

NRL Report 6452

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Corrosion of Metals in Tropical Environments

Part 7 - Copper and Copper Alloys - Sixteen Years' Exposure

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ABSTRACT

The corrosion of copper and nine wrought copper alloys is reported for exposures in five tropical environments for one, two, four, eight, and sixteen years. Weight loss, pitting, and change in tensile strength were measured to evaluate corrosion resistance. Higher corrosion rates are shown for tropical sea water immersion and tropical marine atmosphere than similar exposures in temperate climates. Of the various alloys studied, 5% Al bronze showed the highest general corrosion resistance; its 16-year losses in sea water were only 1/5 that of copper. Copper and the high-copper alloys were resistant to all environments and generally had decreasing corrosion rates with time of exposure. Tensile tests revealed heavy dezincification in the lower-copper brasses when exposed in marine environments, and for two of the brasses in fresh water immersion. As a result of the decreasing corrosion rates or dezincification, antifouling properties of copper alloys decreased with time of exposure. All were moderately to heavily fouled after 16 years in sea water. Galvanic effects were pronounced in tropical sea water. The corrosion of copper alloys was accelerated appreciably by contact with stainless steel (316) of 1/7 their area, while similar carbon steel strips gave effective cathodic protection to plates of brass and bronze over the long term.

Tropical atmospheric corrosion of cupreous metals was generally very low, but dezincification of $\alpha + \beta$ brasses caused average penetrations three to five times greater than alloys of less than 20% zinc content.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem C03-11
Projects RR 007-08-44-5506
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CORROSION OF METALS IN TROPICAL ENVIRONMENTS

PART 7 - COPPER AND COPPER ALLOYS - SIXTEEN YEARS' EXPOSURE

INTRODUCTION

This report is the seventh in a series describing the results of a comprehensive corrosion investigation initiated in 1947 in the Panama Canal Zone. In the complete study, 52 metals and alloys were exposed to five diverse tropical environments for a total of 16 years. Both simple plates and bimetallic couples were included in the program, and sufficient replicates of each were exposed to provide for removal of duplicate samples at 1, 2, 4, 8, and 16 year periods. More than 13,000 individual samples were exposed. Earlier reports on this work were based on data from the first 8 years' exposure and were concerned with the more rapidly corroded ferrous metals (1-5). One sixteen-year report on light metals also has been published (6). The first report in the series (1) presents more detailed information on the program background and test procedures.

From earliest history, copper has been a very important metal for use in marine environments. With the continuing development of many copper alloys, the importance of copper-base metals has increased steadily. The present Panama Canal and proposed designs for future modifications or sea level construction in Panama include a considerable amount of copper and copper alloys. In 1946-1947, as design work on new canal structures was initiated, it became evident that very little quantitative information was available on the corrosion rates of metals in tropical environments. To help supply the necessary data, this comprehensive corrosion study was initiated. Among the metals included were copper and nine of its alloys, the diversity being fairly representative of the complete spectrum of copper alloys in production.

METALS AND METHODS

In addition to electrolytic 99.9% copper, the wrought cupreous metals tested included three high-copper bronzes: 2-1/2% silicon bronze, 4-1/4% tin-phosphor bronze, and 5% aluminum bronze; three alpha-phase copper-zinc alloys: 90-10 commercial bronze, 80-20 low brass, and 70-30 cartridge brass; and three alpha-beta 60-40 bronzes: naval brass, arsenical Muntz metal, and manganese bronze. Complete chemical compositions and physical properties of these metals are given in Tables A1 and A2 in Appendix A.

The Panama Canal Zone has within its 45-mile length a unique variety of exposure conditions. Available here are deep jungle and extensive cleared areas, access to the Caribbean with off-shore reefs and heavy surf and the Pacific with a normally calm shoreline, a large body of tropical fresh water in Gatun Lake, and a brackish-water, constant-level lake at Miraflores. The five sites employed in this investigation included Caribbean-marine and Miraflores-inland atmospheric exposures, fresh-water immersion in Gatun Lake, and continuous and mean tide sea-water immersion in the Pacific. Location of the test sites in the Canal Zone are shown in Fig. 1.

The marine atmospheric site was on the roof of the Washington Hotel, in Cristobal, at a 55-foot elevation and 300 feet from the shore of Limon Bay on the Caribbean coast (Fig. 1(a)). Here the prevailing wind is from the sea, and offshore breakers normally

