the steel pipe before forming the plastic flange face. This is done in order to minimize the restrictive forces[3] that might develop in the plastic as a result of manufacturing procedures and techniques.

In this light the design temperature of certain types of plastic lined pipe must be examined critically in relation to that recommended by the manufacturer and further, services involving even limited thermal cycling should be avoided. It is apparent that PLP manufacturers have not been aware of this type of problem in the past and have lacked sufficient data to adequately pinpoint possible problem areas.

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Sea Water Corrosion of 90-10 and 70-30 Cu-Ni: 14 Year Exposures*

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Fourteen year data for 90-10 and 70-30 cupronickel alloys exposed in sea water at the F. L. LaQue Corrosion Laboratory, Wrightsville Beach, North Carolina are reported. Corrosion rates for both alloys in quiet and flowing as well as in the tidal zone tended to become linear after the first 4 years' exposure. Initially, corrosion rates for 90-10 tended to be much higher in flowing than in either quiet or tidal zone exposures, but at 14 years, rates in all environments were about the same, 0.05 mils per year. Similarly, 70-30 had high initial rates in flowing water, but at 14 years, rates were about the same for all three exposures, 0.03 to 0.08 mils per year.

THE Cu-Ni ALLOYS are becoming increasingly more important in marine engineering systems.[1,2] This is principally due to their good corrosion resistance, ductility, weldability, useful resistance to fouling, and general immunity from stress corrosion cracking in marine environments.

The complete solid solubility of copper and nickel results in a metallurgically *simple* system with an essentially homogeneous structure, and corresponding freedom from corrosion problems associated with heterogeneous alloys, *e.g.,* pitting, stress corrosion cracking, etc.

The alloy compositions in use today were developed over a number of years, with research efforts concentrating on the effects of iron additions.[3-6] These studies confirmed the beneficial effects of dissolved iron in the copper-nickel alloys.

Previous long-term corrosion data for 90-10 and 70-30 Cu-Ni were presented by May and Weldon,[7] Lennox, *et al,*[8] and Reinhart,[9] with all of these being less than 3 years' total exposure. Some 7 year corrosion data were presented by Anderson and Efird,[10] but treatment was not extensive.

Experimental Procedure

Tests were conducted at the Francis L. LaQue Corrosion Laboratory, Wrightsville Beach, North Carolina. The characteristics of sea water at this site are given in Table 1.

TABLE 1 — Characteristics of Sea Water at the Francis L. LaQue Corrosion Laboratory, Wrightsville Beach, North Carolina

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	0.015	PO_4	0.01
Fe	0.001	F	1.5
Zn	0.012	Br	61
		I	0.16

Hardness ($CaCO_3$) 5970 mg/l
Dissolved Solids 38,255 mg/l

Multiple specimens of 90-10 Cu-Ni and 70-30 Cu-Ni [4 x 6 x 1/4 inch (10 x 15 x 0.6 cm)] were used in this investigation with compositions and mechanical properties given in Table 2. Specimens were cut from a single plate of each alloy, and identified by both stencil and notch code to assure positive identification after exposure. The materials were cleaned before exposure by scrubbing with a pumice slurry, rinsing in distilled water, air-drying, and then weighed.

The specimens were exposed in three locations: (1) quiet sea water, (2) flowing sea water, and (3) the tidal zone. The specimens exposed in quiet sea water and the tidal zone were mounted vertically on Monel alloy 400 racks using porcelain insulators, and suspended beneath the laboratory wharf at appropriate levels. The

*Submitted for publication April, 1974.

TABLE 2 – Properties of the Alloys Tested

Alloy	Composition, % Cu	Ni	Fe	Mn	Zn	Pb
90-10 Cu-Ni	Bal	10.21	1.74	0.29	<0.10	<0.02
70-30 Cu-Ni	Bal	30.68	0.61	0.45	0.05	0.01

Alloy	Mechanical Properties: Yield Strength ksi	Yield Strength MN/m^2	Tensile Strength ksi	Tensile Strength MN/m^2	Elongation in 2 Inches
90-10 Cu-Ni	29.6	290	45.9	316	42%
70-30 Cu-Ni	32.4	318	58.7	404	43%

