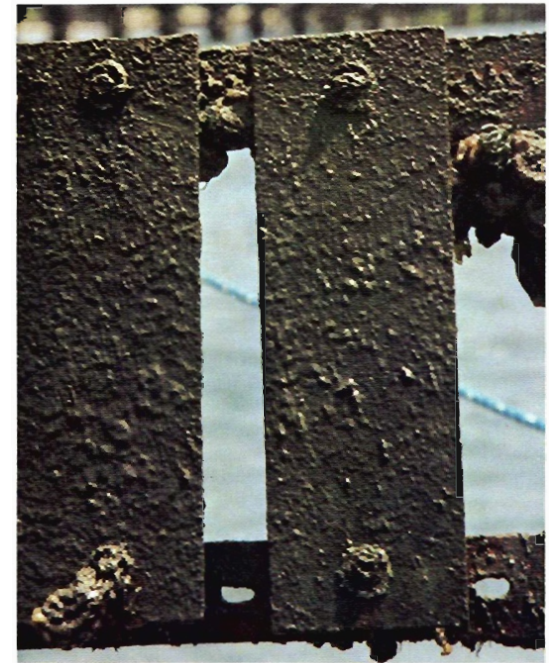
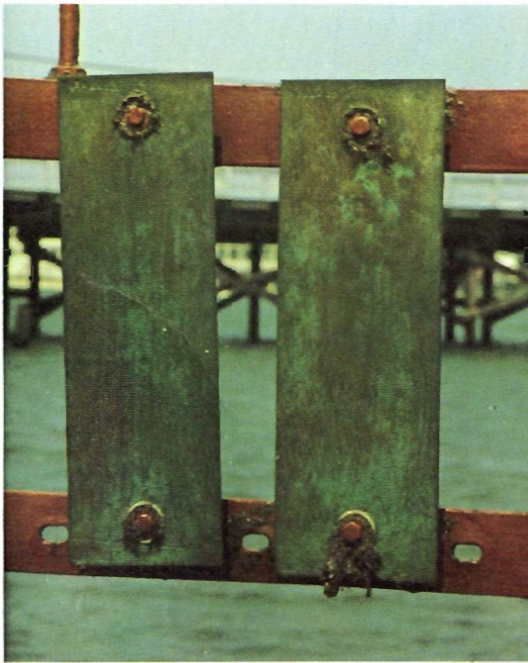


Figure 8. The five-year sequence of fouling on copper (CA 110) in sea water. Exposure periods are (from left to right):
Top—3 months, 9 months, 18 months.
Bottom—36 months, 48 months, 60 months.

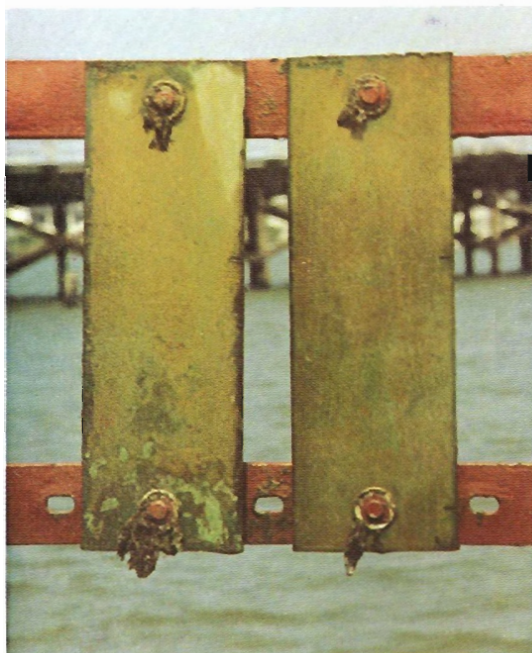


Figure 9. The five-year sequence of fouling on 90-10 Cu-Ni (CA 706) in sea water. Exposure periods are (from left to right):
 Top—3 months, 9 months, 18 months.
 Bottom—36 months, 48 months, 60 months.

