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# The Effects Of Decaying Marine Organisms On The Corrosion Of Copper-Nickel Alloys In Sea Water

by

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Abstract

Recent changes in construction techniques and operational practice have resulted in a number of failures of copper-nickel components in sea water systems, including perforation of 70/30 heat exchanger tubes that was attributed to exposure to sulfide-polluted, stagnant sea water during shutdowns. In an effort to understand the mechanism of these failures, 70/30 copper-nickel specimens were exposed to flowing sea water until protective films were developed. Some of the specimens were then buried in organic debris that had been allowed to accumulate at the bottom of the tank. These specimens were then re-exposed to flowing sea water after two weeks. Corrosion rates were monitored throughout the experiment using linear polarization resistance. The corrosion rate increased by an order of magnitude when the specimens were re-exposed to flowing sea water. The results also suggest that repair of damaged protective films may take longer than initial film formation.

THE EFFECTS OF DECAYING MARINE ORGANISMS ON THE CORROSION OF COPPER-NICKEL ALLOYS IN SEA WATER

by

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# OUTLINE

- BACKGROUND
  - Historical performance
  - Problems with pitting on HALIFAX-class ships
- ELECTROCHEMICAL EXPERIMENTS
  - Polarization resistance
  - Galvanic corrosion
- CONCLUSIONS

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# HISTORY

- PRIOR TO HALIFAX CLASS, MOST SHIPS DREW SEA WATER FOR EQUIPMENT FROM FIREMAIN SYSTEM
  - CONTINUOUS OPERATION
  - RELATIVELY HIGH VELOCITY
- MARINE FOULING RARE



# CHANGE IN PHILOSOPHY TO "WATER ON DEMAND"

- Gentle flow of water in some pipe runs has provided ideal environment for attachment of marine organisms.
- Result: heavy fouling

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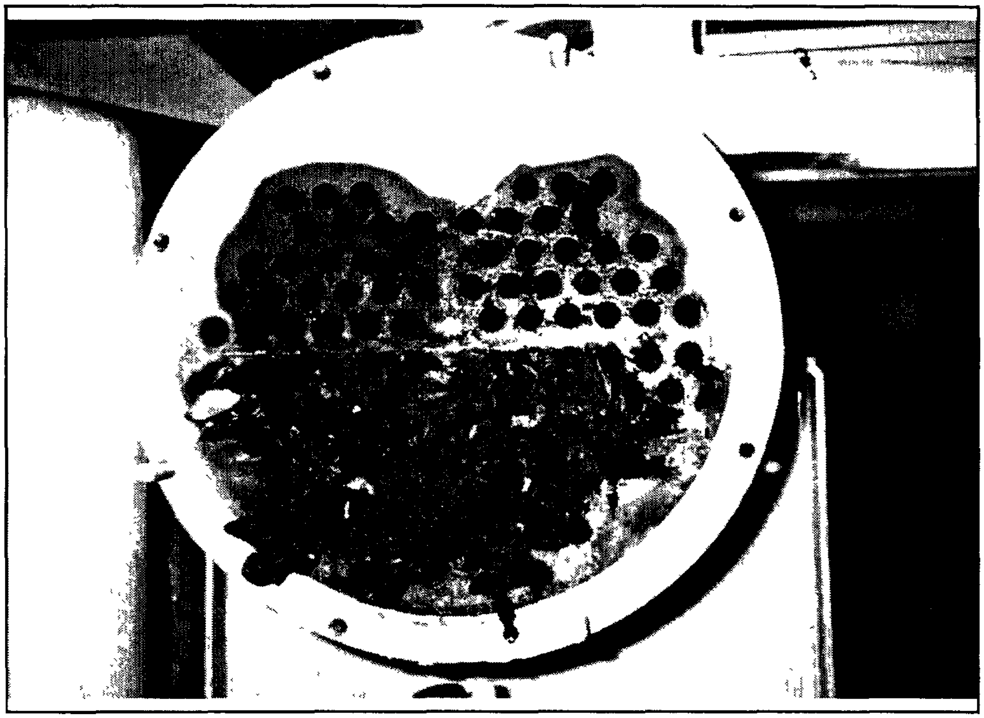

- Blockage on the supply side of a chiller 3 months after a previous cleaning. Most of the material consisted of the remnants of mussels and hydroids that were killed by exposure to fresh water during a visit to Portland, OR. The dead shells broke away from other parts of the system and were trapped at the tube plate. However, this material formed a base for new growth and live four-day old mussels were found in the debris in mid-December, well outside their normal attachment season.