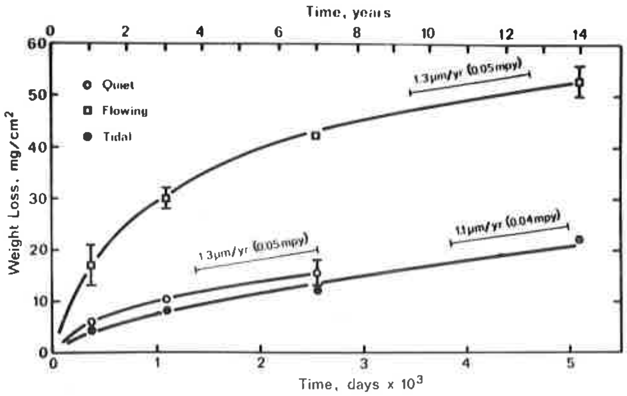

FIGURE 1 – Chronogravimetric curves for 90-10 Cu-Ni in quiet, flowing, and tidal zone sea water.

depth of immersion for the quiet sea water rack ranged from 2 to 6 feet depending upon the tide, while the tidal zone rack was alternately immersed with each changing tide. Specimens for exposure in flowing sea water were mounted horizontally on racks constructed of 1/4 inch (6 mm) wide Micarta[(1)] strips. This exposure was in a covered trough designed to give a constant sea water velocity of 2 fps (0.6 m/s) past the specimens. Removals were made after 1, 3, 7, and 14 year exposures in all 3 locations.

After removal, all specimens were cleaned in 10% sulfuric acid, rinsed in distilled water, and air dried. Measurements of weight loss and depth of localized attack were made on all samples and corrosion rates calculated.

Results and Discussion

Corrosion Resistance

Corrosion data for 90-10 Cu-Ni in quiet sea water, flowing sea water, and the tidal zone are given in Figure 1 as chronogravimetric curves (weight loss vs exposure time). The initial weight loss in flowing sea water is much higher than the other two exposures, reflecting a lower rate of protective film formation under these highly aerated and somewhat turbulent flow conditions. However, it should be noted that after long exposure times, the corrosion rates for all 3 zones are similar. Unfortunately, the 14 year panels of 90-10 Cu-Ni in quiet sea water were lost; however, 7 year data for this exposure are available. The 14 year corrosion rates for 90-10 Cu-Ni, taken as the slope of the chronogravimetric curves, are 1.3 μm/yr (0.05 mpy) in flowing sea water and 1.1 μm/yr (0.04 mpy) in the tidal zone. Of specific interest is the time required for the corrosion rate to become linear. For 90-10 Cu-Ni, this occurs after approximately 4 years' exposure in quiet sea water and 8 years' exposure in the tidal zone. It is still decreasing and has not stabilized after 14 years' exposure in flowing sea water. This change in

[(1)] Registered tradename, Conroy and Knowlton, Inc., Los Angeles, California.

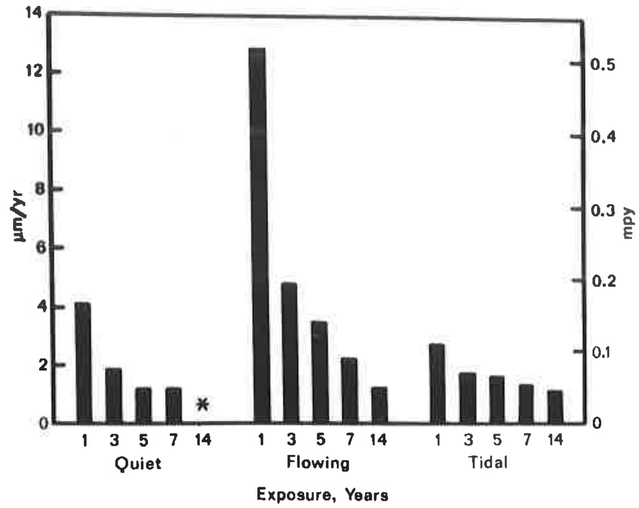

FIGURE 2 – The change in corrosion rate with time for 90-10 Cu-Ni in quiet, flowing, and tidal zone sea water. Rates calculated from the slope of the chronogravimetric curve.

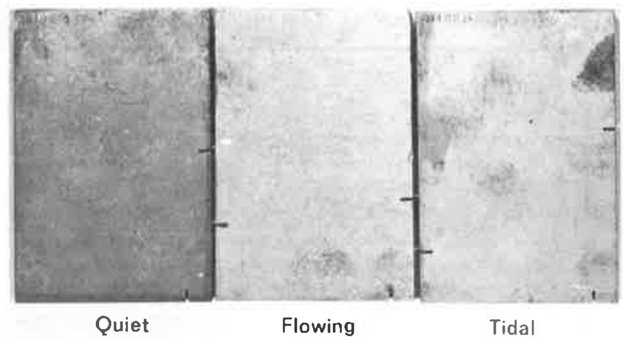

FIGURE 3 – 90-10 Cu-Ni panels after 7 years' exposure in quiet sea water and 14 years' exposure in flowing and tidal zone sea water.