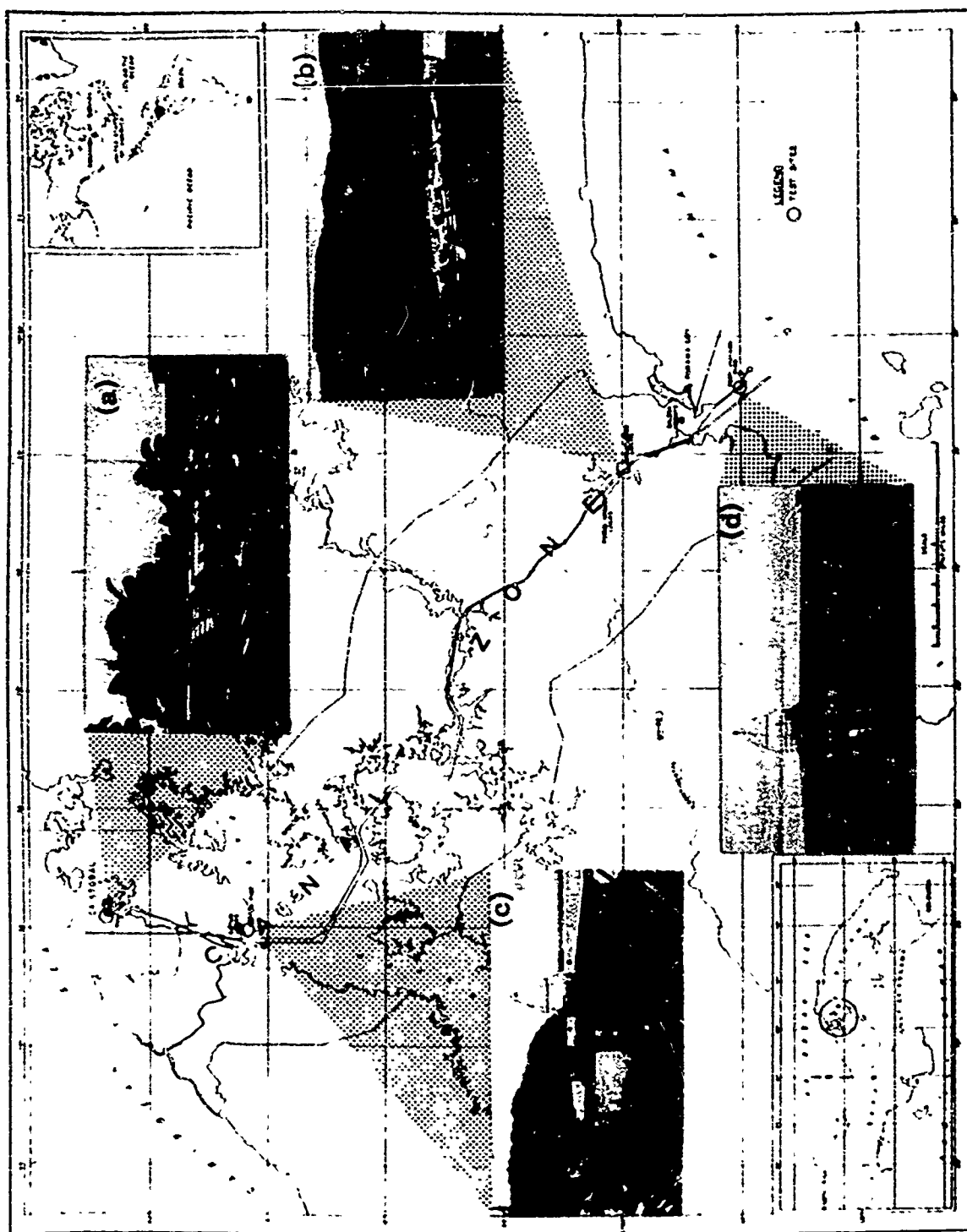


Fig. 1 - Location of test sites

provide a salt-bearing atmosphere. The inland open site was located at Miraflores, C.Z. (Fig. 1(b)), about 5 miles inland from the Pacific coast. The prevailing wind at this site is from the land, and atmospheric conditions can best be classified as tropical, semirural. Two immersion sites were used; one in tropical fresh water, in Gatun Lake (Fig. 1(c)), where the test pier is about 50 feet from the natural shore line. Samples were submerged here an average of 6 feet below the surface in 30-foot water. There is no measurable current flow at this location. The second pier was located over the Pacific Ocean off the Fort Amador causeway, about 1-1/2 miles out from the natural shore line (Fig. 1(d)). The average water depth is about 40 feet, average tidal range is 13 feet, and the maximum currents measured 1/2 foot per second. Two elevations, 14 feet apart, were employed for the ocean exposures. The upper rack was at half-tide level, and the lower at an elevation just under minimum low tide.

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

RESULTS

Comprehensive Tabulation

Table 1 presents a comprehensive summary of results for the ten copper-base metals evaluated for 1, 2, 4, 8, and 16 years' exposure in five tropical environments. All values represent the average of duplicate panels for each exposure period. In order to conform to generally accepted corrosion terminology, weight loss is presented in grams per square decimeter, while penetration values are presented in mils (0.001 in.). The average penetration is calculated from the weight loss and specific gravity, and thus in effect is a volume loss. Corrosion losses of metals of diverse densities are more directly comparable on the basis of average penetration than on the basis of loss in weight. Depth of pitting is given as the average of the 20 deepest pits, which is calculated from the five deepest on both sides of duplicate panels. Maximum penetration on any of the four surfaces is recorded in the table as the deepest pit. Percent tensile loss is shown for the 8 and 16 year samples. As there is a difference in sample thickness between the atmospheric sheets (1/16 in.) and the immersion plates (1/4 in.), the percentage losses must be adjusted by a factor of four if direct comparisons of atmospheric and immersion tensile results are desired.

Comparison of Tropical and Temperate Climate Corrosion

One of the principal objectives of the investigation was to compare corrosion rates in the tropics with those reported for temperate climates. Results from several temperate climates using some of the same metals and alloys have been published. Those used here for comparison with data from the tropical environments include copper, silicon bronze, and naval brass exposed at Eastport, Maine (7), copper and silicon bronze at Kure Beach, North Carolina (8), copper and naval brass at Port Hueneme, California (9), and copper and 70-30 brass at Key West, Florida (10). Figure 2 compares results from these exposures with the Canal Zone data. Bar graphs are used to show temperate climate losses, as these are reported for one or two time periods only, while the curves represent the Canal Zone data.