## CHANGE IN PHILOSOPHY TO "WATER ON DEMAND"

- Sea water flow shut off when equipment not in use. Fouling organisms die from lack of oxygen.
- Sulfides released from decaying organisms interfere with protective films on Cu-Ni alloys.

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## PITTING OF 70-30 COPPER-NICKEL

- IN ADDITION TO CAUSING OTHER PROBLEMS, HAS FOULING CONTRIBUTED TO PITTING OF 70-30 COPPER-NICKEL ALLOYS?
- PITTING FAILURES HAVE OCCURRED IN DIESEL LUBE OIL COOLERS, AIR EMISSION COOLERS AND HYDRAULIC OIL COOLERS.
- WHAT IS THE MECHANISM?

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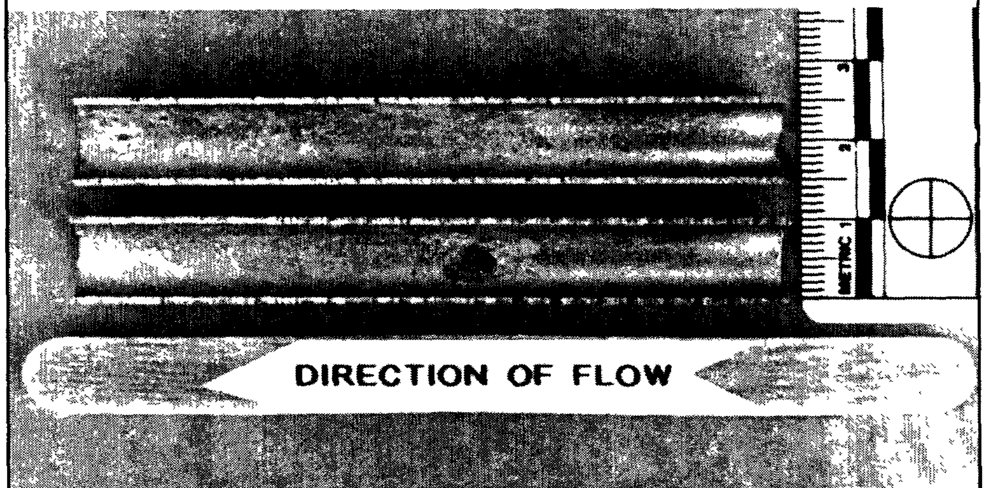


# PITTING IN A HYDRAULIC OIL COOLER

- Leak developed after 15 months
- Constant flow of sea water through cooler at sea.
- Flow shut off in port, leaving cooler full of stagnant sea water.
- Temperature of oil entering cooler normally 30 - 40 Celsius
- If temperature reaches 65 C, alarm activated: never happened.

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# POLARIZATION RESISTANCE

- Measure the current required to maintain a small voltage offset from the corrosion potential.
- Plot of Voltage vs. Current has slope in ohms: Polarization Resistance

- Polarization resistance is inversely proportional to the corrosion rate: method provides instantaneous corrosion rate at the time the measurement was taken

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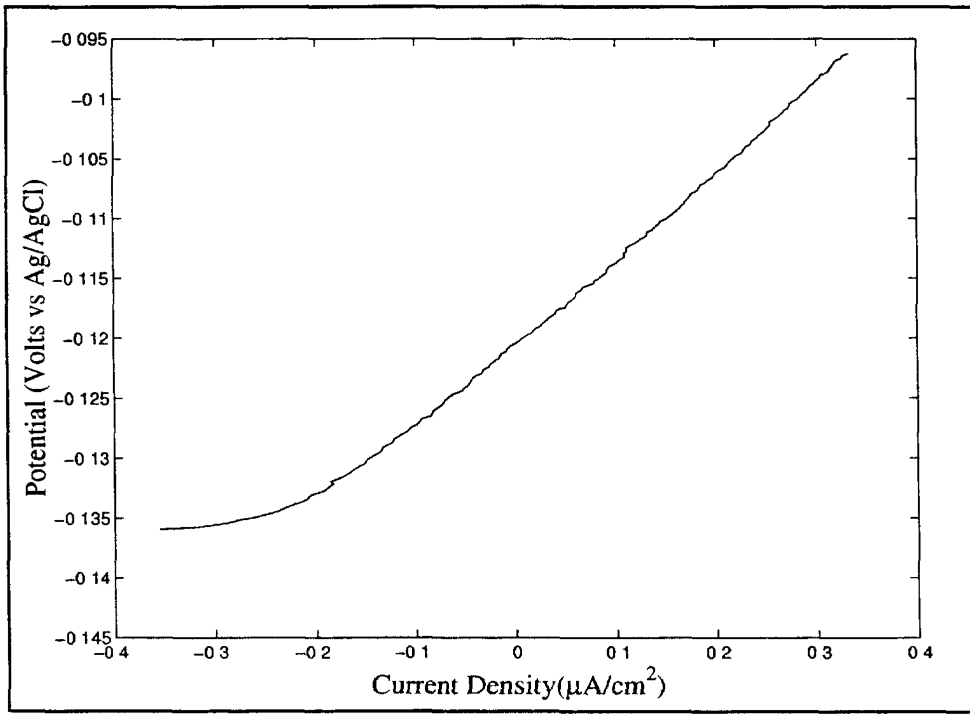

