NRL Report 6592

Corrosion of Metals in Tropical Environments

Part 8 - Nickel and Nickel-Copper Alloys - Sixteen Years' Exposure

October 4, 1967

NAVAL RESEARCH LABORATORY
Washington, D.C.

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"Corrosion of Metals in Tropical Environments, Part 2 – Atmospheric Corrosion of Ten Structural Steels," C. R. Southwell, B. W. Forgeson, and A. L. Alexander, NRL Report 5002, Dec. 1957

"Corrosion of Metals in Tropical Environments, Part 3 – Underwater Corrosion of Ten Structural Steels," B. W. Forgeson, C. R. Southwell, and A. L. Alexander, NRL Report 5153, Aug. 1958

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"Corrosion of Metals in Tropical Environments, Part 5 – Stainless Steels," A. L. Alexander, C. R. Southwell, and B. W. Forgeson, NRL Report 5517, Sept. 1960

"Corrosion of Metals in Tropical Environments, Part 6 – Aluminum and Magnesium," C. R. Southwell, C. W. Hummer, and A. L. Alexander, NRL Report 6105, Dec. 1964

"Corrosion of Metals in Tropical Environments, Part 7 – Copper and Copper Alloys – Sixteen Years' Exposure," C. R. Southwell, C. W. Hummer, Jr., and A. L. Alexander, NRL Report 6452, Oct. 1966

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Part 8 - Nickel and Nickel-Copper Alloys - Sixteen Years' Exposure

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Chemistry Division

October 4, 1967

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ABSTRACT

Corrosion of nickel and nickel-copper alloys in five natural tropical environments is reported for exposure periods of 1, 2, 4, 8, and 16 years. Data collected include weight loss, pitting, change in tensile strength of simple plates, and weight loss of galvanic couples. Corrosion in the tropics is compared with available exposure results from temperate latitudes in the United States, and generally the tropical corrosion was appreciably higher. The weight-loss-vs-time curves are normally curvilinear relations but considerable variation in the direction and magnitude of the curvature was observed for the different metals and environments. With respect to pitting, the high nickel alloys developed severe early pitting under sea water. However, the initial high penetration rates leveled off to very low rates after the first 1 to 2 years' exposure. Comparison under tropical sea water of monel and copper-nickel with various other nonferrous metals shows copper-nickel with comparatively high corrosion resistance, but monel with the lowest sea-water resistance of the group. Galvanic corrosion results show the long-term efficiency of carbon steel anodes in cathodically protecting nickel-copper alloys in sea water. Additional galvanic data reveal that considerable anodic corrosion can be induced in a normally sea-resistant metal if coupled with certain nickel alloys. The nickel metals were highly resistant to corrosion in the tropical atmospheres. There was no measurable pitting in these terrestrial exposures and only small weight losses. The losses that were measured though showed increasing resistance of the metals with increasing nickel content. Since tropical corrosion is near the upper limit of corrosiveness of natural environments, these long-term results should afford safe, practical information for design and protection of structures in all latitudes.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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CORROSION OF METALS IN TROPICAL ENVIRONMENTS

PART 8 - NICKEL AND NICKEL-COPPER ALLOYS - SIXTEEN YEARS' EXPOSURE

INTRODUCTION

This report is the eighth in a series describing results of a comprehensive environmental corrosion investigation which was initiated in 1947 in the Panama Canal Zone. In the complete study, 52 metals and alloys were exposed to five different tropical environments for 16 years. Both single plates and bimetallic couples were included, and sufficient replicates of each were exposed to permit removal of duplicate samples at intervals of 1, 2, 4, 8, and 16 years. More than 13,000 individual pieces were exposed. Earlier reports (1-5) were based on data from the first 8 years of exposure and were concerned with the more rapidly corroded ferrous metals. The first of two subsequent reports included 16-year data on the light metals (6), and the second described the results with wrought-copper alloys (7). The initial report in the series (1) contains detailed information on the program background and test procedures.

From earliest times, nickel has been used in alloys with copper, but the pure metal was not known until Cronstedt isolated and identified it in 1751. In the present century, nickel has become an increasingly important structural metal. Its principal uses are as alloying additions to iron and copper, but ever-increasing amounts are being used as pure nickel and to produce high nickel alloys. From 1950 to 1960 the annual world production of nickel more than doubled to a total exceeding 300,000 tons (8). Future needs of the hydrospace age will, in all probability, assure a continued and accelerating demand for nickel and its alloys.

METALS AND METHODS

The metals for which 16-year-exposure results are presented in this report include nickel, cold-rolled monel, hot-rolled monel, 70-30 copper-nickel, nickel-silver, and copper. Comparative data in sea water is also included for 5%-aluminum bronze, 6061T aluminum, sheet lead, and commercially pure zinc. Complete chemical compositions and physical properties of these metals are given in Tables A1 and A2 in the Appendix.

Geographical locations and photographs of the test sites are shown in Fig. 1. Immersion studies were made from two piers, one a tropical fresh water site in Gatun Lake (Fig. 1c) and the other for marine immersion in the Pacific Ocean off the Fort Amador causeway, about 1-1/2 miles beyond the natural shoreline (Fig. 1d). The ocean exposures were made at two elevations 14 feet apart, the upper rack at half-tide level and the lower just below minimum low tide. At this ocean pier the average water depth is about 40 feet, the average tidal range is 13 feet, and maximum currents measure less than 1 ft/sec. A marine atmospheric site was located on the rooftop of the Washington Hotel by the shore of Limón Bay, Caribbean Sea, at an elevation of 55 ft above sea level (Fig. 1a). There the prevailing wind is from the sea, and offshore breakers generally provide a salt-bearing atmosphere. The inland atmospheric site was near the Miraflores locks on the Pacific side of the Canal Zone (Fig. 1b), where the prevailing wind is from the land. Exposure conditions at this location can be classified best as tropical semirural. Analyses of the test environments and a summary of Canal Zone climatic conditions during a 20-year period can be found in Tables A3 and A4 and Fig. A1 in the Appendix.

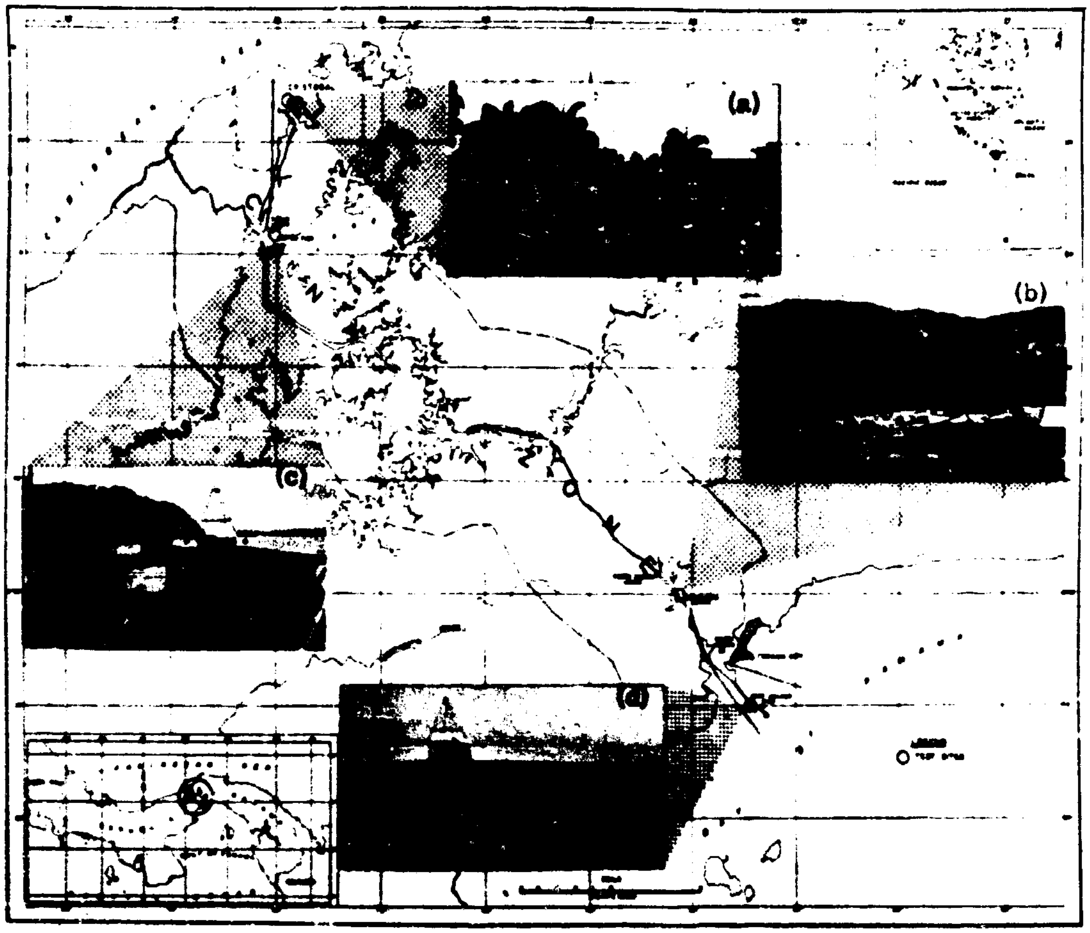


Fig. 1 - Location of test sites

Weight loss, pit depths, and dimensional changes were determined by standard procedures. Loss in tensile strength was measured by comparing the average of three to seven tensile coupons cut from the exposed plates with the average of three to 15 control samples retained in dry storage in the laboratory during the exposure period.