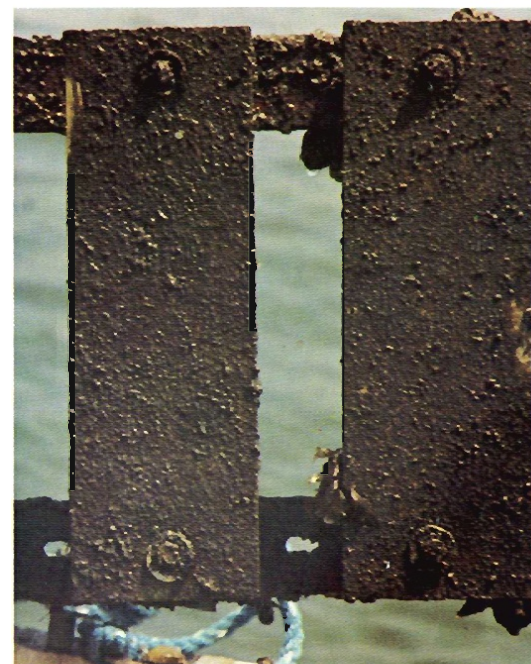
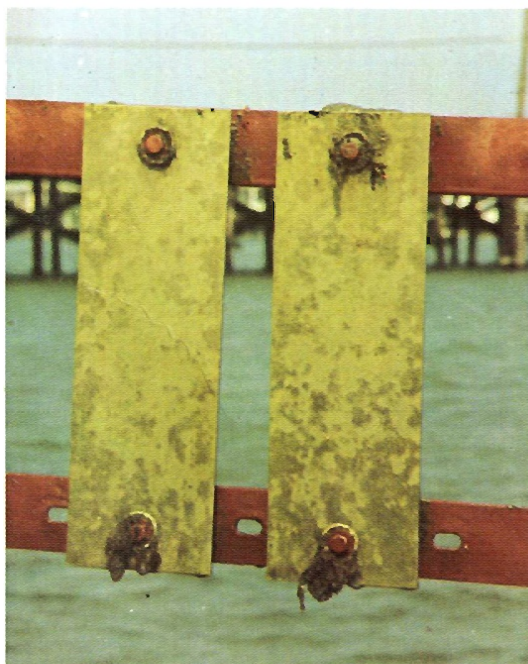


Figure 10. The five-year sequence of fouling on 70-30 Cu-Ni (CA 715) in sea water. Exposure periods are (from left to right): Top—3 months, 9 months, 18 months. Bottom—36 months, 48 months, 60 months.

The striking thing about this series of experiments is that there is no significant difference in the fouling properties of Cu, 90-10 Cu-Ni and 70-30 Cu-Ni with fouling of all three minimal after 4 years' exposure and 70% fouling coverage after 5 years.

Samples were removed at the end of five years' sea water exposure since fouling had occurred on all the alloys. After cleaning and weighing, corrosion rates were calculated, and (along with data from an earlier exposure of zinc, lead and silver) the corrosion rates converted to average leaching rates for metal ions given in Table III. Of particular note is that the copper is corroding at a rate three times that of CA 706 or CA 715 (0.3 mpy compared to 0.1 mpy), while all three alloys fouled in the same time period. This would indicate that the corrosion product form provides the fouling resistance for these materials, not the leaching rate of copper per se from the surface. This concept was further substantiated by a removal in another experiment⁵ where 70-30 Cu-Ni panels that had been exposed in sea water for 14 years, with corrosion rates of .05 mpy, were only slightly fouled as shown in Figure 11. This is in conflict with the leaching theory for fouling resistance of copper-base alloys in sea water, which requires a minimum corrosion rate of 0.7 mpy to prevent fouling.³

4. Effect of Copper Alloy Corrosion on Adjacent Surfaces

If, in fact, leaching were not a factor in the fouling resistance of copper-base alloys, there would be no "throwing power" for the fouling resistance. That is, an inert surface would not be protected by the corrosion of an adjacent copper-base alloy, while if leaching were a factor it would be. As shown in Figure 12, initially there appears to be an effect of the 90-10 Cu-Ni on the adjacent painted surface. However,

after seven weeks, this effect has disappeared, and after longer exposure periods fouling has occurred right up to and is beginning to overlay some of the 90-10 Cu-Ni. There was no effect of the relative orientation of the exposed 90-10 Cu-Ni with respect to the vinyl surface. The ability of serpulids to build shells directly over the copper alloy surface also gives strong indication that the toxic properties of the copper-base alloys are not due to a substance released into the sea water itself. It is the copper-containing film that is resistant to fouling, not copper ion present in the sea water medium poisoning the organisms.