Generally, the tropical environments caused considerably higher weight losses in the copper-base metals than comparable temperate climate exposures. Exceptions were at mean tide, where the copper and silicon bronze corroded appreciably less in the Canal Zone. Because of the very high tides and calm seas, exposure of the metals in the highly corrosive splash zone is of relatively short duration at the Amador site. This condition,

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Table 1
Comprehensive Evaluation of Corrosion Damage for Copper and Copper Alloys in Five Tropical Environments

Symbol	Metal	Exposure	Weight Loss (g/dm ²)					Average Penetration (Mils)					Depth of Pitting (Mils)										Tensile Strength Loss % (b)	Type Corrosion Attack (c)		
													Average 20 Deepest Pits (a)					Deepest Pit								
			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				
A	Copper	Immersion Sea Water	2.74	5.03	5.95	12.06	13.61	1.21	2.22	2.62	3.33	6.02	27(15)	36(22)	16(11)	28	31	46	75	21	53	57	1.7	5.2	E, R	
		Mean Tide	1.47	1.85	4.30	2.45	2.99	0.65	0.82	1.90	1.08	1.32	9(2)	6(1)	7(2)	10	11	11	11	8	23	(2)	1.7	1.0	E, R	
		Fresh Water	0.50	0.81	1.29	1.86	2.33	0.22	0.36	0.57	0.82	1.03	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	2.0	2.6	A	
		Atmospheric Marine Inland	0.37	0.52	0.66	1.29	1.73	0.17	0.23	0.38	0.57	0.77	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	3.7	4.5	A	
		Inland	0.18	0.26	0.34	0.43	0.60	0.06	0.12	0.15	0.19	0.27	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	1.3	0.1	A	
B	Silicon Bronze	Immersion Sea Water	5.17	3.43	7.56	13.30	12.75	2.38	1.58	3.47	6.10	5.85	15(18)	40(14)	19	21	21(17)	37	80	51	46	36	1.9	3.5	E, R	
		Mean Tide	1.81	2.09	2.61	3.35	4.45	0.74	0.96	1.20	1.53	2.04	(0)	(0)	21(7)	14	41(7)	(0)	(0)	38	42	65	1.3	0.2	R	
		Fresh Water	0.71	1.10	1.56	2.20	2.44	0.33	0.51	0.72	1.01	1.12	(0)	(0)	(0)	(0)	9(2)	(0)	(0)	(0)	(0)	(0)	1.2	1.6	A, R	
		Atmospheric Marine Inland	0.87	0.87	1.41	2.36	4.06	0.31	0.40	0.65	1.09	1.86	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.0	3.9	B, A	
		Inland	0.35	0.44	0.64	0.82	1.33	0.16	0.20	0.30	0.38	0.61	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	1.4	1.5	B, A	
C	Phosphor Bronze	Immersion Sea Water	2.42	3.40	4.88	9.07	12.38	1.07	1.51	2.16	4.01	5.48	4(6)	15(16)	14	13(10)	2(18)	9	35	22	22	29	1.1	7.0	E	
		Mean Tide	1.09	1.70	2.50	4.65	7.85	0.48	0.75	1.28	2.05	3.47	(0)	(0)	(0)	(0)	11(2)	(0)	(0)	(0)	(0)	11	3.6	2.4	E	
		Fresh Water	0.26	0.56	0.71	1.04	1.65	0.12	0.24	0.31	0.45	0.72	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.1	1.9	A	
		Atmospheric Marine Inland	0.44	0.64	0.91	1.37	2.16	0.20	0.29	0.40	0.61	0.96	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	6.6	2.4	K, A	
		Inland	0.13	0.24	0.38	0.56	0.81	0.08	0.11	0.16	0.25	0.36	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	2.0	0.0	K, A	
D	Aluminum Bronze	Immersion Sea Water	0.39	0.75	1.25	1.58	2.62	0.18	0.36	0.60	0.76	1.26	(0)	(0)	(0)	14(3)	(0)	(0)	(0)	(0)	21	(0)	1.9	3.2	J	
		Mean Tide	0.20	0.35	0.58	0.77	1.19	0.09	0.17	0.28	0.37	0.58	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	1.8	1.7	K	
		Fresh Water	0.13	0.20	0.31	0.57	0.87	0.06	0.19	0.15	0.27	0.42	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	1.7	2.3	K	
		Atmospheric Marine Inland	0.18	0.22	0.31	0.47	0.54	0.08	0.11	0.15	0.23	0.39	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	1.5	2.4	K, A	
		Inland	0.10	0.15	0.20	0.28	0.57	0.05	0.07	0.10	0.13	0.25	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.5	0.4	K, A	
E	Commercial Bronze	Immersion Sea Water	2.01	4.67	5.32	10.63	11.01	0.90	2.08	2.39	4.75	4.93	72	65(16)	28(19)	25	33(20)	158	174	54	44	51	2.6	5.1	R, O, J	
		Mean Tide	0.88	1.02	1.26	1.62	2.33	0.40	0.46	0.56	0.72	1.04	6(10)	(0)	(0)	8(4)	(0)	(0)	(0)	(0)	(0)	(0)	1.4	1.8	C	