GENERAL RESULTS

Comprehensive Tabulation

Table 1 presents a comprehensive summary of all results for the six nickel-copper metals, evaluated for 1, 2, 4, 8, and 16 years' exposure in five tropical environments. To conform to general corrosion terminology, weight loss is shown in grams per square decimeter, and penetration values are shown in mils (0.001 in.). The average penetration is calculated from the weight loss and specific gravity, and in effect is a volumetric loss. Depth of pitting is shown as the average of the 20 deepest pits, calculated from the five deepest on both sides of duplicate panels. The maximum penetration on any of the four surfaces is recorded in the table as the deepest pit. Percent loss in tensile strength is shown for the 16-year samples. Si[illegible] is a difference in sample thickness between the atmospheric sheets (1/16 in.) [illegible] mersion plates (1/4 in.), the atmospheric

Table 1
Comprehensive Tabulation of Corrosion Damage for Nickel-Copper Alloys and Comparison Metals

Symbol	Metal	Exposure	Weight Loss (g dm⁻²)					Average Penetration (mils)					Depth of Pitting (mils)										Tensile Strength Loss (%)†	Type Corrosion Attack‡
													Av 20 Deepest*					Deepest Penetration						
			1 yr	2 yr	4 yr	8 yr	16 yr	1 yr	2 yr	4 yr	8 yr	16 yr	1 yr	2 yr	4 yr	8 yr	16 yr	1 yr	2 yr	4 yr	8 yr	16 yr	16 yr	16 yr
A	Nickel	Immersion																						
	99%	Sea water	5.40	7.55	11.8	28.4	43.4	2.40	3.35	5.22	12.6	19.3	125	143	121	120	142	245	248	248	245	249	9	jqhk
		Mean tide	0.73	1.30	2.99	5.77	9.89	0.35	0.58	1.33	2.56	4.39	(0)	37	47	65	61	0	58	105	103	121	2	jq
		Fresh wtr	0.00	0.00	0.00	0.03	0.08	0.00	0.00	0.00	0.01	0.04	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	<1	k
		Atmospheric																						
		Marine	0.02	0.03	0.06	0.13	0.26	0.01	0.02	0.03	0.06	0.12	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	0	k
		Inland	0.01	0.04	0.06	0.09	0.21	0.01	0.02	0.03	0.04	0.09	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	0	k
B	Monel	Immersion																						
	(cold	Sea water	3.67	5.14	9.38	14.2	19.5	1.64	2.29	4.18	6.32	6.66	17	32	27	40	33	42	56	41	55	55	8	rj
	rolled)	Mean tide	0.23	0.30	1.11	3.02	6.00	0.10	0.22	0.50	1.34	2.67	(0)	(0)	(0)	14	14	0	0	00	24	21	2	jr
	67 Ni-	Fresh wtr	0.00	0.20	0.03	0.25	1.36	0.00	0.09	0.01	0.11	0.61	8(1)	12(10)	19(15)	29(8)	30(11)	8	16	27	53	52	<1	r
	30 Cu-	Atmospheric																						
	1.8 Fe	Marine	0.10	0.08	0.14	0.28	0.49	0.04	0.04	0.07	0.12	0.22	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	2	ak
		Inland	0.02	0.05	0.06	0.14	0.30	0.01	0.03	0.04	0.06	0.13	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	1	ka
C	Monel	Immersion																						
	(hot	Sea water	4.68	5.46	9.05	14.40	18.72	2.09	2.44	4.05	6.44	8.37	43	40	53	50	56	90	61	82	68	80	-	rj
	rolled)	Mean tide	0.25	0.63	1.58	3.09	5.74	0.11	0.28	0.71	1.38	2.57	(0)	(0)	16(15)	17	24	0	0	20	25	36	-	jr
	67 Ni-																							
	30 Cu-																							
	2.1 Fe																							
D	Copper-	Immersion																						
	nickel	Sea water	1.15	2.34	3.13	3.38	5.11	0.51	1.03	1.38	1.49	2.25	11(8)	12	24(10)	6(7)	7(14)	15	18	37	8	10	<1	jr
	30 Ni-	Mean tide	0.19	0.31	0.61	0.97	1.71	0.08	0.14	0.27	0.43	0.75	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	<1	ka
	69 Cu	Fresh wtr	0.36	0.60	1.20	2.18	2.96	0.17	0.28	0.53	0.96	1.31	(0)	(0	(0)	(0)	(0)	0	0	0	0	0	<1	k
		Atmospheric																						
		Marine	0.38	0.14	0.27	0.52	0.83	0.03	0.06	0.12	0.23	0.41	(0)	(0)	(0)	2(2)	(0)	0	0	0	0	0	1	ak
		Inland	0.34	0.11	0.18	0.30	0.62	0.02	0.05	0.08	0.13	0.27	(0)	(0)	(0)	3(1)	(0)	0	0	0	0	0	1	ak
E	Nickel	Atmospheric																						
	silver	Marine	0.09	0.15	0.28	0.49	0.83	0.04	0.06	0.12	0.22	0.37	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	0	ak
	18 Ni-	Inland	0.04	0.09	0.16	0.29	0.63	0.02	0.04	0.07	0.13	0.28	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	0	ak
	64 Cu																							
	17 Zn																							
F	Copper	Immersion																						
	99.9%	Sea water	2.74	5.03	5.95	12.1	13.6	1.21	2.22	2.62	5.33	6.02	27(15)	36(17)	16(11)	28	31	46	75	21	53	57	5	er
		Mean tide	1.67	1.85	4.30	2.45	2.99	0.65	0.82	1.90	1.08	1.32	9(2)	(0)	7(2)	10	(0)	11	0	8	23	0	1	er
		Fresh wtr	0.50	0.81	1.29	1.84	2.33	0.22	0.36	0.57	0.82	1.03	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	2	a
		Atmospheric																						
		Marine	0.37	0.52	0.86	1.29	1.73	0.17	0.23	0.38	0.57	0.77	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	4	a
		Inland	0.18	0.26	0.34	0.43	0.60	0.08	0.12	0.15	0.19	0.27	(0)	(0)	(0)	(0)	(0)	0	0	0	0	0	<1	a
		Immersion																						
G	Al-bronze	Sea water	0.39	0.75	1.25	1.58	2.62	0.19	0.36	0.60	0.76	1.26	(0)	(0)	(0)	14(3)	(0)	0	0	0	21	0	3	jk
H	6061 Al	Sea water	0.19	0.33	0.30	0.50	0.63	0.28	0.48	0.56	0.73	0.92	(0)	(0)	13(10)	23	14	0	0	32	49	79	<1	ja
J	Lead	Sea water	1.67	3.37	4.93	8.18	14.0	0.58	1.17	1.72	2.85	4.88	(0)	20	(0)	23	28	0	34	0	40	48	0	ajh
K	Zinc	Sea water	3.18	4.73	6.03	9.08	15.7	1.76	2.61	3.33	5.01	8.23	20(14)	36(17)	52	53	62	50	72	70	90	107	[illegible]	erq

*Numbers in parentheses indicate number of measurable pits when less than 20. A measurable pit is ·5 mils.
†Percent tensile losses are for samples of 1/4 in. thickness for immersion exposure and 1/16 in. thickness for atmospheric exposure.
‡Corrosion types are described in detail in the appendix to Part I (Ref. 1). Those referred to here are: a—uniform attack, e—local attack (uniformly distributed), r—local attack (randomly located), h—concentration cell, j—fouling contact, k—no visible attack, q—pitting (randomly distributed).

percent losses must be divided by 4 if direct comparison of atmospheric and immersion tensile results are desired. Visual ratings of corrosion attack shown in the last column of Table 1 were made according to standards described in the appendix to the first report of this series (1).

Comparison of Tropical Vs Temperate Climate Corrosion

A principal objective of the investigation was to compare corrosion damage in the tropics with corrosion losses reported for temperate climates. Unfortunately, there are few comparable data for corrosion of nonferrous metals in temperate waters. Published data are usually for a single-point short-period exposure. In Fig. 2, available data for nickel and monel from North Carolina (9), California (10,11) and Florida (11) have been plotted as bar graphs and compared to applicable portions of the tropical corrosion curves.