After an extended time period in sea water, the copper-base alloys appear to alternately lose and regain their fouling resistance, as evidenced by the attachment and growth of small barnacles and their easy removal, and periodic sloughing off of attached serpulids. The duplex nature of the copper alloy corrosion product in sea water explains this phenomenon. The initial film formed, which is resistant to fouling, is the cuprous oxide corrosion product. It oxidizes after a period of time to green cupric hydroxychloride, which does not appear to be as toxic to marine organisms, since barnacles have been found on this corrosion product as shown in Figure 13. This is in spite of a significantly higher solubility for cupric hydroxychloride over cuprous oxide, and the resulting higher copper ion concentration in the environment. The cupric hydroxychloride corrosion product is not tightly adherent to the sample surface and is easily removed, preventing secure fouling attachment.

<u>Metal/alloy</u>	<u>Corrosion</u> <u>Rate (mpy)</u>	<u>Metal Ion Conc'n</u> <u>($\mu\text{g}/\text{cm}^2/\text{d}$)</u>
Cu	0.3	18.6
Pb	0.4	31.5
Zn	0.6	29.8
Ag	0.5	36.5
CA 706	0.1	6.2
CA 715	0.1	6.2

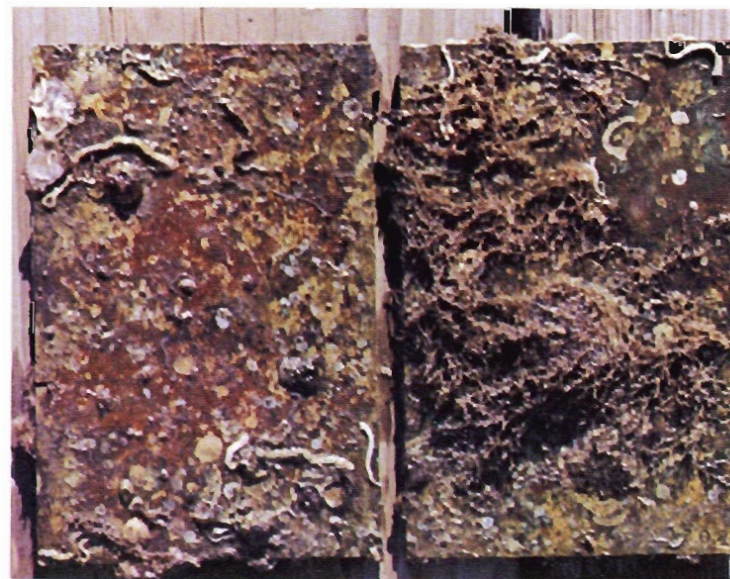


Figure 11. Fouling on 70-30 Cu-Ni after 14 years sea water exposure.⁵

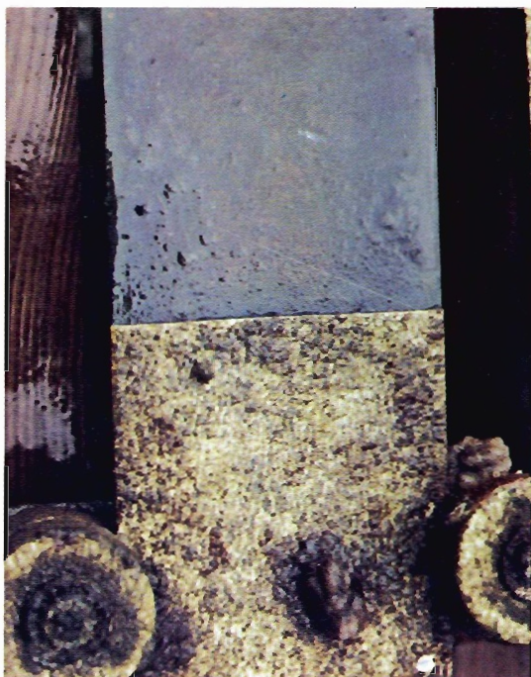
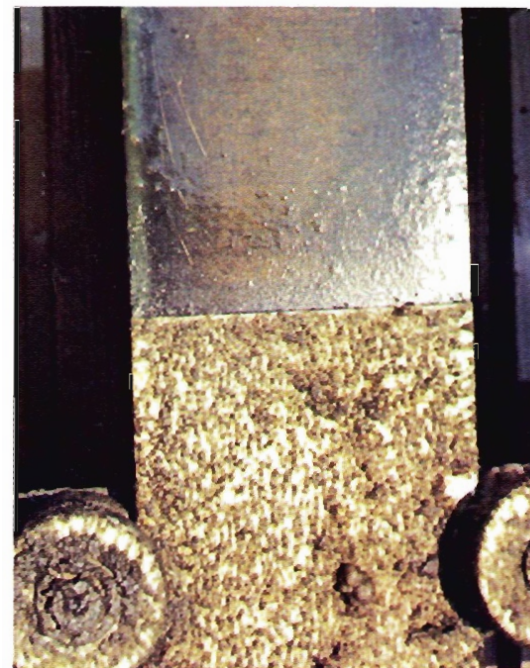
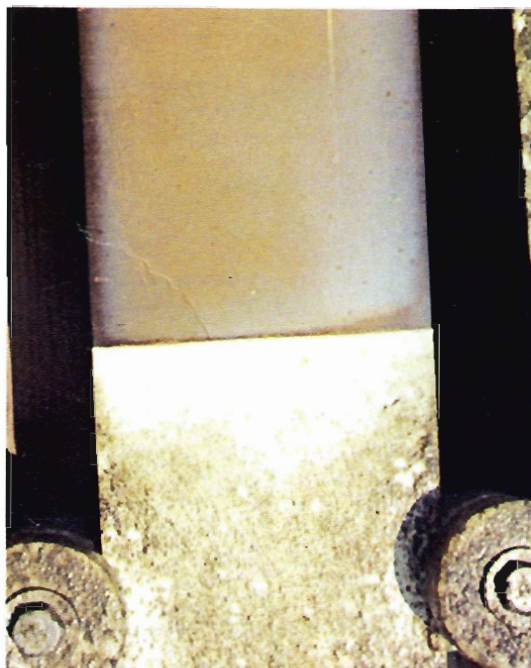