		Fresh Water	0.50	0.88	1.39	2.23	2.98	0.22	0.40	0.62	0.99	0.34	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	1.6	1.8	C	
		Atmospheric Marine Inland	0.25	0.32	0.50	0.67	1.10	0.12	0.14	0.22	0.30	0.40	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	2.3	3.3	A, K	
		Inland	0.11	0.19	0.31	0.42	0.71	0.05	0.08	0.14	0.19	0.32	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.6	0.0	A, K	
F	Low Brass	Immersion Sea Water	1.43	2.75	4.09	6.54	8.18	0.66	1.25	1.82	2.97	3.73	8(9)	53(18)	18(12)	32	22	22	130	23	53	46	1.7	3.3	O, C, Q	
		Mean Tide	0.70	0.69	0.76	1.09	1.44	0.32	0.55	0.50	0.66	0.66	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.7	2.0	O	
		Fresh Water	0.61	1.06	1.64	2.52	3.32	0.28	0.48	0.74	1.15	1.66	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	1.6	3.0	O	
		Atmospheric Marine Inland	0.18	0.23	0.35	0.49	0.81	0.08	0.11	0.16	0.23	0.37	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	3.8	3.0	A	
		Inland	0.08	0.15	0.24	0.35	0.65	0.04	0.07	0.11	0.16	0.30	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.7	0.2	A	
G	Cartridge Brass	Immersion Sea Water	1.01	2.17	3.39	5.28	8.45	0.47	1.00	1.56	2.43	3.90	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	13.7	20.0	O, C	
		Mean Tide	0.37	0.34	0.55	0.82	1.93	0.17	0.16	0.25	0.37	0.89	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	1.3	4.2	O, K	
		Fresh Water	0.75	1.30	1.87	2.84	5.87	0.34	0.60	0.86	1.31	1.75	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.6	2.7	O, A	
		Atmospheric Marine Inland	0.11	0.15	0.24	0.39	0.72	0.05	0.07	0.11	0.18	0.33	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	5.3	3.6	A, R	
		Inland	0.05	0.19	0.17	0.26	0.54	0.03	0.05	0.08	0.12	0.25	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.6	0.0	A, R	
H	Naval Brass	Immersion Sea Water	6.26	6.51	12.71	15.01	26.52	2.94	3.96	5.97	7.04	12.44	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	34.6	57.6	C	
		Mean Tide	2.05	3.45	4.43	8.80	12.70	0.96	1.82	2.08	4.03	5.96	(0)	(0)	(0)	7	(0)	(0)	(0)	(0)	7	(0)	18.2	21.7	C	
		Fresh Water	0.66	1.48	1.89	3.29	3.96	0.52	0.70	0.85	1.55	1.86	(0)	(0)	(0)	8(5)	(0)	(0)	(0)	(0)	11	(0)	15.8	12.0	C	
		Atmospheric Marine Inland	0.13	0.16	0.28	0.44	0.81	0.06	0.08	0.13	0.21	0.39	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	2.7	6.8	K, A	
		Inland	0.07	0.10	0.18	0.30	0.61	0.03	0.05	0.09	0.14	0.29	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.4	1.4	K, A	
I	Moniz Metal	Immersion Sea Water	2.49	3.27	5.68	9.12	17.33	1.13	1.53	2.87	4.30	8.18	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	32.7	45.5	C, B	
		Mean Tide	1.73	2.84	4.02	7.73	12.00	0.81	1.33	1.89	3.62	5.85	4(4)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	31.8	38.2	C, B	
		Fresh Water	1.15	2.30	3.51	5.01	7.36	0.54	1.08	1.64	2.35	3.47	3(9)	(0)	(0)	(0)	11(15)	(0)	(0)	(0)	(0)	(0)	7.7	10.5	O	
		Atmospheric Marine Inland	0.14	0.18	0.30	0.45	0.97	0.07	0.09	0.14	0.23	0.45	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	4.3	8.4	K	
		Inland	0.09	0.13	0.21	0.34	0.68	0.04	0.06	0.11	0.16	0.32	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	1.3	3.5	K	
J	Manganese Bronze	Immersion Sea Water	6.45	7.33	12.32	25.00	36.58	3.03	3.54	5.79	11.75	17.19	22(2)	(0)	(0)	(0)	12	21(13)	27(13)	(0)	(0)	20	36	33.1	45.8	O, C
		Mean Tide	2.10	2.81	4.83	8.18	16.03	0.99	1.32	2.27	3.84	7.53	(0)	(0)	(0)	(0)	(0)	12(1)	(0)	(0)	(0)	(0)	12	6.3	13.8	O, C
		Fresh Water	0.32	0.57	0.85	1.25	1.98	0.19	0.28	0.40	0.59	0.93	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.0	0.2	C	
		Atmospheric Marine Inland	0.38	0.40	0.63	0.70	1.26	0.18	0.19	0.30	0.33	0.60	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	6.0	8.0	K, A	
		Inland	0.33	0.32	0.44	0.45	1.67	0.15	0.15	0.20	0.21	0.50	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	0.8	4.2	K, A	