During continuous immersion in tropical sea water, nickel and nickel-copper (monel) were more rapidly corroded than in temperate latitudes. The greatest difference appeared

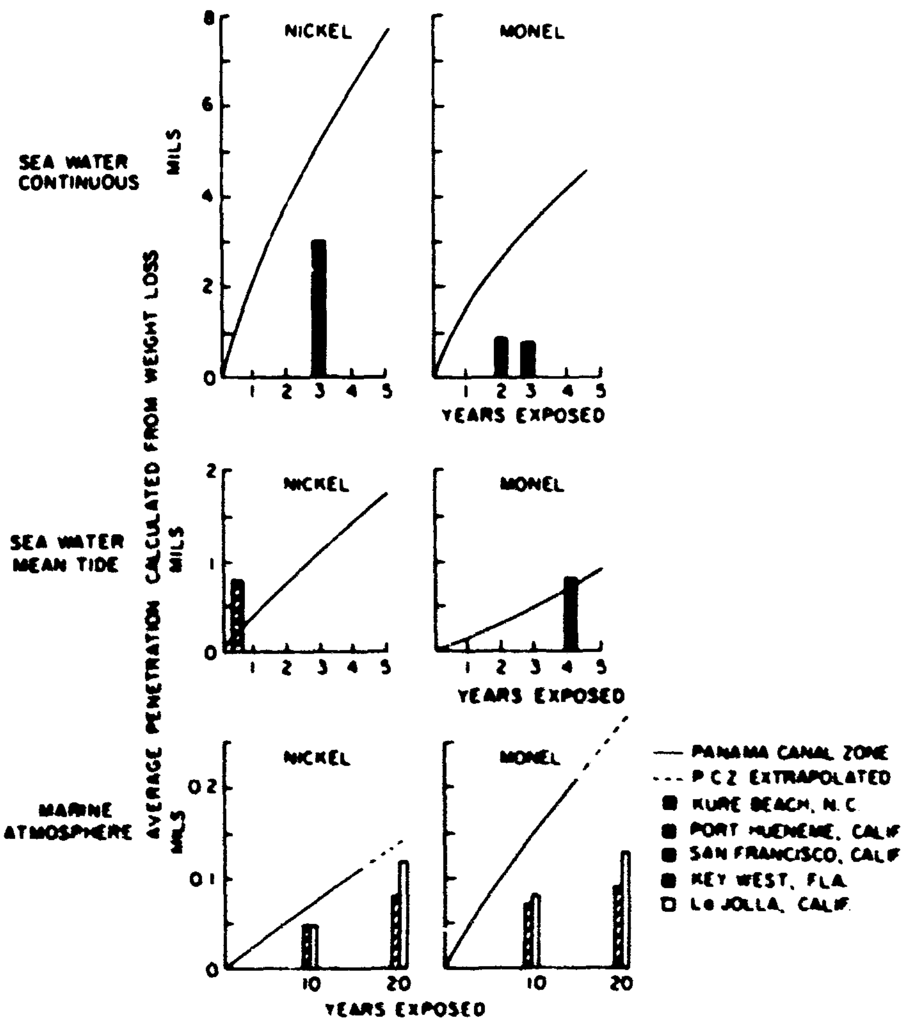


Fig. 2 - Comparison of corrosion in tropical and temperate climates

in the monel-corrosion losses at Kure Beach and in the Canal Zone. For the same period of exposure the loss in the Canal Zone was about 4 times as high as that at Kure Beach.

Losses at mean tide in the tropics were lower than those reported from temperate mean tide exposures. This agrees with results for other nonferrous metals that have been compared similarly at mean tide. Because of the greater tidal range and the calm seas on the Pacific side of Panama, exposure of the metals to the highly corrosive splash zone was of relatively short duration. This condition, combined with rinsing of the samples by tropical showers while exposed to the atmosphere during low tides and the rapid drying from tropical sunshine, probably accounts for the lower corrosion losses sustained by samples subjected to this environment.

Corrosion in the marine atmosphere in the tropics was appreciably higher than losses reported from the lower temperate zone at Key West, Fla., and La Jolla, Calif. These higher losses from the true tropics in Panama were as expected, but were probably caused principally by the high salinity and humidity of the Caribbean coastal atmosphere rather than by average temperature differentials. Ambler and Bain (12) and May (13) have reported the important influence of airborne salinity on metal corrosion in natural atmospheres. A prevailing high salinity at the Caribbean site and the generally high tropical humidity combined to provide ideal conditions for hygroscopic solution of positive salts on the metallic surfaces. Corrosion rates of high-nickel metals in this environment range from 1.3 to 2.5 times the comparable losses in the more temperate latitudes.

UNDERWATER CORROSION OF NICKEL-COPPER METALS

Fresh-water continuous immersion, sea-water continuous immersion, and sea-water mean-tide exposure are included in underwater corrosion. Weight-loss-vs-time curves and pitting-vs-time relations are given for four metals representing a wide ratio of nickel to copper content. In addition, for the two sea-water environments, a hot-rolled surface-finish monel was added. Thus, for monel a comparison between hot-rolled and cold-rolled surface finish in sea water is included in the data.

As a concession to general corrosion practice, mixed units (English-system mils and metric-system g/dm^2) are used to report the corrosion data. However, these concessions are not carried to the point of reporting results as time-averaged (secant) corrosion rates. Such rates are found frequently in the corrosion literature as mdd (milligrams/decimeter^2-day) or ipy (in./yr), but are considered by the authors to be very misleading, especially when based, as they often are, on short periods of exposure. Undoubtedly such published rates often will be accepted by engineers as implying a linear relation of corrosion with time and will be used to establish design criteria for enduring underwater structures. In this comprehensive study, one of the most recurrent conclusions is that corrosion does not generally proceed at a constant rate during the first years of exposure. With the slope of the corrosion curves rapidly changing in early periods, any exposure rate established from a single exposure period will be inherently inaccurate over most of the time scale.

Corrosion rates presented here are the final tangent or asymptotic rates. This value, coupled with the 16-yr corrosion loss, should provide a fairly accurate extrapolation for evaluation of long-term service life.

The first group of curves (Fig. 3) are for continuous immersion in Gatun Lake. In this tropical fresh water, corrosion losses for all four metals were very low, with the maximum 16-year weight loss of 3.1 g/dm^2 being measured on 70-30 copper-nickel. The low fresh-water losses are interesting, however, because of the considerable variation in corrosion rate changes. Copper shows a constantly decreasing rate of corrosion,

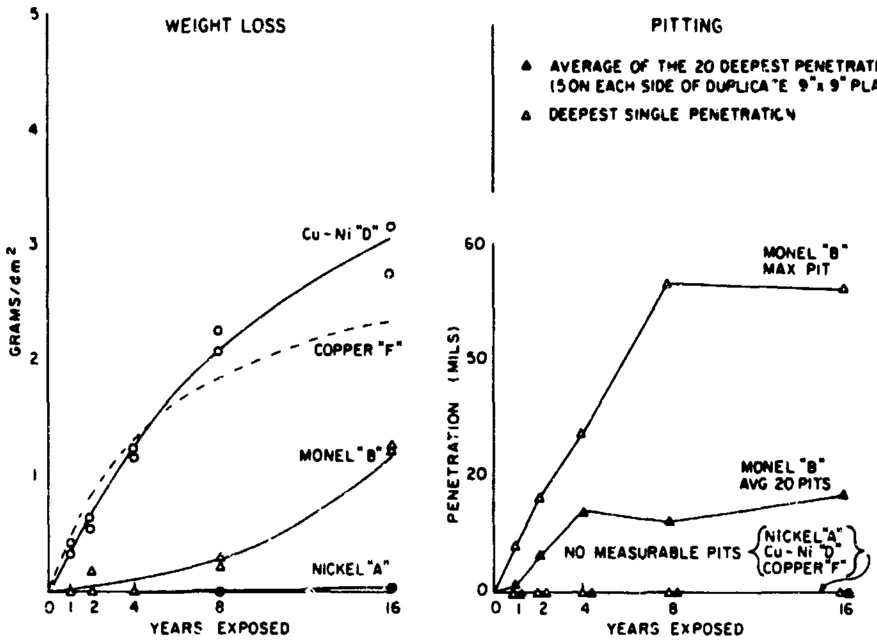


Fig. 3 - Weight loss and pitting as a function of time for nickel and nickel-copper alloys continuously immersed in tropical fresh water

resulting in a 16-year loss of 2.4 g/dm^2 and a final tangent rate of 0.04 g/dm^2-yr. The corrosion rate of copper-nickel also decreased with time but the rate of decrease was somewhat less than for copper, resulting in the slightly higher 16-year loss of 3.0 g/dm^2 and a final tangent rate of 0.11 g/dm^2-yr. Monel sustained very low weight losses during the early portions of the exposure period, which resulted in a lower 16-year loss of 1.2 g/dm^2, but the increasing corrosion rate revealed by the long-term data indicated a final rate of about 0.15 g/dm^2-yr. Pure nickel was practically unaffected by exposure to fresh water, showing a barely discernible weight loss after 16 years.

The pitting of these four metals is shown in the right-hand side of Fig. 3. In the tropical fresh water, nickel, copper, and copper-nickel remained free of measurable pits throughout the 16-year exposure. For monel, though, there was some pitting; the average 20 deepest pits had increased to a depth of 17 mils by 16 years. The progression of maximum pitting is also shown for monel. The deepest penetration measured during the 16 years was 52 mils. This maximum pit occurred on an 8-year panel. Straight line connection of points is used with all pitting data, because variation in pitting is greater than for weight loss, and smooth curves are not very practical.