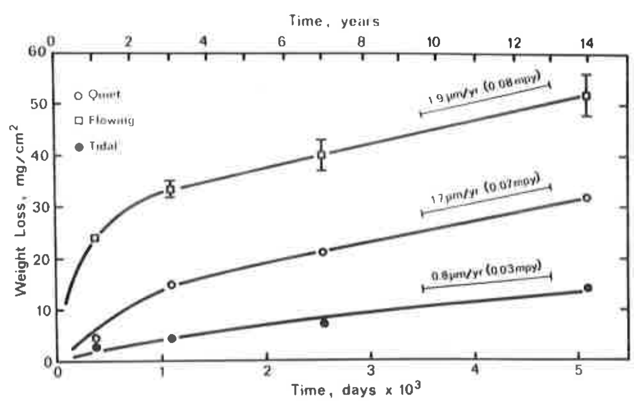

FIGURE 4 – Chronogravimetric curves for 70-30 Cu-Ni in quiet, flowing, and tidal zone sea water.

corrosion rate with time, taken from the curves, is shown graphically in Figure 2. The appearance of the long-term 90-10 copper-nickel exposure panels, after cleaning, is shown in Figure 3. Of particular note is the lack of localized attack on the samples after these long exposure periods.

Corrosion data for 70-30 copper-nickel in quiet, flowing, and tidal sea water are shown in Figure 4. After 14 years' exposure, the

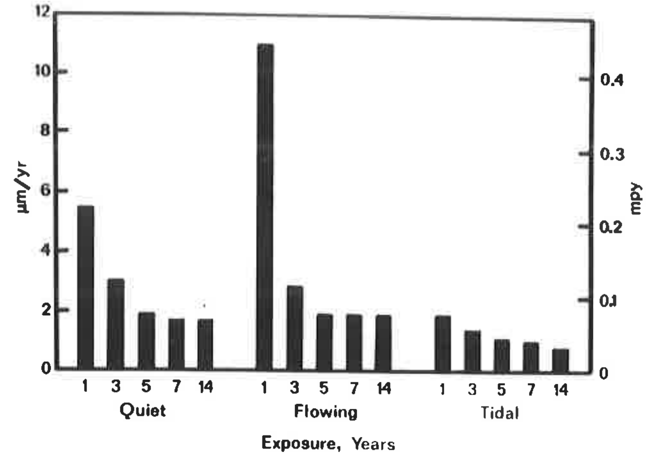

FIGURE 5 — The change in corrosion rate with time for 70-30 Cu-Ni in quiet, flowing, and tidal zone sea water. Rates calculated from the slope of the chronogravimetric curve.

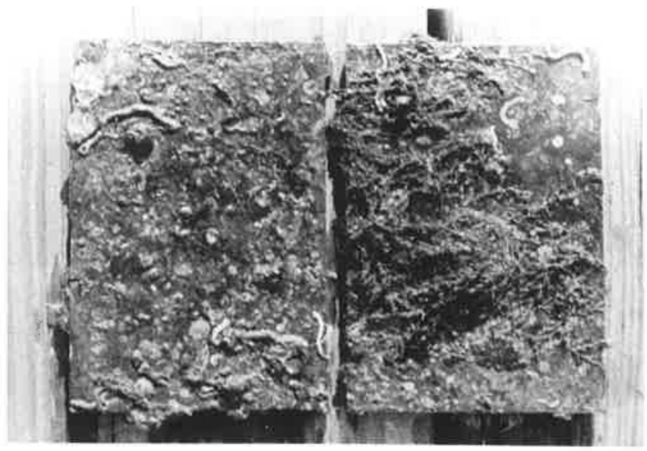

FIGURE 8 — 70-30 Cu-Ni after 14 years' exposure in quiet sea water before cleaning. Light fouling has occurred consisting of anomia, serpula, crisia bryozoa, and barnacles.

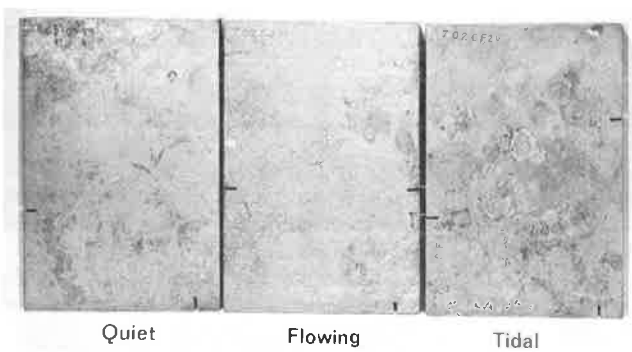

FIGURE 6 — 70-30 Cu-Ni panels after 14 years' exposure in quiet, flowing, and tidal zone sea water.