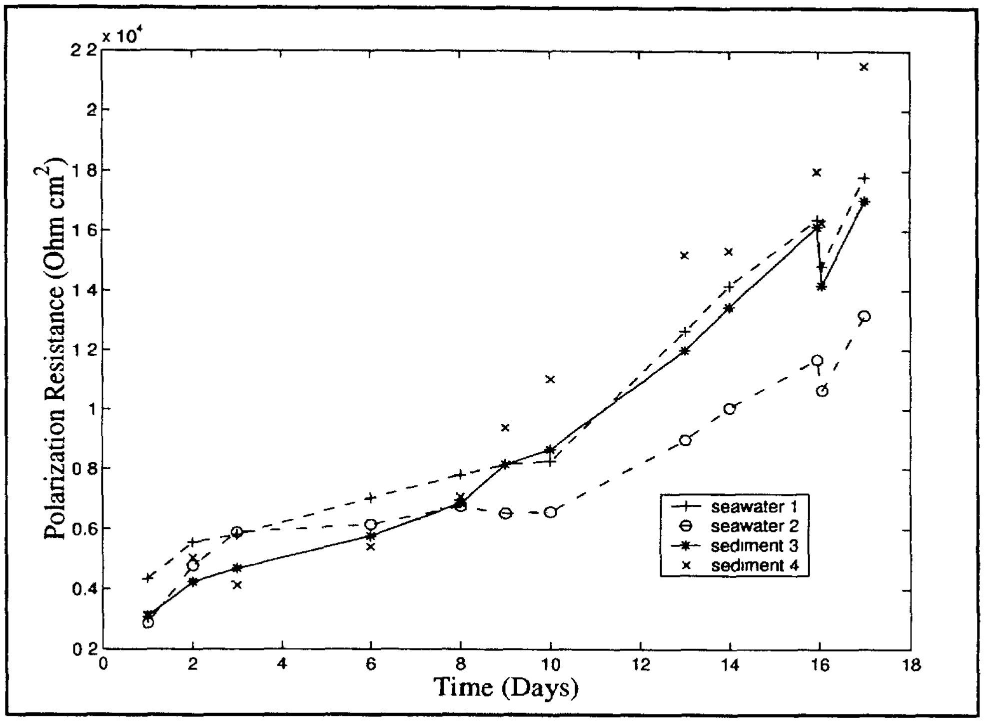


- Polarization resistance measurements for 4 specimens of 70-30 Cu-Ni that, at this point, had been continuously exposed to flowing sea water. Observe the decrease in polarization resistance (increase in corrosion rate) that occurred on Day 16, one hour after the sea water delivery pumps were changed. The switchover introduced a small amount of sulfide (from marine organisms that have died in the stagnant line) into the water in the tank for a few minutes. Note that, in this case, the interruption in the development of the protective film is temporary and any damage is repaired by continuing exposure to clean sea water.

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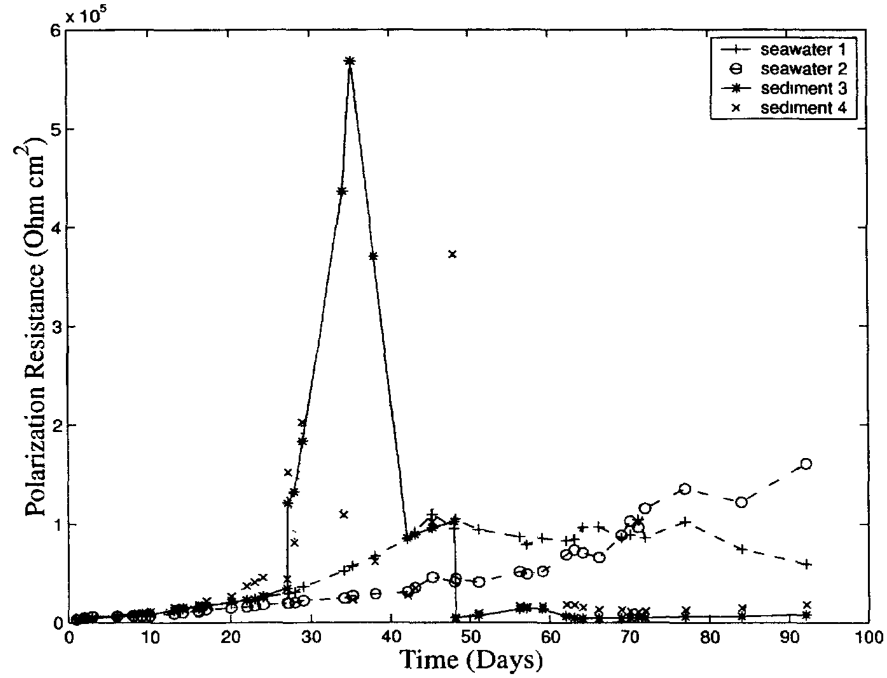