All 16-year tensile losses are presented in Table 1. Results show there was no measurable reduction in strength for fresh-water-exposed nickel-copper metals. Evaluation of selective or intergranular corrosion was the primary reason for including tensile testing in the study. Analysis of all tensile results on the nickel-copper metals discloses that in no instance was the percent loss in tensile strength significantly greater than the percent reduction in average thickness calculated from weight loss. From this evidence it can be concluded that there was no measurable internal or selective attack on any of the nickel-copper metals for any of the five environments. Therefore no further reference to the tensile data will be made in the following discussions of marine and atmospheric corrosion.

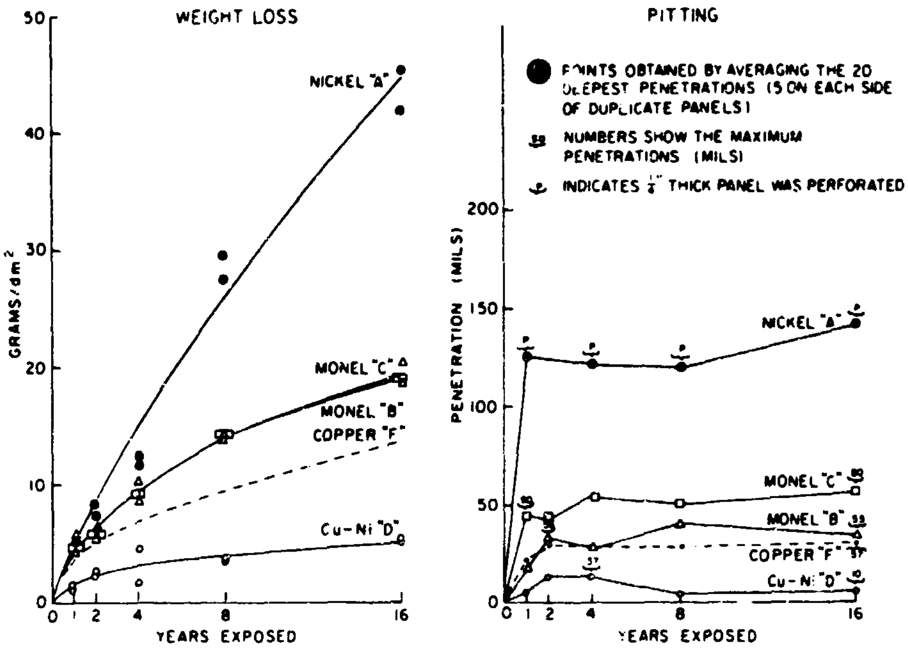


Fig. 4 - Weight loss and pitting as a function of time for nickel and nickel-copper alloys continuously immersed in tropical sea water

In Fig. 4 the progression of weight loss and pitting during 16 years' continuous immersion in tropical sea water are shown for the same nickel-copper metals. In addition, results with monel "C" are included. This metal is quite similar in composition to monel "B" but was hot-rolled finished, rather than cold-rolled. Weight losses of the metals subjected to continuous sea-water immersion show some rather surprising differences from the fresh-water results. The 70-30 copper-nickel, most heavily corroded of the metals in fresh water, was the least corroded in sea water; while the "A" nickel, the metal most resistant to fresh-water corrosion, was the most severely corroded in sea water. No doubt this reversal is to some extent due to the heavy marine fouling of Panama ocean water. The copper-nickel is less affected by fouling. Because of its high copper content it is somewhat resistant to fouling attachment, and even when fouled it did not develop deep underfouling pits. Corrosion weight loss at 16 years for copper-nickel in sea water was only 1.6 times higher than in fresh water. On the other hand, sea-water-corrosion loss of nickel at 16 years was about 20 times the loss sustained in fresh water. Weight loss of nickel was almost entirely the result of intensive pitting attack. Although the pits were fairly infrequent, those which did develop were large and deep. This deep pitting was most probably initiated in oxygen-deficient areas under marine fouling. In such areas the passivity of the nickel is interrupted, and a much more aggressive attack develops at the resulting anodic areas. Undercutting of the surface in established pits or on edges of the panels caused the bulk of the corrosion weight loss of nickel in sea water. Because of this concentrated localized attack the weight loss is of lesser significance for nickel than for the other metals which corrode more uniformly, but it is included to complete the data. The 16-year loss is 45 g/dm^2 and the final rate is 2.1 g/dm^2-yr.

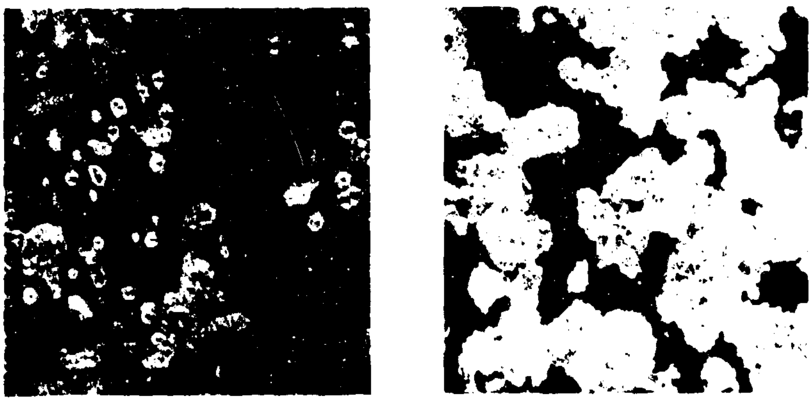
Sea water was about 5 times as corrosive to monel as fresh water. Weight-loss curves indicate a decreasing rate of corrosion throughout the exposure period, with a constant rate fairly well established within 8 years. No measurable difference could be found between cold-rolled and hot-rolled surface finishes. Weight-loss values for the two monels were closely grouped at each of the five time periods. Thus, monel, with 20 reliable weight-loss points, provides one of the best defined corrosion-time curves in the study. The slight separation at the end of the weight-loss curve in Fig. 4 is only for clarification and does not indicate any real difference. The 16-year loss for each monel is 20 g/dm^2, and the final corrosion rate is approximately 0.59 g/dm^2-yr.

Most of the corrosion of the monels seems to be attributable to pitting or local attack. As with nickel, some of these pits were probably initiated under marine fouling, although the fact that there was some pitting on the monel in fresh water leaves some doubt concerning the role of marine fouling in initiating these pits.

The pits that developed on monel in sea water were of quite a different character than the fast-perforating types found in nickel. During the first 1 to 2 years, penetration of the monels developed rapidly to an average depth of 35-45 mils, after which deepening of the pits ceased. During the remaining 14 years of exposure, no appreciable increase in depth of penetration of the metal occurred. This effect can be seen in the 20-pit average curves shown on the right side of Fig. 4. Numbers above the data points show the depth of deepest penetration at the time of occurrence; these also reached their maximum depth within the first 2 years of exposure. Although there was no appreciable difference in weight loss of the cold-rolled and hot-rolled finished monels, the pitting depth shows some advantage for the cold-rolled metal, which had a maximum penetration of 56 mils vs 90 mils for the hot-rolled finish.

Pitting of 70-30 copper-nickel was quite low in sea water, and similarly showed no tendency to increase in depth after the early exposure period. The maximum depths of penetration for this metal occurred at 4 years and measured 37 mils. Weight loss of copper-nickel also was very low, measuring only 5.3 g/dm^2 at 16 years with a final constant-loss rate of only 0.14 g/dm^2-yr.

The photographs in Fig. 5 show the change in character of corrosion of 69%-nickel monel between 1 year and 16 years of exposure. The 1× views of typical areas of the sample plates show rather clearly the type of corrosion to which this metal is subject. After 1 year a heavy pitting attack had developed at numerous points on the surface. The maximum depth measured at this time was 42 mils. The nonpitted areas of the plates were practically unattacked. At the end of 16 years these pits had deepened very little,



I YEAR EXPOSURE 16 YEARS EXPOSURE

Fig. 5 - Typical areas of nickel-copper (monel) panels after 1 year and 16 years of immersion in tropical sea water, showing changing character of pitting attack (1×)

the maximum depth being only 55 mils. However, they had broadened considerably in area, so that approximately 50% to 60% of the surface area had corroded. Thus, they no longer appear as pits but rather as wide shallow areas of local attack. Such pitting effects on nickel-copper (monel) may restrict this metal for service in thin sheets or as sheathing, but it should provide long-term service where adequate thickness is provided.

Weight-loss and pitting data from the sea-water mean-tide exposure are shown in Fig. 6. The weight-loss curves on the left show that after 16 years the metals appear in the same order of corrosion resistance as in continuous immersion. However, the general magnitude of 16-year loss at mean tide was only about 1/5 of that for continuous exposure.