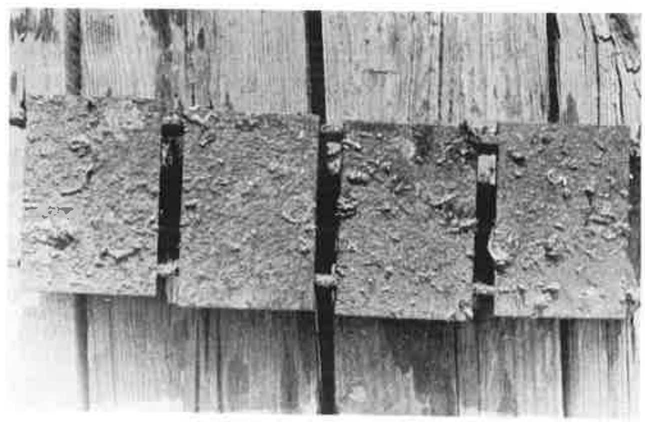

FIGURE 9 — 90-10 Cu-Ni (left 2 panels) and 70-30 Cu-Ni (right 2 panels) after 14 years' exposure in flowing sea water before cleaning. Very light fouling consisting of serupla, anomia, and small barnacles has occurred.

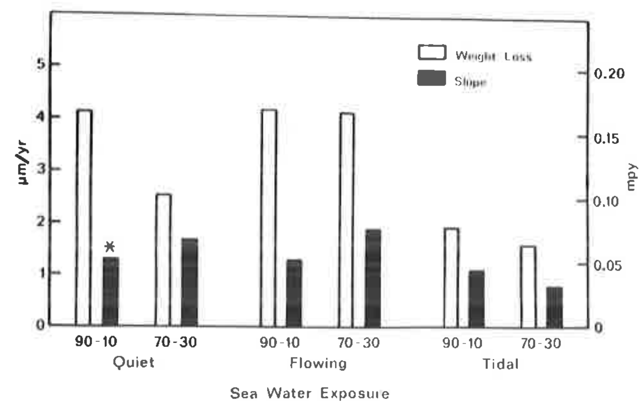

FIGURE 7 — Fourteen years' corrosion rate data.

corrosion rate of 70-30 Cu-Ni, taken from the slope of the curve, is 1.7 μm/yr (0.07 mpy) for quiet sea water, 1.9 μm/yr (0.08 mpy) for flowing sea water, and 0.8 μm/yr (0.03 mpy) for tidal zone exposures. Stabilization of the corrosion rate occurred after approximately 14 years' exposure in quiet sea water and flowing sea water, but is still decreasing slightly after 14 years' tidal zone exposure. This is shown diagrammatically in Figure 5. The appearance of 70-30 Cu-Ni samples after 14 years' exposure in all 3 zones is shown in Figure 6. There was no significant localized attack.

The corrosion rates after 14 years for 90-10 and 70-30 Cu-Ni in quiet, flowing, and tidal zone sea water are compared in Figure 7. Comparison is also made between the corrosion rate determined from the weight loss measurements (average corrosion rate over the total exposure period) and as determined from the slope of the chronogravimetric curve (the corrosion rate at a specific point in time). The greatest difference in these two methods of corrosion rate determination occurs when the initial weight loss is very high, as was observed in these flowing sea water exposures. Thus, while the steady state corrosion rates are equal, and in some cases less in flowing sea water than in quiet sea water or tidal zone exposures, the corrosion rate taken from total weight loss measurements is considerably higher. The steady state values calculated from the chronogravimetric curves are more applicable to accurately predict metal loss during continuing exposures.

Fouling Resistance

Of special interest, particularly due to the low corrosion rates observed after long time exposure, was the condition of the specimens on removal with respect to fouling. Uncleaned samples of 70-30 Cu-Ni exposed 14 years in quiet sea water are shown in Figure 8. The 90-10 Cu-Ni samples were unfortunately lose. Even on the 70-30 Cu-Ni samples, however, fouling is minimal after 14 years' quiet sea water exposure, consisting of serpula, anomia, small barnacles, and crisia bryozoa.