NOTES

(a) Numbers in parenthesis indicate number of measurable pits when less than 20 - a measurable pit is one > 5 mils

(b) Percent losses are for samples of 1/4 inch thickness for immersion exposure and 1/16 inch thickness for atmospheric exposure

(c) Corrosion types are described in detail in the Appendix of Part I. Those referred to here are:

A - uniform attack, B - granular reaction, C - uniform desiccation, D - random desiccation, E - local attack (uniformly distributed), R - local attack (randomly located), J - fouling contact, K - no visible attack.

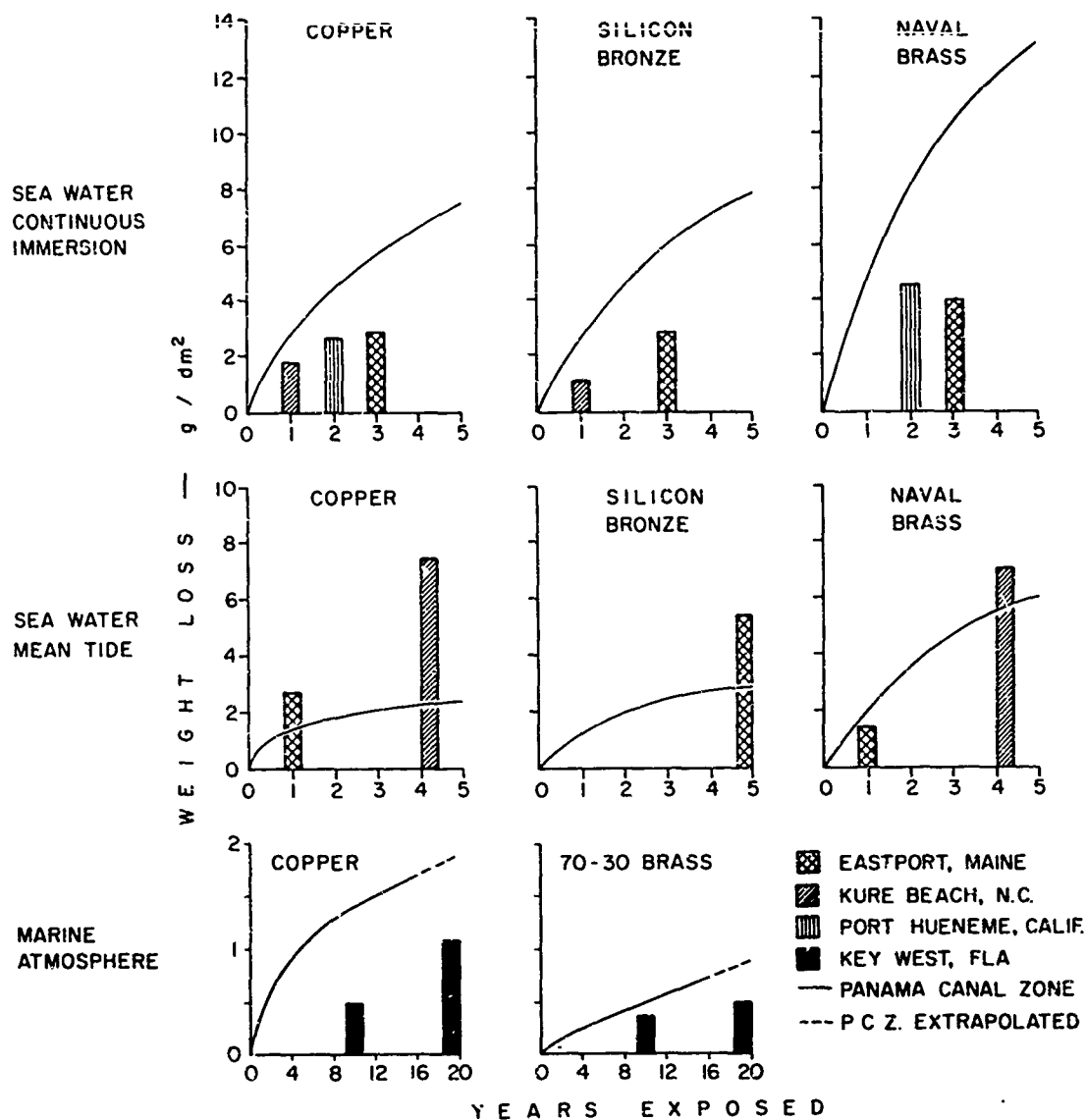


Fig. 2 - Comparison of tropical and temperate climate corrosion

combined with the rinsing of samples when they are above the sea level by frequent tropical showers and the rapid drying from tropical sunshine, probably accounts for the lower mean tide corrosion rates in this tropical exposure.

During continuous immersion in sea water, the copper-base metals corroded more rapidly at Fort Amador than in temperate latitudes. The largest differences were between Eastport, Maine, and the Canal Zone, where the difference in losses of all three metals was more than a factor of two. Corrosion losses at Kure Beach and Port Hueneme were somewhat closer to those found at Fort Amador. Copper, after one year at Kure Beach, corroded 40% less than copper exposed to the sea at Fort Amador. As marine fouling and its effects have a reduced significance on copper and its alloys, the continually higher temperature is perhaps the most important factor contributing to the greater tropical losses.

Corrosion in the marine atmosphere in Panama was appreciably higher than losses for similar periods reported from Key West, Florida. Small temperature differences between these two geographical locations were certainly of less significance than differences in the

constituents in the atmosphere. As reported by Ambler and Baine (11) and May, et al. (12), concentration of salt in the atmosphere has much greater effect on metallic corrosion than existing differences in temperature. The high atmospheric salinity on the Caribbean Coast of Panama and the continuously higher tropical humidity combine to provide ideal conditions for hygroscopic solution of the positive salts, providing a continuing corrosive environment on the metals. These conditions, in all probability, account for the higher atmospheric corrosion rates at the Canal Zone site.