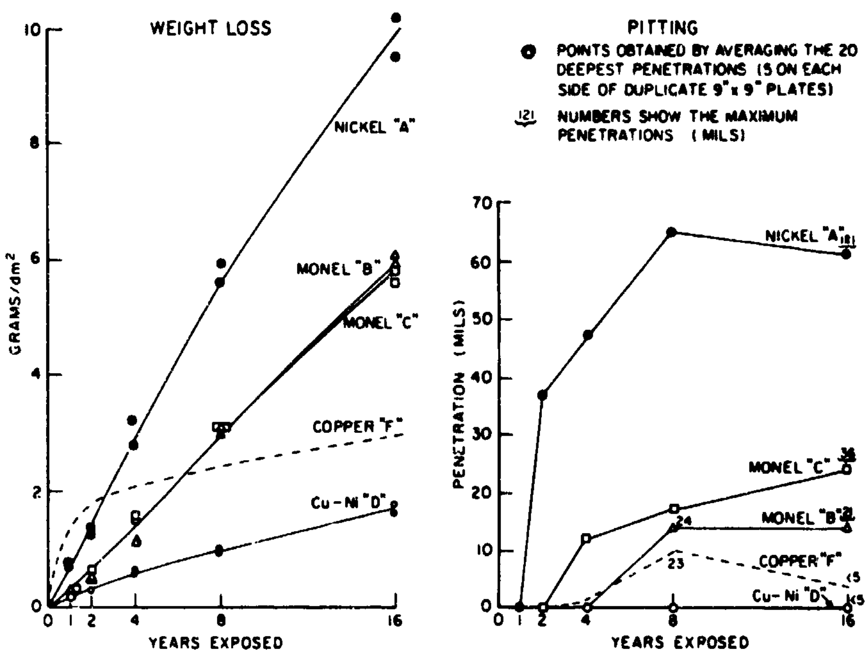


Fig. 6 - Corrosion of nickel and nickel-copper alloys exposed at mean tide elevation in tropical sea water

Hot-rolled and cold-rolled monel again showed no measurable difference in weight loss; the data are in such close agreement that one curve can be drawn to represent both metals.

These mean-tide curves most clearly exemplify the dangers inherent in extrapolating short-term or one-point corrosion rates to extended service. If, for example, a comparison between copper and monel had been made solely on the basis of the 1 or 2 years of exposure, a completely erroneous conclusion would have resulted. One-year secant rates would have shown copper as having only one-half the corrosion resistance of nickel, whereas the actual losses after 16 years were 10 g/dm^2 for nickel, and 3.0 g/dm^2 for copper. The final corrosion rates were 0.51 g/dm^2-yr for nickel vs 0.07 g/dm^2-yr for copper.

At mean tide the development of pitting in the nickel metals was considerably different than that resulting from continuous immersion in sea water. While most of the high nickel alloys in continuous immersion pitted rapidly during the first year or two, and then ceased pitting, a nearly opposite effect was found for nickel and monel at mean tide.

As can be seen in the right half of Fig. 6, no measurable pits developed on any of the metals during the first year. Pitting of the nickel was apparent after 1 year, but none appeared on the monels until after 2 or 4 years at mean tide. After these initial periods of resistance pitting commenced and progressed until, at 16 years, nickel "A," monel "C," and monel "B" had maximum pits of 121 mils, 36 mils, and 21 mils respectively. As with weight loss, short-term data on pitting would have been completely misleading.

Copper-nickel was almost immune to pitting at mean tide. There was no pit greater than 5 mils on this metal at any period.

Comparison of Nickel-Copper Alloys With Other Sea-Resistant Metals

With the current high interest in oceanography and undersea mining and construction, the need for comparative long-term corrosion data is becoming more apparent. Without such information, economical design of structures and machinery for undersea environments is practically impossible. The data given in Fig. 7 are presented for the specific purpose of supplying useful information on sea-resistant metals currently available from the undersea portion of this investigation. The six metals for which 16-year-corrosion curves and pitting data are given in the figure were selected from the 52-metal array of the complete study as representative of those most resistant to sea-water corrosion. When a number of metals of one class were exposed, e.g., ten copper alloys, the metal included in Fig. 7 is the most sea-water resistant of the group. Among the nickel alloys both 70-30 copper-nickel and 70-30 nickel-copper (monel "B") are included.

Since comparisons are made here between metals of widely divergent densities, the weight losses have been converted to average mils penetration; this permits evaluation on a comparable volumetric-loss basis.

Of the six metals compared, copper-nickel, 5%-aluminum bronze, and 6061T aluminum were superior on the basis of total metal lost. Their respective 16-year losses were 2.2, 1.3, and 0.92 average mils penetration, and the final constant corrosion rates were 0.07, 0.05, and 0.03 mil/yr. Lead was intermediate at 4.9 mils loss and 0.25 mil/yr final rate while zinc and monel had 8.5 and 8.8 mils average penetration and 0.41 and 0.30 mil/yr final rate. For periods beyond the tested 16 years, weight-loss rates combined with the pitting data presented in the upper box of Fig. 7 predict a relative order of long-term durability in which aluminum-bronze has the highest resistance by a slight margin, closely followed by 6061 aluminum and copper-nickel, and then, in order of decreasing resistance, lead, monel, and zinc.

The comparative position of monel "B" is somewhat surprising, since this metal is reputed to be highly resistant to sea-water corrosion. Zinc, on the other hand, is not normally considered outstanding in this respect. Yet, during the 16 years in the quiet sea water, monel was actually less resistant to corrosion (weight loss) than the commercial zinc and considerably less resistant than lead.

Galvanic Effects

Undoubtedly, the reputed resistance of monel to sea water is largely based on its very noble position in the galvanic series. Its potential in sea water is such that when coupled with other structural metals it is almost always the protected metal in the couple. For example, if a bronze propeller is attached to a monel shaft, the monel would be completely protected and would appear to be a highly resistant alloy. The propeller bronze, on the other hand, would be galvanically corroded at an accelerated rate and leave the impression that it is considerably less resistant to sea-water corrosion.

PITTING PENETRATION (MILS)						
METAL →	B	D	G	H	J	K
AVG 20 DEEPEST PITS *	40	12	< 5	23	28	62
DEEPEST PIT	56	37	21	79	48	107

* - FIVE MEASUREMENTS ON EACH SIDE OF DUPLICATE PANELS

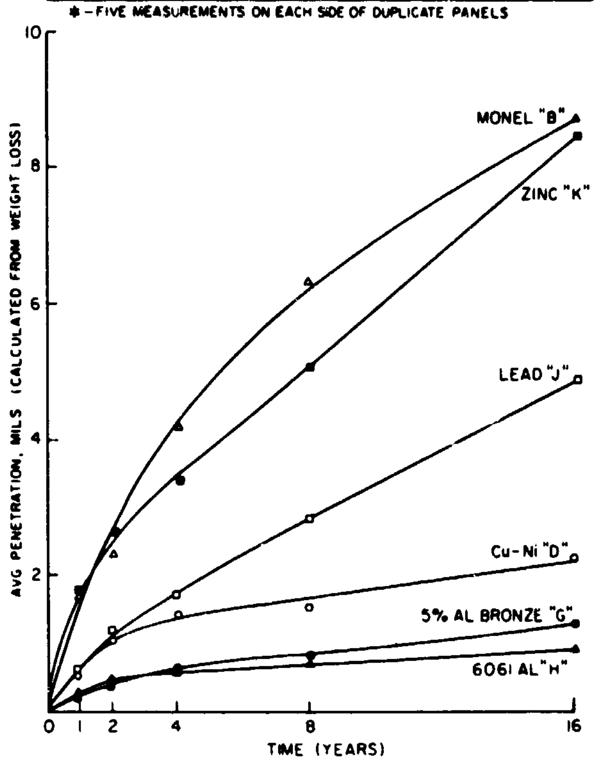


Fig. 7 - Comparison of various sea-resistant metals for 16-years' immersion in tropical sea water

In bimetallic systems containing two noble metals the driving potential is low and, as both metals are normally considered durable in sea water, galvanic corrosion effects are not always anticipated. That these effects in warm tropical sea water can be significant is evident from Fig. 8. The figure shows the results of coupling nickel-bearing alloys with smaller areas of a normally corrosion-resistant phosphor-bronze. The bars of solid background represent the normal corrosion of the metals, and the hatched bars show the galvanic corrosion when the metals are coupled at area ratios of bronze strip to nickel-alloy plate of 1 to 6.9.