The as-removed condition of both 90-10 and 70-30 Cu-Ni samples after exposure in flowing sea water for 14 years is shown in Figure 9. Here again fouling attachment is minimal with barnacles,

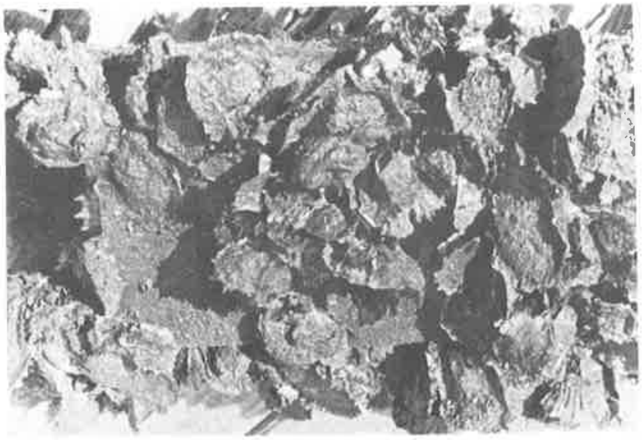

FIGURE 10 — 90-10 Cu-Ni (left) and 70-30 Cu-Ni (right) after 14 years' exposure in the tidal zone, before removal from the exposure rack, showing heavy oyster growth.

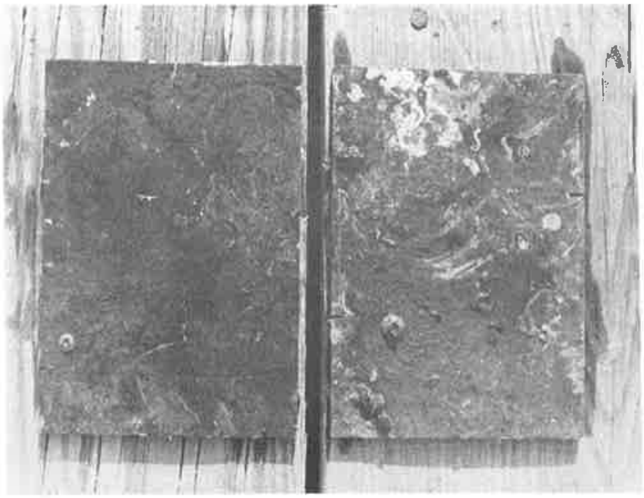

FIGURE 11 — Panels in Figure 10 after removal from the rack, before cleaning. The 90-10 Cu-Ni (left) has one barnacle attached, with no evidence of oyster attachment. The 70-30 Cu-Ni (right) has several small barnacles and mussels attached, and evidence of some oyster attachment.

anomia, and some serpula present, although none developed to significant size.

The fouling condition of 90-10 and 70-30 Cu-Ni after 14 years' tidal zone exposure is shown in Figures 10 and 11. In Figure 10, the samples, before being removed from the exposure racks, show a great deal of oyster fouling. However, after removal from the racks (Figure 11), it can be seen that most of the oysters are not attached but had bridged over from the Monel alloy 400 support racks. Other fouling consists of small serpulids and barnacles. The differences in the fouling communities which developed in the 3 exposure conditions reflect abilities of specific organisms to adapt to natural ecological variables, particularly intermittent versus continuous immersion and the presence or absence of sunlight.

Conclusions

1. The measured corrosion rates of 90-10 Cu-Ni are 1.3 μm/yr (0.05 mpy) after 7 years' exposure in quiet sea water, 1.3 μm/yr (0.05 mpy) after 14 years' exposure in flowing sea water, and 1.1 μm/yr (0.04 mpy) after 14 years' exposure in the tidal zone.
2. Stabilization of the corrosion rate for 90-10 Cu-Ni occurs after approximately 4 years' exposure in quiet sea water, and 8 years' exposure in the tidal zone, and is still decreasing after 14 years' exposure in flowing sea water.
3. The measured corrosion rates for 70-30 Cu-Ni after 14 year exposures are 1.7 μm/yr (0.07 mpy) in quiet sea water, 1.9 μm/yr (0.08 mpy) in flowing sea water, and 0.8 μm/yr (0.03 mpy) in the tidal zone.
4. Stabilization of the corrosion rate for 70-30 Cu-Ni occurs after approximately 4 years' exposure in quiet sea water and flowing sea water, and is still decreasing after 14 years' tidal zone exposure.
5. The initial corrosion rate in flowing sea water for both 90-10 and 70-30 Cu-Ni is higher than for exposures in quiet sea water and the tidal zone, but stabilizes at equally low values after long exposure times.
6. The use of the slope of the chronogravimetric curve provides more useful corrosion rate data than the total weight loss method, particularly where the initial weight loss is high followed by significant decrease in the rate of weight loss.
7. 90-10 and 70-30 Cu-Ni continue to provide useful fouling resistance after 14 years' exposure in quiet, flowing, and tidal zone sea water.

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