Underwater Corrosion of Copper Alloys

Most of the corrosion rates of immersed nonferrous metals found in handbooks or treatises on corrosion are determined from one short-term exposure of the metal in a particular environment. From this result, a rate, usually mils per year (mpy) or milligrams per square decimeter per day (mdd), is calculated as the rate of corrosion in the medium, e.g., copper at 1.1 mils per year in Galveston Bay, determined with a 130-day test (13). However, with durable metals, such as these high-copper alloys, the short-term loss is usually of minor significance and can be quite misleading, because early establishment of a linear relation does not appear to be typical for these metals in underwater exposure. Bulow (14) has reported a time relation for copper corroding in sea water as:

$$\text{Total corrosion} = Ct^{1/3}$$

where C is a constant and t is the time of exposure. In these long-term exposures in tropical sea water the relation was found to be closer to:

$$\text{Total corrosion} = Ct^{1/2}$$

where (for average penetration in mils) C = 1.5 and t is the time of exposure in years. This approximate relationship reveals the magnitude of error inherent in the use of the commonly accepted one-year secant rates. From the one-year rate, the average penetration for 50 years' exposure of copper in tropical sea water would be predicted as 75 mils, while actually the 50-year penetration, computed from the equation, is only 11 mils. Comparison of the average corrosion penetration of 75 mils predicted from the one-year rate with that calculated from Bulow's equation would have resulted in an even larger discrepancy, since the calculated 50-year penetration would be only 5.7 mils.

The considerable variation in the shape of the curves for the different environment-alloy combinations precluded the establishment of one comprehensive empirical relation for the copper group; however, an accurate prediction of the service life of each specific combination can be made by extrapolating its 16-year curve. This has been done for a few metals in Table 2, which, for comparison, includes predictions based on the one-year rate. From Table 2, it is apparent that the selection of copper alloys for underwater use on the basis of the short-term results can be most unreliable. For example, a copper alloy might be rejected for use as a thin sheathing material in sea water because of the predicted loss of 32 to 45 mils over 50 years, whereas the true loss of 3 to 9 mils might make it the logical choice. Also, selection between alloys of different metals, such as copper alloy vs nickel alloy, would probably lead to even more erroneous conclusions.

The American Society for Testing Materials and the National Bureau of Standards have conducted sufficient long-term atmospheric and soil burial exposures of metals to provide a reasonable basis for corrosion rates in these environments; but for underwater use, structural designers often must rely on rates established from a few inadequate short-term exposures. In view of recently expanded interest in undersea development, with almost unlimited possibilities for mining, transportation, and living in the environment, oceanographic engineers may find themselves seriously handicapped by a fundamental

Table 2
Service Life Predictions

Alloy	Environment	Average Penetration at 50 years (mils)	
		Predicted From One-Year Rate	Extrapolated From 16-Year Curve
Silicon Bronze	Continuous fresh water	16.5	1.49
Commercial Bronze	Continuous fresh water	11.0	2.86
Phosphor Bronze	Mean tide level	25.0	9.45
Silicon Bronze	Mean tide level	39.0	4.25
Low Brass	Continuous sea water	32.0	3.40
Commercial Bronze	Continuous sea water	45.0	8.70

materials knowledge gap, similar to, but of much more widespread significance than that encountered by the Panama Canal design engineers in 1946. It is hoped the following 16-year data will contribute significantly in this area and that these results will serve to highlight the pressing need for additional investigations of open-ocean corrosion-time relations.

The next three figures will show weight loss as a function of time for nine copper alloys in the three underwater environments. The first group of curves, shown in Fig. 3, are for continuous immersion in fresh water. Corrosion losses in fresh water were reasonably close to predictions, with the high-copper bronzes showing the least corrosion. The α -phase copper-zincs were next in corrosion magnitude and were closely grouped in exact order of zinc content; i.e., the higher the zinc content, the higher the loss. The maximum fresh-water corrosion loss was found in the $\alpha + \beta$ group (Fig. 3(c)). However, the corrosion rates of the three $\alpha + \beta$ bronzes were much more varied than those in the other two groups, so that a considerable range of corrosion magnitude was included.

Arsenical Muntz metal (metal I), containing 0.2% arsenic, was the least resistant to corrosion in fresh water. Apparently the addition of arsenic as an inhibitor for the high brass was ineffective in this environment. The small tin addition in naval brass (metal H) was a somewhat more efficient inhibitor, as this metal corroded at about the same rate as lower zinc 70-30 alloy (metal G). The best corrosion inhibition for the 60-40 bronzes exposed to fresh water appeared to result from the small additions of aluminum, iron, and manganese in manganese bronze (metal J).

The curves of Fig. 4 show the weight loss of the copper alloys during continuous immersion in tropical sea water. These have been scaled down from the previous fresh-water curves by a 5 to 1 change in ordinate, since the corrosion magnitude of the group is generally about 5 times higher than the fresh-water corrosion.