In the first combination high-copper bronze is connected with 70-30 copper-nickel. This was an innocuous couple in all environments, with the slight effect measured indicating the bronze strip was slightly protected. In the second bimetallic combination, in which monel plates were coupled with bronze strips, a highly accelerated attack was induced in the bronze. In continuous sea-water immersion the corrosion loss of the bronze at 8 years was 14 times normal, while corrosion of the monel plate was reduced by one-half. Even in fresh water and at mean-tide elevation, the galvanic effect of the larger area of monel caused a 5- to 8-fold increase in corrosion loss of the bronze. Cathodic protection of the monel plates, however, was not measurable in fresh water and showed

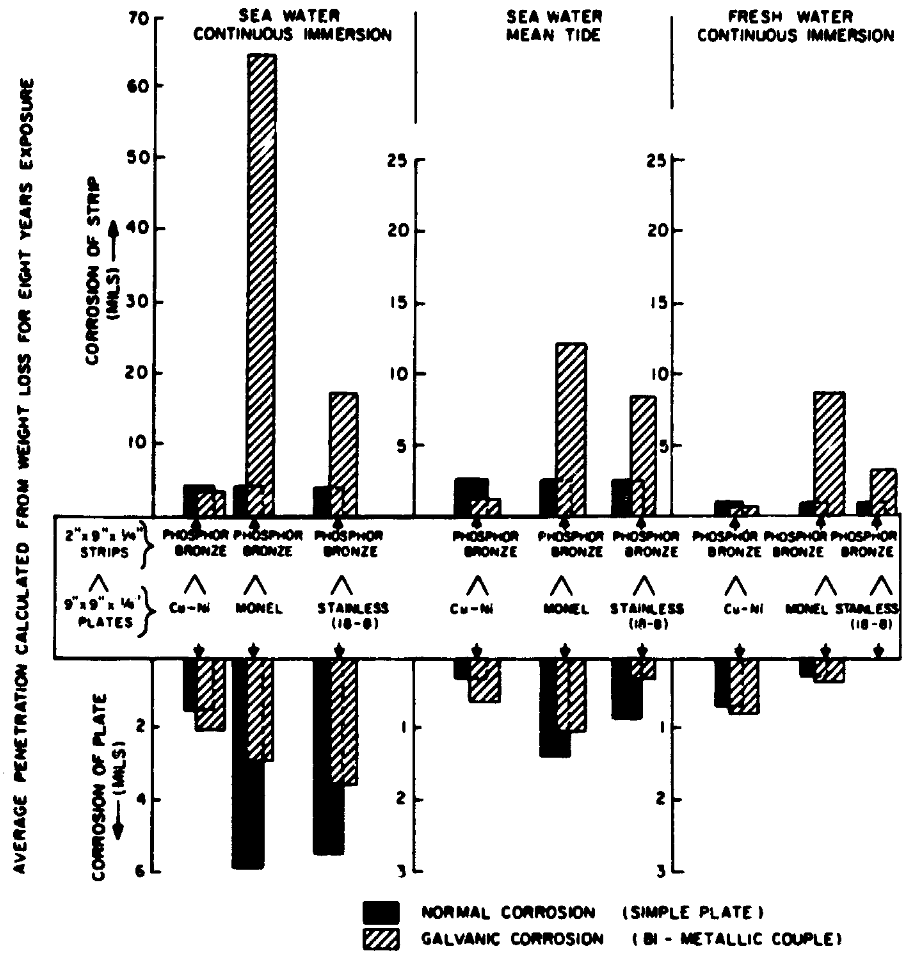


Fig. 8 - Galvanic effects with binoble metal couples in tropical sea water

only slight effect at mean tide. The third couple, included for comparison, is an 18 chromium-8 nickel austenitic stainless steel coupled to strips of the same bronze alloy. Although passive stainless steel is almost as noble as monel, its galvanic effect in all three exposures was considerably less, probably due to the lower conductivity of its surface passivating film. It would appear, then, that the 70-30 nickel-copper monel, with its top noble potential and with limited tendency to polarize, is among the most galvanic corrosion-inductive of the structural metals reported.

Although there was considerable galvanic acceleration of bronze in these couples, it can be seen that, to obtain efficient cathodic protection, a higher potential anode than bronze or copper will be needed. Undoubtedly, the common anode metals such as zinc, aluminum, and magnesium would be effective, but another choice might be regular carbon steel. If the intermediate nobility, low-cost steel, can provide satisfactory long-term protection of the seminoble metals, it should show some advantages in both initial cost and/or less frequent anode replacement.

Results of using carbon-steel anodes for protecting larger areas of copper-nickel and nickel-copper (monel) are shown in Fig. 9. At the anode-to-cathode-area ratio of 1 to 6.9, copper-nickel was almost completely protected during 8 years' exposure, at the

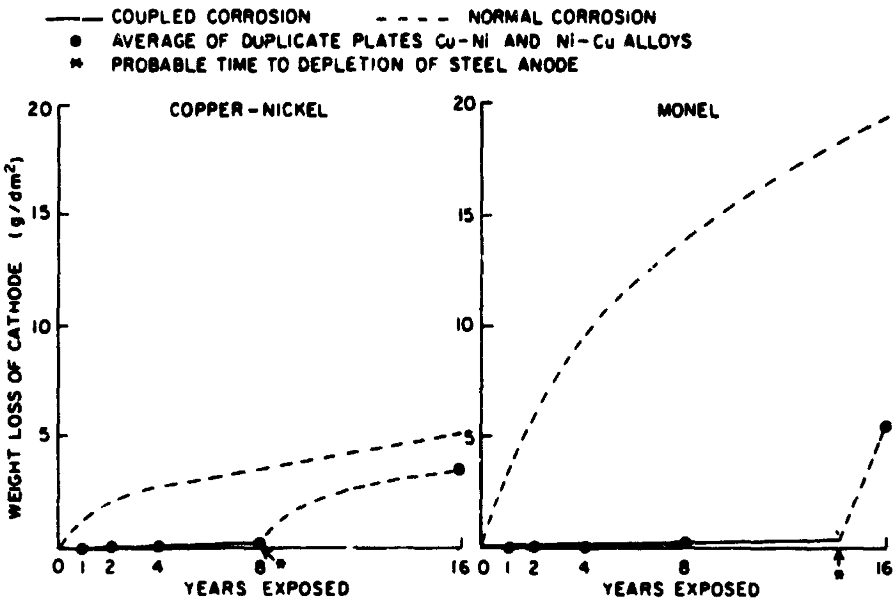


Fig. 9 - Effectiveness and duration of cathodic protection of nickel alloys with 1/7 area carbon-steel anodes

end of which the steel anodes were depleted and corrosion of the copper-nickel proceeded at its normal rate. Monel plates were equally well protected, and the anodes lasted for more than 8 years. During the life of the anodes, highly effective protection was afforded the two nickel alloys. Weight loss was insignificant, and no crevice or underfouling corrosion developed. Panels were entirely free of pitting during the protected period. The opposite sides of the test plates were as corrosion free as the sides to which the anodes were attached. In previous reports, exposure results have shown that carbon steel anodes were also equally effective in providing cathodic protection for stainless steels and high-copper bronzes.

All test data thus point to possible practical uses of carbon-steel anodes for protecting the seminoble construction metals from the corrosive effects of sea water. The use of such bimetallic systems should certainly be among the materials considered for future designs of permanent undersea structures.

ATMOSPHERIC CORROSION OF NICKEL-COPPER METALS

Figure 10 shows the results of exposure of the nickel-copper metals to the Caribbean seashore and the Miraflores inland tropical atmospheres. Data are presented for the same group of metals as tested underwater, with the exception of hot-rolled monel, which was not exposed. In addition, a 65 copper, 18 nickel, 17 zinc nickel-silver (actually nickel brass) alloy was exposed in the atmosphere and the results are included in Fig. 10. Only the weight-loss curves are plotted, as there were no measurable pits on any of these metals in these environments. Weight losses were quite low in each case, but some significant differences appeared during 16 years' exposure.

For the marine atmosphere, shown on the left side of Fig. 10, the most resistant metal was pure nickel, with a loss of less than 0.3 g/dm² at 16 years. This low loss places it among the most resistant of all the 52 metals exposed in this environment. Monel "E" (second highest nickel content) was almost as good, losing only 0.5 g/dm² at

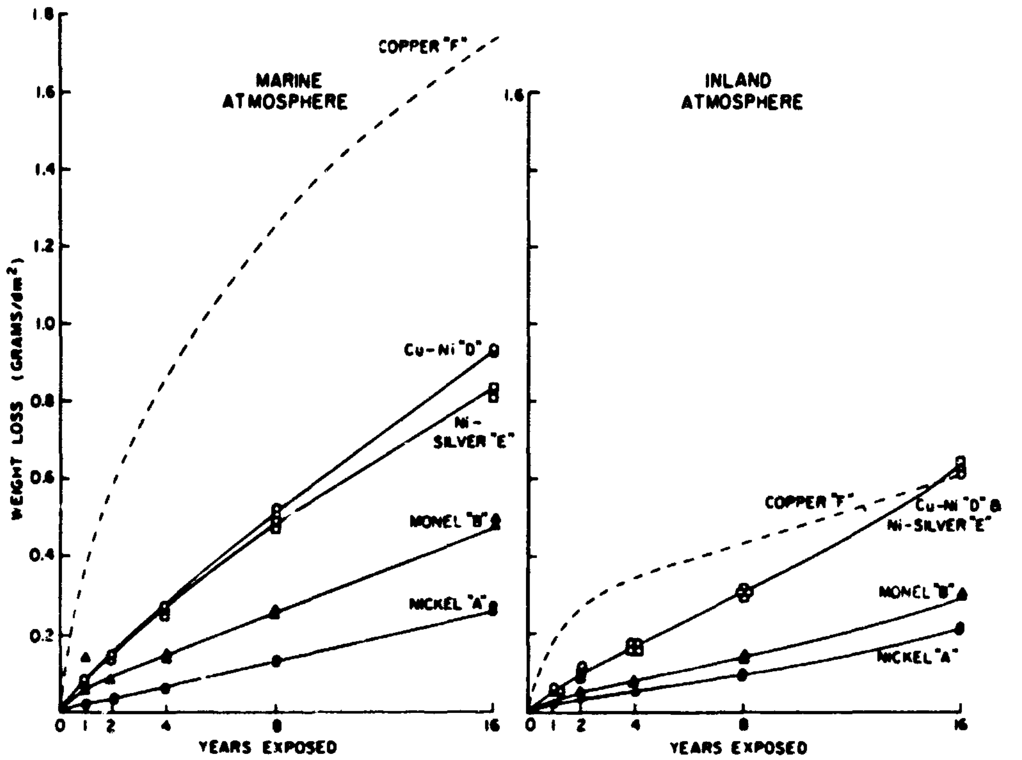


Fig. 10 - Corrosion of nickel and nickel-copper alloys in tropical atmospheres

16 years and showing a final rate of 0.03 g/dm^2-yr; the extrapolated loss at 50 years for monel would be only 1.5 g/dm^2 or about 2/3 mil average penetration. The corrosion losses for these five metals increase with decreasing nickel content of the metals, and pure copper at 1.8 g/dm^2 is considerably higher at 16 years than any of the metals containing nickel.