- Polarization resistance measurements for 4 specimens of 70-30 Cu-Ni. Until Day 27, all specimens were exposed to clean, flowing sea water, with the brief exception of the introduction of a small amount of sulfide on Day 16, as described in a previous slide. On Day 27, specimens 3 and 4 were lowered into organic debris that had been allowed to accumulate at the bottom of the exposure tank. The immediate increase in polarization resisitance (decrease in corrosion rate) is associated with the lack of oxygen in the sediment. The sediment was loosely packed and had little effect on the solution resistance (iR drop). On Day 48, specimens 3 and 4 were lifted back into the flowing sea water.

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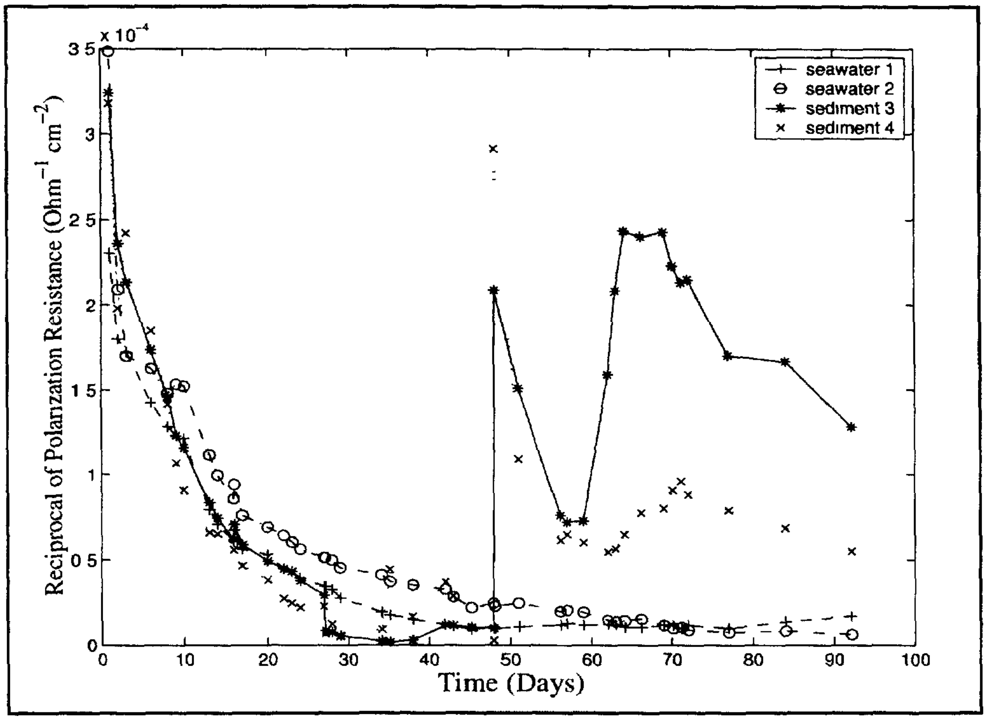
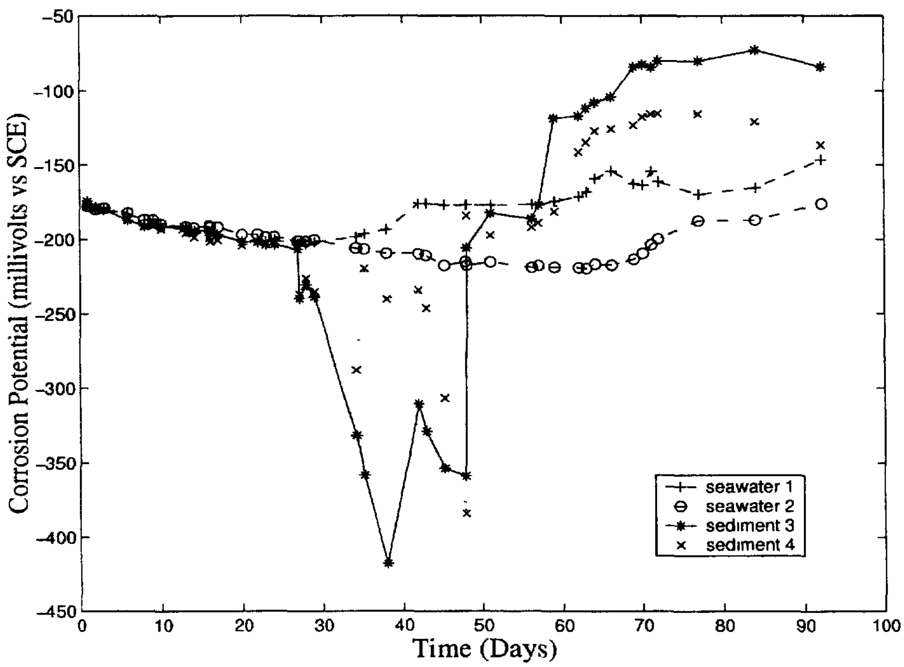