Silicon bronze (metal B) and phosphor bronze (metal C) were both about equal to copper in their undersea corrosion, fouling, and pitting resistances. Five-percent Al bronze (metal D) was consistently more resistant to sea-water corrosion than the other copper metals; after 16 years it showed only 1/5 as much weight loss as copper. Because of the low corrosion rate of this metal, there was a heavier accumulation of marine fouling than on the other high-copper metals; but fouling-initiated pitting, which has been occasionally reported for aluminum bronzes, was insignificant during these exposures. During its 16 years in the ocean there were only three measurable pits, with a maximum depth of 20 mils. This was slightly less pitting than the other two bronzes and copper, all of which

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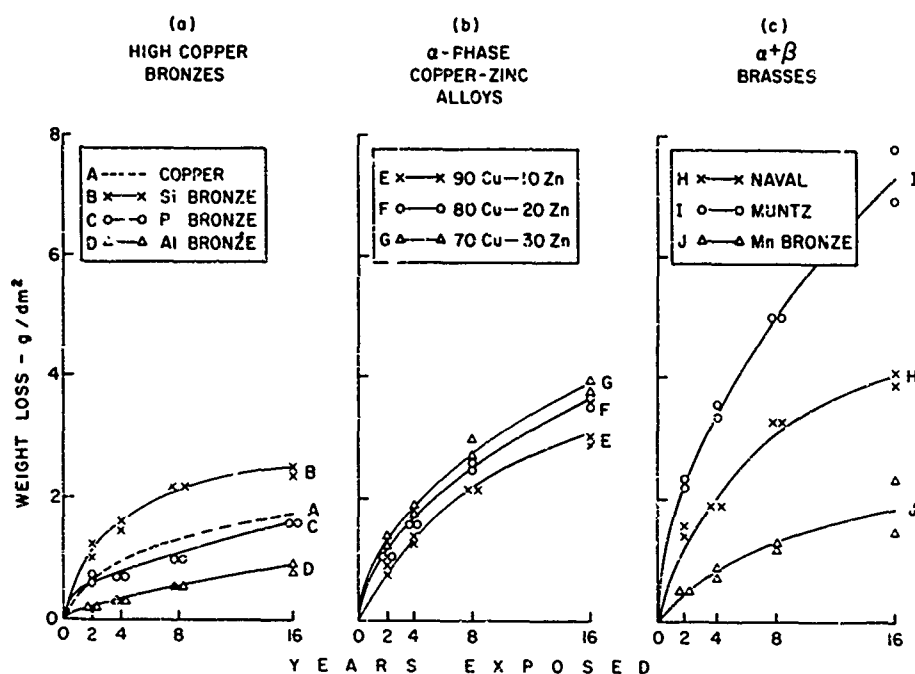


Fig. 3 - Corrosion weight loss as a function of time for copper alloys continuously immersed in tropical fresh water

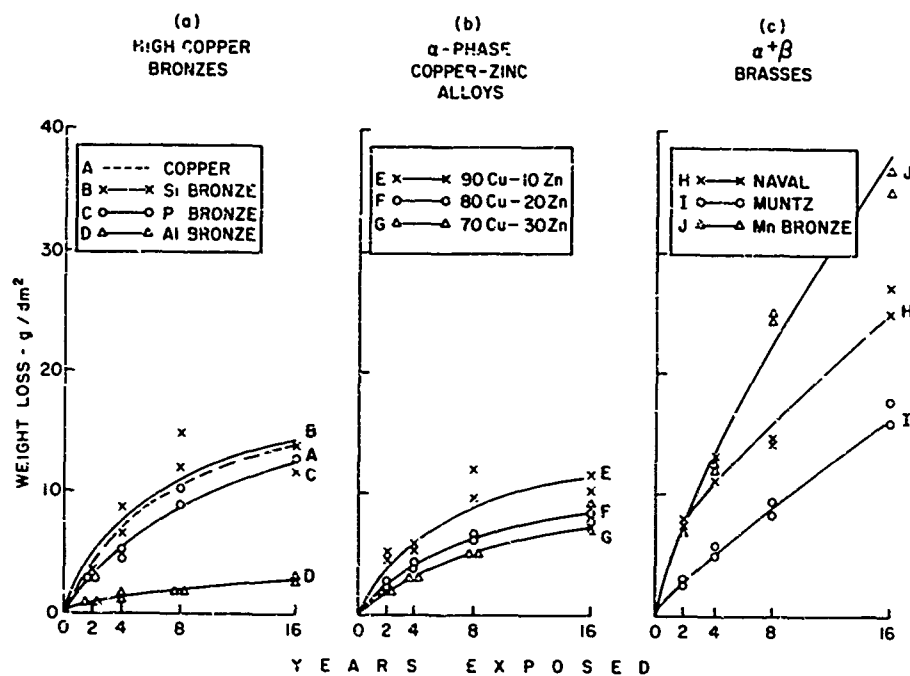


Fig. 4 - Corrosion weight loss as a function of time for copper alloys continuously immersed in tropical sea water

had some scattered light pits at each of the time periods. However, a definite relation of pitting with time did not develop for any of the copper metals. Pit depth measurements for all the metals are included in table 1.

On the basis of weight loss, the α -phase copper-zinc alloys with 10, 20, and 30 percent zinc content were very resistant to this quiet sea-water exposure. All corroded at a lower rate than pure copper, and the curve positions seem to indicate a slight increase in resistance with increasing zinc content; but, because these were uninhibited alloys, some dezincification occurred on the 70-30 samples (metal G). This tends to confuse the weight loss results for this brass, as only part of the corrosion effect is measured by weight loss on dezincified metal.

The two-phase brasses in Fig. 4(c) had the highest weight losses of any of the copper alloys in any of the three environments. Again, because of dezincification, the residue of which could not be removed by cleaning, the actual corrosion penetration of these metals is even greater than indicated. Tensile losses discussed later will give a better quantitative evaluation of corrosion penetration for alloys subject to dezincification attack.