The right side of Fig. 10 shows that the inland semirural atmosphere at Miraflores, C.Z., was about 30% to 40% less corrosive to nickel and nickel-copper alloys than the Caribbean marine atmosphere. Pure nickel was again the most resistant, with monel losses being only slightly higher. With the exception of copper at 16 years, resistance of the metals increased with increasing nickel content. The nickel metals corroded almost linearly with time, but between 4 and 16 years a very slightly increasing corrosion rate for monel and nickel is indicated by the data.

The close duplication of points obtained in these atmospheric evaluations reflects the precise control that was held on cleaning and weighing procedures, and permits establishment of accurate corrosion time curves.

The curve for unalloyed copper revealed that it corroded more rapidly than nickel metals during the early years. At 2 years it had sustained 3 times the loss of copper-nickel; but the copper corrosion rate decreased sharply between 2 and 4 years, and by 16 years its corrosion loss was down to that of copper-nickel. The shape of the curves reveals that for longer periods of exposure there will probably be some advantage for unalloyed copper.

For all metals in this environment, though, the losses measured were very low, and it can be generally concluded that the nickel metals exposed are extremely resistant to tropical atmospheric corrosion.

The widely used high-nickel monel, for example, had a 16-year loss of only 0.3 g/dm^2 and a final tangent corrosion rate of 0.02 g/dm^2-yr. On the basis of these values, the extrapolated 50-year loss for monel in the inland atmosphere would be only 1.0 g/dm^2 or approximately 1/2 mil average penetration.

CONCLUSIONS

Nickel and nickel-copper alloys continuously immersed in tropical sea water and exposed in tropical atmospheres had corrosion weight losses up to 4 times higher than losses reported for comparable exposures on the east and west coasts of the United States. For mean-tide exposures the large tidal range on the Pacific side of the Canal Zone results in conditions that are less aggressive to nickel-copper metals than temperate climate mean-tide exposures.

No single metal had highest resistance in all environments. Pure nickel had the lowest losses in fresh water and in marine and inland atmospheres, but was the most corroded in the two tropical sea water exposures. Copper-nickel (70-30) had the best resistance in both sea water environments but had the greatest loss in fresh water.

Nickel-copper (monel) was less resistant in sea water than anticipated, because it was subject to a rapid, high-density pitting attack. However, depth of these pits did not continue to increase with time. After the first year to 2 years' exposure, the approximate terminal depth was reached and the 16-year pits were only slightly greater than those found at 2 years.

Mean tide was generally about 1/5 as corrosive as continuous immersion. In this environment, there was considerable shift in relative corrosion rates of pure copper and the high-nickel metals. The nickel metals appeared superior during the first few years' exposure, but after this there is an increasing advantage for pure copper.

Comparison of nickel-copper alloys with a few of the more sea-resistant materials from other metal groups showed the sea-water resistance to be highest for 5%-aluminum bronze followed closely in order of resistance by 6061T aluminum and 70-30 copper-nickel, then by commercially pure lead, monel, and commercially pure zinc.

The nickel metals were all extremely resistant in the marine and inland tropical atmospheres. The slight differences observed for the different metals indicated that resistance increased with increasing nickel content. Pure nickel was one of the most resistant of the 52 metals tested in the tropical atmospheres, with only austenitic stainless steel showing slightly lower losses.

For all metal-environment combinations, tensile-strength losses generally approximated the average reduction-in-thickness, indicating no measurable intergranular or selective corrosion of the subject metals.

Bimetallic couples made up of carbon-steel strips on nickel-copper alloy plates revealed that very effective, long-term protection (8 to 12 years) was afforded both the nickel-copper metals by the structural steel anodes. Such results suggest effective, low-cost methods for protecting the nickel-copper metals for continuous use in sea water.

Other bimetallic combinations disclosed the possibilities of severe galvanic attack on noble metals in tropical sea water; couples with bronze and high-nickel alloys induced anodic corrosion in the bronze up to 14 times normal.

The long-term results repeatedly emphasize the value of obtaining such lengthy data. Study of the completed tests reveals that many misevaluations and gross errors in corrosion rates would have resulted if evaluations had been based solely on measurements from the early periods of exposure.

ACKNOWLEDGMENTS

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Appendix A

ANALYSES OF METALS AND ENVIRONMENTS

So that exact test conditions would be known, considerable effort was expended during the course of the investigation in analyzing the metals under study and the environments in which they were exposed. Tables A1 through A4 and Fig. A1 give summaries of the pertinent results of these tests.

All sampling and testing for the appendix data were done by personnel of the Canal Zone Corrosion Laboratory with the exception of the 20-year meteorological summary, which was supplied by the Panama Canal Company.

Table A1
Chemical Composition of Test Metals

Code	Type	Specification	Ni	Cu	Zn	Fe	Mn	C	S	Si	Cr	Al	Co	Sn	Pb	Mg
		Submerged Metals														
A	Nickel	ASTM B-162-41T, Cold Rolled, Sheet, Annealed	98.46	0.02		0.34	0.20	0.07	0.01	0.04			0.90			
B	Monel	Navy 46M7f, Class A, Cold Rolled, Annealed	66.59	30.37		1.83	0.91	0.15	0.008	0.14		Trace				
C	Monel (Hot Rolled)	Navy 46M7f, Class A, Hot Rolled, Annealed	66.03	30.42		2.06	0.98	0.15	0.003	0.11		Trace				
D	Copper-Nickel	Navy 46C6, Type III, Soft	30.03	68.75	0.42	0.31	0.91							0.015	0.056	
F	Copper	QQ-C-501a, Amend. 2, Class A, Soft		99.92		0.002			0.001							
G	Al Bronze (5% Al)	QQ-B-666, Type IV, Grade A, Amend. 3, Hard		94.84	0.01	0.08						5.07*				
H	Aluminum (6061T)	QQ-A-327, Condition T		0.23	0.015	0.15	0.01			0.55	0.30	97.91*				0.80
J	Lead	QQ-L-201, Amend. 1, Grade A		0.058	0.001	0.002							0.0046	0.002†	99.92*	
K	Zinc	QQ-Z-301A, Type III			99.46*	0.006						Trace			0.49	
		Atmospheric Metals														
a	Nickel	ASTM-B-162-41T, Cold Rolled, Sheet, Annealed	99.24	0.15		0.14	0.14	0.07	0.002	0.05						
b	Monel	Navy 46M7, Class A, Cold Rolled, Annealed	67.43	28.68		2.38	0.40	0.06	0.015	0.03						
d	Copper-Nickel	Navy Specs. 46C6A, Type IV, Soft	29.28	69.74	0.20*	0.09	0.56							0.10	0.03	
e	Nickel Silver	ASTM B-122-42T, Alloy #2, Half Hard	18.49	64.06	17.33*	0.05	0.034								0.004	
i	Copper	QQ-C-501A, Amend. 3, Class A, Soft		99.94												

*Value obtained by difference.
†Sn, Pb, and As.