- Same data as previous graph, but y-axis converted to reciprocal of polarization resistance, which is directly proportional to corrosion rate. Note the sharp increase in corrosion rate when specimens 3 and 4 are re-exposed to flowing sea water. They show at least an order of magnitude higher corrosion rates than the control specimens that were continuously exposed to flowing sea water. Furthermore, these specimens do not develop protective films as quickly as they did when first exposed to sea water at the start of the experiment Fully protective films did not develop even after another 45 days of exposure to flowing sea water.




- Plot of corrosion potential for the specimens described on the previous two pages. The shift in corrosion potential for specimens 3 and 4 between Day 27 and Day 48 results from the anaerobic conditions in the sediment. The fluctuations in corrosion potential during this time period suggest the possibility of biological activity within the sediment.

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# GALVANIC CORROSION

- **USE "ZERO-RESISTANCE AMMETER" TO MEASURE CURRENT FLOW BETWEEN INDIVIDUAL SPECIMENS IN A PAIR AS A RESULT OF DIFFERENT EXPOSURE CONDITIONS.**
- **ATTEMPT TO DETERMINE CONDITIONS UNDER WHICH GALVANIC CORROSION WILL OCCUR**

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- Specimens of 70-30 Cu-Ni that were 1 cm wide by 18 cm long were coated with two coats of an underwater epoxy paint so that 1 $cm^2$ of Cu-Ni was exposed on one side. Pairs of specimens were placed in the sea water tank so that the exposed faces were 2 cm apart as shown in the next photograph. All specimens exposed to flowing sea water for 21 days. Of the six pairs, on Day 21, two sets of pairs were lowered into the organic debris and for three pairs, only one specimen in each pair was lowered into the debris. The sixth pair served as a control and remained exposed to flowing sea water. After another 21 days, one specimen from each pair was lifted back into the flowing sea water. A silver-silver chloride reference electrode was placed between each specimen pair.