Figure 12. The influence of 90-10 Cu-Ni on the fouling of an adjacent non-toxic (vinyl paint) surface in sea water during the summer fouling season. Exposure times are (from left to right):
Top—1 week, 3 weeks, 7 weeks.
Bottom—10 weeks, 24 weeks.

The fouling resistant properties of copper-base alloys appear to be due to their corrosion to the cuprous oxide state. The alloys remain fouling resistant because of the looseness of the cupric hydroxychloride overlayer, which is easily removed and sloughs off in a manner similar to that for the highly corrodible alloys, except that instead of exposing bare metal, the adherent cuprous oxide film is exposed, which is toxic. The exposed cuprous oxide surface will then oxidize to cupric hydroxychloride. The sequence is diagrammed in Figure 14. All indications are that the slight attachment of fouling to the copper-base alloys when immersed in sea water does not increase their corrosion rate to any measurable extent⁵

5. Waterline Effects

The waterline is probably the most severe and rapid fouling exposure possible. The appearance of the waterline area of the panels in Experiment 3 after 4 months' exposure is shown in Figures 15 and 16.

The "normal" waterline fouling of heavy algae and barnacle attachment occurring on a non-toxic surface is shown by the vinyl coated sample (Figure 15). Some algae attachment is evident on the Cu_2O antifouling coating in the same figure. The copper sample shows some waterline barnacle attachment and heavy sliming, while the 90-10 Cu-Ni and 70-30 Cu-Ni show only heavy sliming (Figure 16).