Table A2
Physical and Mechanical Properties of Test Metals

Code	Type	Physical Properties			Mechanical Properties				
		Surface Condition	Grain Size (diam-mm)	Density (g/cc)	Ultimate Tensile Strength (psi)	Yield Strength 0.2% Offset (psi)	Hardness (BHN) with kg load	Free Bond	
								Elong. (%)	Final Cond.
Submerged Metals (nominal thickness 1/4 in.)									
A	Nickel	As rec.	0.120	8.87	62,800	13,770	144	40	O.K.
B	Monel	As rec.	0.065	8.84	76,900	30,150	102	50	O.K.
C	Monel (hot rolled)	Pickled	0.064	8.81	76,600	25,100	97	50	O.K.
D	Copper-nickel	As rec.	0.035	8.92	61,930	37,570	131	40	O.K.
F	Copper	Pickled	0.035	8.91	31,570	7,880	45	50	O.K.
G	Al-bronze (5% Al)	As rec.	0.045	8.20	50,730	38,330	135	50	O.K.
H	Aluminum (6061T)	As rec.	0.090	2.70	44,700	41,967	99	33	Cracked
J	Lead	As rec.	0.010	11.31	2,170	—	4	50	O.K.
K	Zinc	As rec.	0.025	7.13	21,770	11,600	40	50	Cracked
Atmospheric Metals (nominal thickness 1/16 in.)									
a	Nickel	As rec.	0.090	8.88	65,100	39,800	—	—	—
b	Monel	As rec.	0.045	8.85	68,900	34,100	—	—	—
d	Copper-nickel	As rec.	0.015	8.93	56,070	22,000	—	—	—
e	Nickel-silver	As rec.	0.025	8.76	79,530	74,570	—	—	—
f	Copper	Pickled	0.035	8.91	67,700	31,500	—	—	—

Table A3
Summary of Individual Analyses of Water Samples Obtained at the Immersion Test sites

Constituent or Property Determined	Fresh Water Gatun Lake at Gatun			Sea Water, Pacific Ocean at Fort Amador					
				Upper Rack Level Elevation 0.0 ft			Lower Rack Level Elevation 14.0 ft		
	Maximum	Minimum	Av.	Maximum	Minimum	Av.	Maximum	Minimum	Av.
Elec. conductivity (mhos × 10^{-3} at 81°F)	0.12	0.091	0.11	51.7	21.3	42.2	51.7	35.4	45.4
Total dissolved solids (ppm)	165	69	113	42,776	22,613	35,832	41,480	26,390	35,735
Total suspended solids (ppm)	23	0.0	7.6	220	0	64	173	0	49
Turbidity (ppm)	<5	<5	<5	20	<5	<5	25	<5	<5
Oxygen saturation (percent)	98	78	90	105	62	90	103	64	87
Oxygen consumed (ppm)	2.4	0.7	1.4	2.5	0.6	1.6	2.6	0.4	1.6
Biochemical oxygen demand (ppm)	2.2	0.1	1.0	3.4	0.2	1.6	2.3	0.0	1.5
pH (colorimetric)	8.0	6.9	7.5	8.4	7.8	8.2	8.4	7.8	8.1
Organic and volatile matter (ppm)	65	6.6	34	10,379	2,150	6,226	10,632	2,759	6,236
Sulfate (ppm)	7.2	0.0	2.6	3,240	1,590	2,431	3,177	1,837	2,473
Chloride (ppm)	12.5	0.0	7.0	20,098	11,300	17,415	19,949	10,379	17,357
Nitrate (ppm)	Trace	0.0	Trace	0.01	0.00	Trace	0.01	0.00	Trace

Table A4
Summary of Individual Analyses of Air Samples Obtained at the Atmospheric Test Sites

Constituent (determined in mg per 100 cu ft)	Cristobal Test Site			Miraflores Test Site		
	Maximum	Minimum	Av.	Maximum	Minimum	Av.
Total Dissolved Solids	5.48	0.30	1.70	2.58	0.15	0.86
Organic and Volatile Matter	1.72	0.16	0.74	0.69	0.11	0.34
Sulfate	0.64	0.030	0.20	1.13	0.011	0.25
Chloride	0.42	0.035	0.23	0.16	0.013	0.055
Nitrate	0.11	0.00	0.031	0.12	0.00	0.040

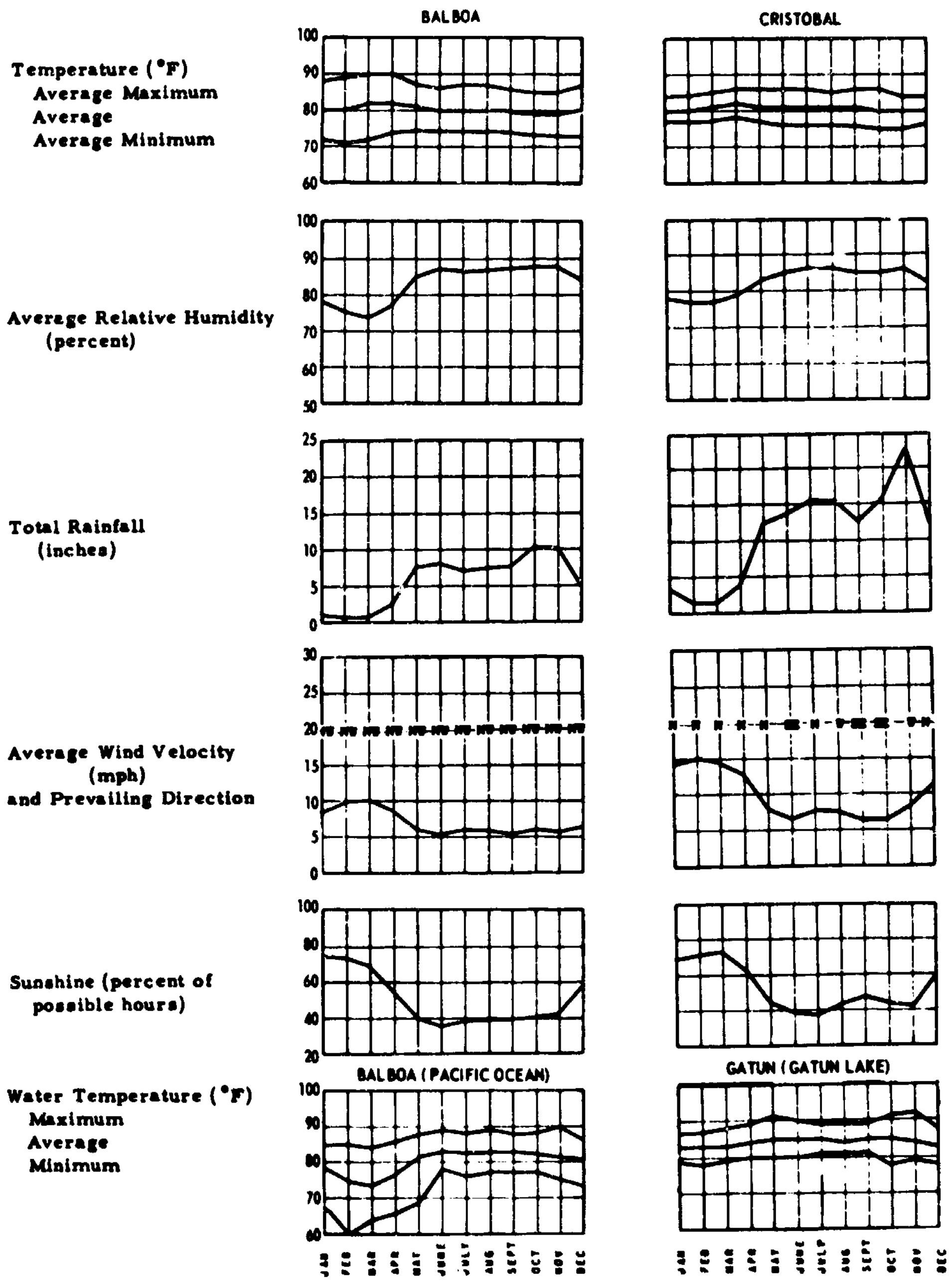
BALBOA
CRISTOBAL
Temperature (°F)
Average Maximum
Average
Average Minimum
Average Relative Humidity
(percent)
Total Rainfall
(inches)
Average Wind Velocity
(mph)
and Prevailing Direction
Sunshine (percent of
possible hours)
Water Temperature (°F)
Maximum
Average
Minimum
BALBOA (PACIFIC OCEAN)
GATUN (GATUN LAKE)

Figure A1

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13. ABSTRACT

Corrosion of nickel and nickel-copper alloys in five natural tropical environments is reported for exposure periods of 1, 2, 4, 8, and 16 years. Data collected include weight loss, pitting, change in tensile strength of simple plates, and weight loss of galvanic couples. Corrosion in the tropics is compared with available exposure results from temperate latitudes in the United States, and generally the tropical corrosion was appreciably higher. The weight-loss-vs-time curves are normally curvilinear relations but considerable variation in the direction and magnitude of the curvature was observed for the different metals and environments. With respect to pitting, the high nickel alloys developed severe early pitting under sea water. However, the initial high penetration rates leveled off to very low rates after the first 1 to 2 years' exposure. Comparison under tropical sea water of monel and copper-nickel with various other nonferrous metals shows copper-nickel with comparatively high corrosion resistance, but monel with the lowest sea-water resistance of the group. Galvanic corrosion results show the long-term efficiency of carbon steel anodes in cathodically protecting nickel-copper alloys in sea water. Additional galvanic data reveal that considerable anodic corrosion can be induced in a normally sea-resistant metal if coupled with certain nickel alloys. The nickel

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Marine corrosion Fresh water corrosion Atmospheric corrosion Corrosion resistance Pitting Weight loss Tensile strength reduction Tropical environments Sixteen Years' Exposure Nickel Nickel alloys Sea-resistant metals						

metals were highly resistant to corrosion in the tropical atmospheres. There was no measurable pitting in these terrestrial exposures and only small weight losses. The losses that were measured though showed increasing resistance of the metals with increasing nickel content. Since tropical corrosion is near the upper limit of corrosiveness of natural environments, these long-term results should afford safe, practical information for design and protection of structures in all latitudes.