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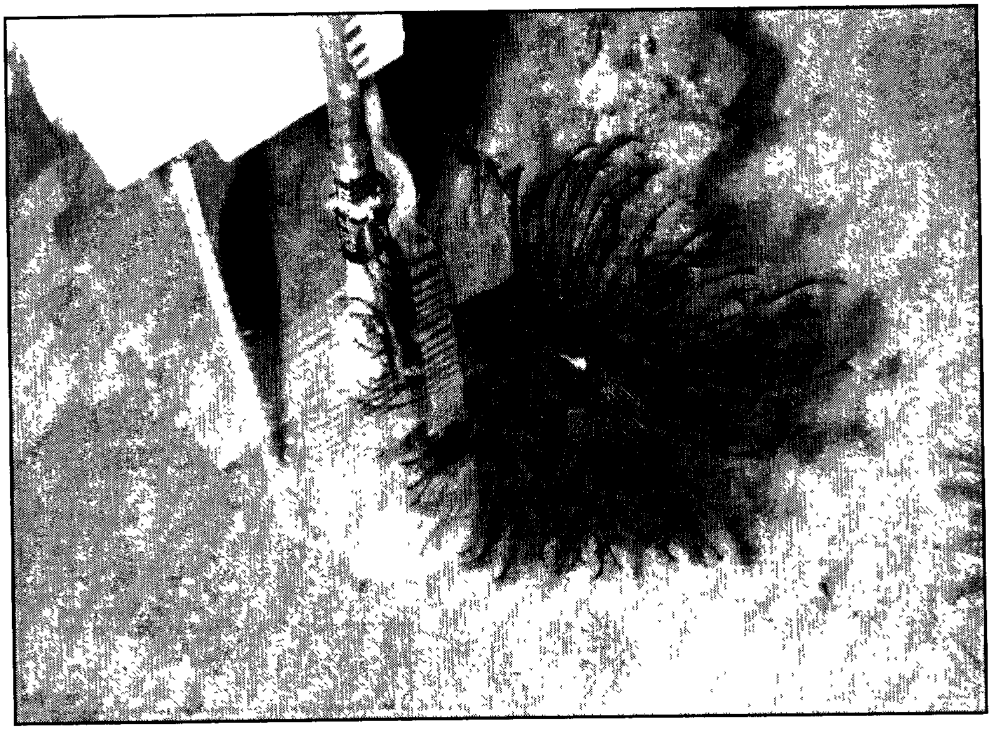
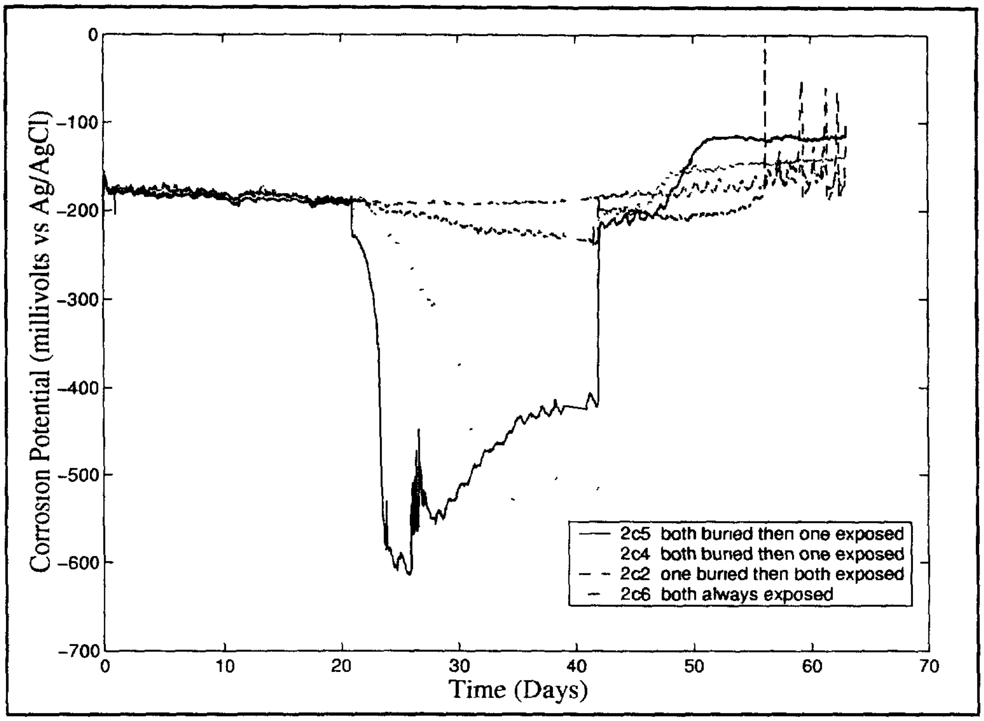


- General arrangement for measuring galvanic corrosion. In the above photograph, fecal matter from a sabellid worm (Eudistylia vancouveri) can be seen to be contributing to the organic debris on the bottom of the tank.




- As observed during the polarization resistance measurements, there was a marked shift in the corrosion potential for the two pairs of specimens for which both members of the pair had been lowered into the debris between Day 21 and Day 42. No such dramatic shift was observed for any of the three pairs in which only one specimen was lowered into the debris or for the control. The sharp spikes in the potential for specimen 2c2 (dotted line) after Day 56 were caused by a sea cucumber (Eupentacta quinquesemita) crawling up and down the reference electrode.