Figure 13. Barnacles attached to cupric hydroxychloride corrosion product on a copper specimen corroding at 6.5 mpy after becoming coupled to the MONEL alloy 400 mounting bolt.

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CONCLUSIONS

1. The fouling properties of metals in sea water are influenced by their corrosion characteristics, and may be placed into one of three classes: (a) highly corrodible metals, (b) passive metals and (c) toxic film forming metals.
2. The highly corrodible metals such as steel will foul, and the fouling is easily removed with the loose corrosion product sloughing off at intervals during exposure.
3. Passive metals and alloys readily foul and this fouling is tightly adherent. The only effect on corrosion results when the material is sensitive to oxygen concentration cells, where crevice corrosion occurs beneath the fouling organisms.
4. Not all metals which would be expected to form toxic films, e.g., beryllium and lead, will be antifouling when immersed in sea water.

5. The copper-base alloys possess fouling resistance because of the formation of an adherent cuprous oxide corrosion product which is toxic to the organisms. The overlayer of cupric hydroxychloride which often forms is not as toxic and may foul, but is easily removed and prevents firm attachment of the fouling organisms.
6. The antifouling properties of the copper-base alloys do not affect adjacent structures. The toxic property is not due to a release of poisonous ions into the sea water, but to a toxic surface layer.
7. The fouling resistance of pure copper, 90-10 Cu-Ni and 70-30 Cu-Ni are virtually identical for five years' exposure in sea water.
8. The copper-base alloys are not highly susceptible to fouling at the waterline in sea water.

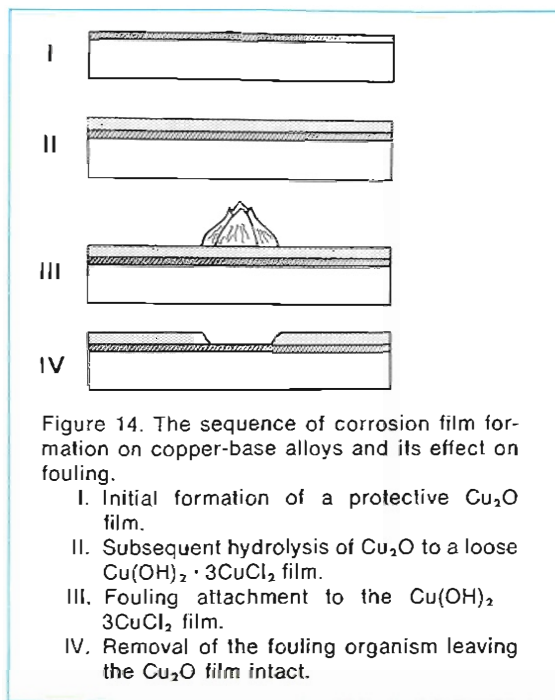


Figure 15. Fouling at the waterline of steel panels coated with white vinyl (left) and Cu_2O antifouling paint (right) after 4 months' exposure in quiet sea water during the heavy fouling season at Wrightsville Beach, N.C.

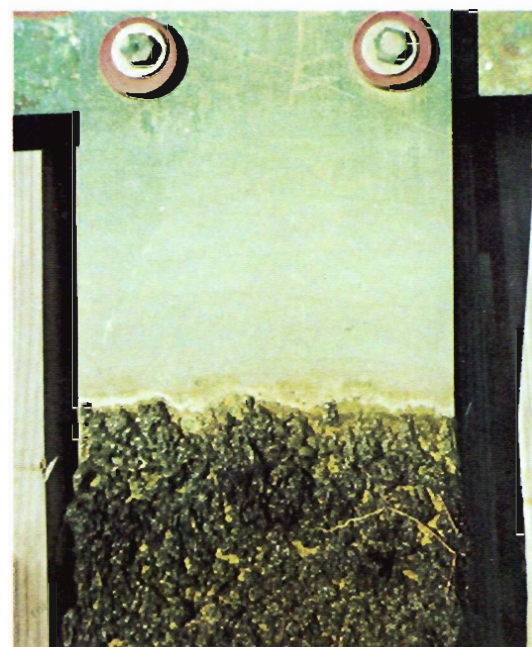
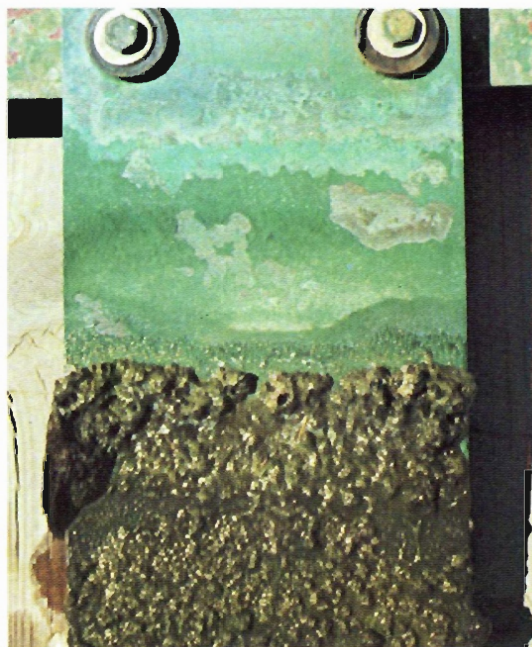
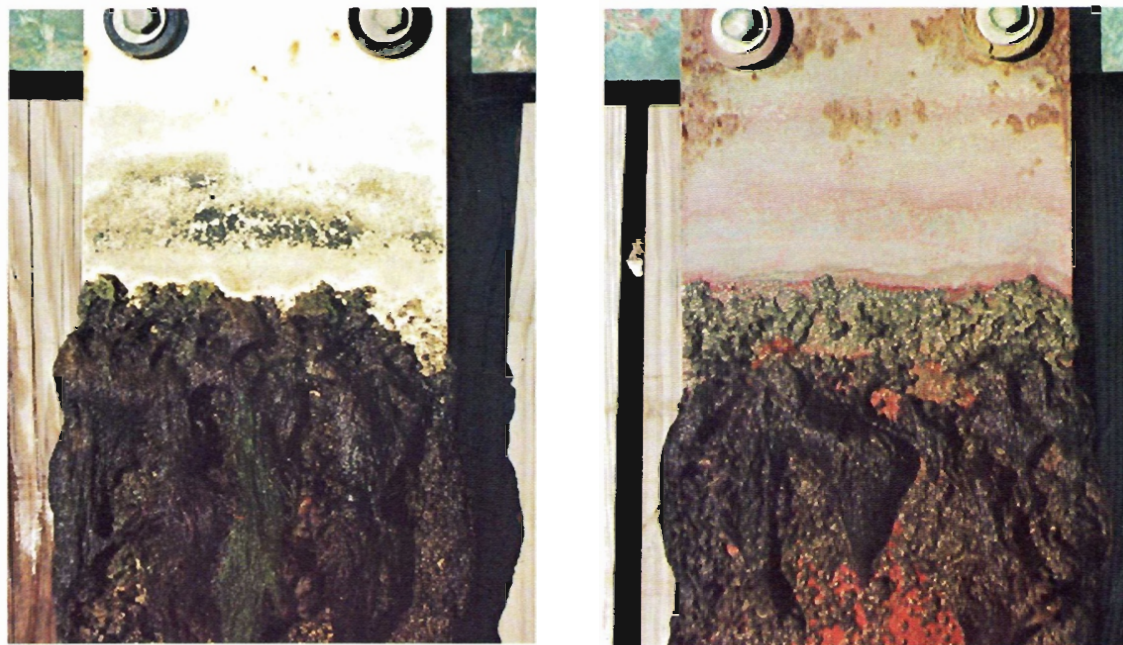


Figure 16. Fouling at the waterline of copper (left), 90-10 Cu-Ni (center), and 70-30 Cu-Ni (right) after 4 months' exposure in quiet sea water during the heavy fouling season at Wrightsville Beach, N.C.