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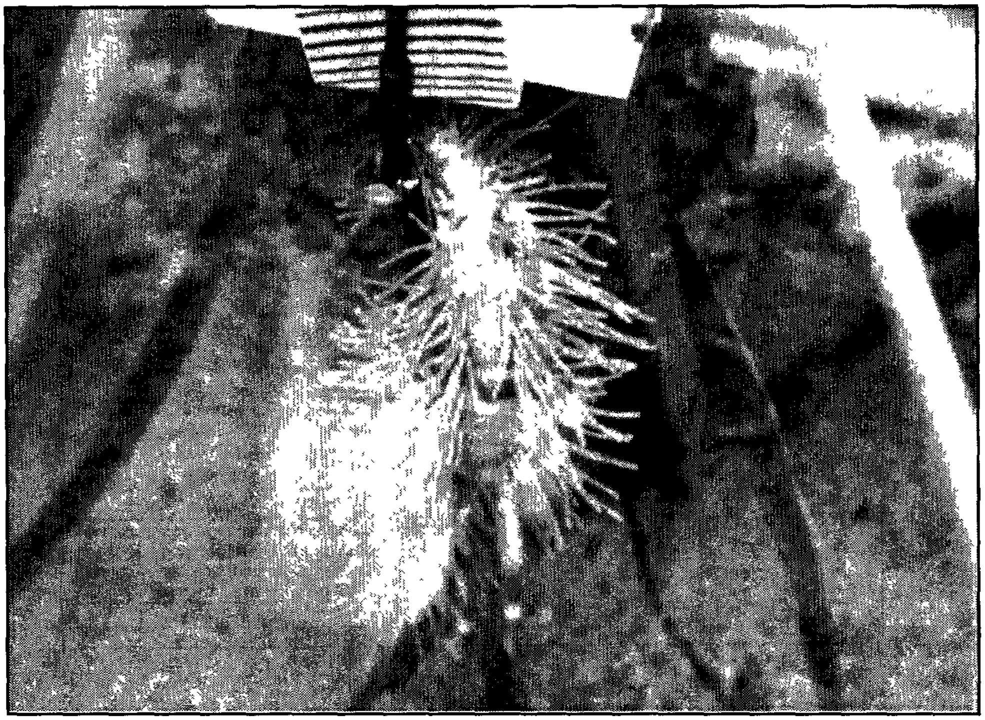
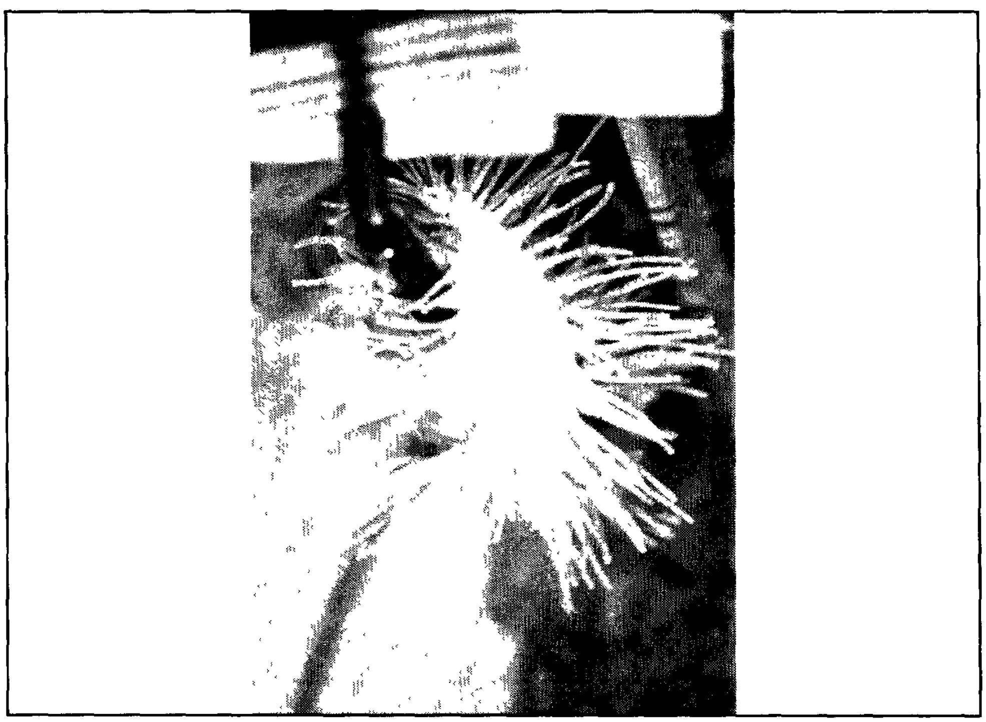
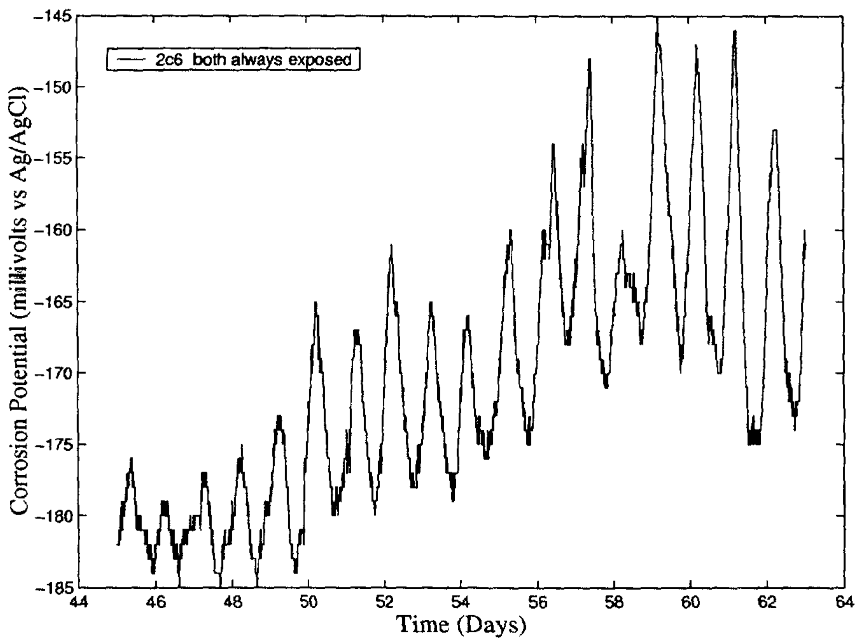
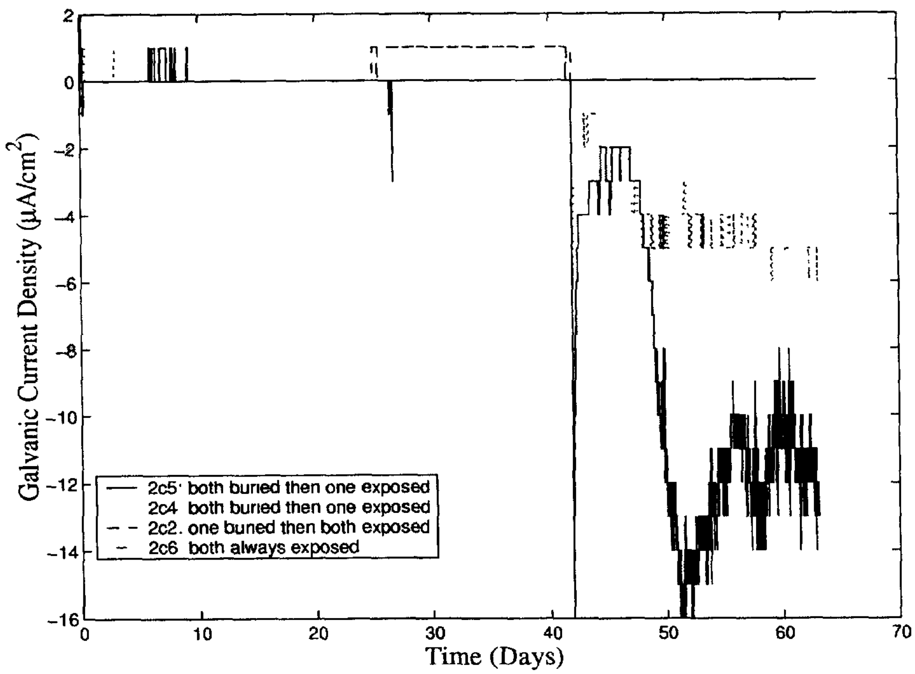







- Blow up of the region of the previous graph between Day 45 and Day 63 for the control cell (2c6). The daily variation is presumed to be caused by variations in the oxygen concentration as a function of biological activity.




- Substantial galvanic current was observed for the two pairs of specimens in which both members of the pair had been buried in the organic debris (2c4 and 2c5). This current was observed as soon as one member of each pair was lifted back into the flowing sea water and persisted throughout the remainder of the experiment. The direction of current was determined to be such that the specimen that remained buried in the sediment suffered accelerated corrosion. This conclusion was supported by the fact that the specimens in these pairs that were lifted back into the sea water were rapidly fouled, indicating that the cathodic protection resulting from the galvanic current prevented the release of copper ions, which have biocidal properties, from these specimens

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# CONCLUSIONS

- Exposure to decaying organic matter results in high corrosion rates after re-exposure to clean sea water. Under conditions of this experiment, repair of protective films was slower than initial film formation and not complete after 6 weeks.
- Conditions can be created in which high galvanic corrosion rates can occur for Cu-Ni under organic debris.

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# CONCLUSIONS

- Pitting may be a continuing problem in some systems on HALIFAX-class ships.
- TO AVOID PROBLEMS IN FUTURE SHIP CONSTRUCTION:
  - Maintain flow rate above 0.9 m/sec (macro-fouling organisms have difficulty attaching).
  - Flush, drain and blow dry systems during periods of shutdown.

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