Weight losses for the copper alloys at mean tide are shown by the group of curves in Fig. 5. In general, these losses are about double those for fresh water and 2/5 those for continuous sea water. Five percent Al bronze (metal D) was again the least corroded of the ten metals, losing about 1/3 as much weight as copper after 16 years. Silicon bronze (metal B) had a rate of loss in this environment slightly higher than copper. Phosphor bronze (metal C) showed a lower initial loss than either copper or silicon bronze, but after 16 years weight loss was 2.6 times that of copper and 1.8 times that of Si bronze. Further divergence is indicated for longer exposures.

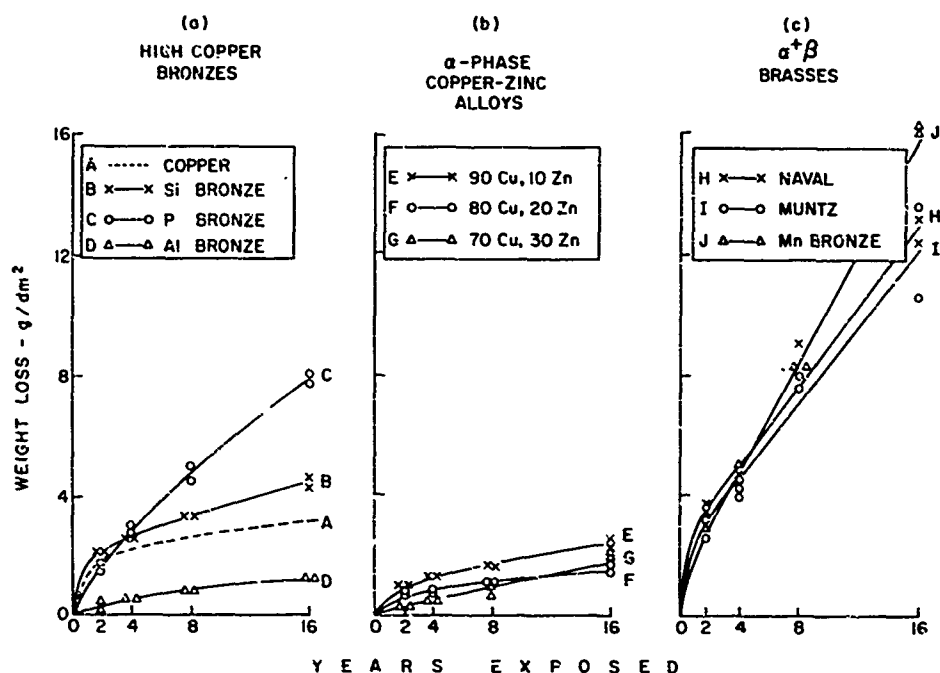


Fig. 5 - Corrosion weight loss as a function of time for copper alloys exposed at mean-tide elevation in tropical sea water

The corrosion rates of the α -phase copper-zinc alloys were quite low at mean tide. Weight losses at 16 years were only 1/2 to 3/4 those of pure copper. As in continuous immersion, 70-30 brass (metal G) incurred some dezincification, as revealed by tensile tests. No measurable dezincification occurred with the 80-20 low brass (metal F), which appears to be optimum among α brasses in this quiet sea water.

The $\alpha + \beta$ high brasses (Fig. 4(c)) sustained the highest losses of any of the metals in the mean tide exposure. At 16 years their order of loss was identical to their ranking in continuous immersion; i.e., the Mn bronze had the highest loss, closely followed by naval brass and arsenical Muntz metal.

In both marine environments all the high brasses reached a fairly definite linear relation with time after the first 2 to 4 years' exposure. In contrast, most of the higher copper alloys did not approach a linear relation until 8 or more years.

Dezincification of Brasses

Dezincification of copper-zinc alloys is still not a clearly understood phenomenon, and, while it is known to be a selective type of attack occurring only in copper alloys containing more than 15% to 20% zinc, some confusion exists pertaining to the mechanism of zinc removal. Regardless of the exact mechanism of attack, however, the insidious and destructive results of dezincification are quite real when certain copper-zinc alloys are used in or near the ocean, and this characteristic is the cause of considerable misunderstanding and apprehension in the use of all copper alloys in marine environments.

The photographs in Figs. 6 and 7 show some of the effects of long-term dezincification in tropical ocean water. Polished and etched end sections of the 2, 4, 8, and 16 year samples of naval brass from continuous sea-water exposure are shown in Fig. 6. The progression of the very uniform dezincification and the sharp line of demarcation between the dark dezincified material and the bright-colored sound metal center can be seen in this picture. With the thick layer of dezincified metal incasing the uncorroded core, a stifling effect on further corrosion is suggested, but it is obvious from this photograph and the preceding curves, showing straight line relations after 2 to 4 years' exposure, that this did not occur.

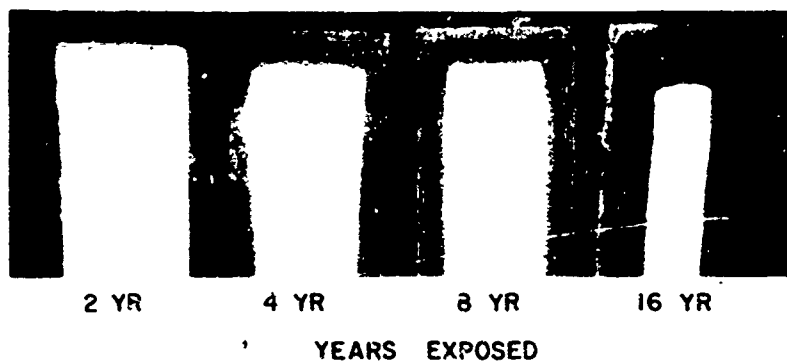


Fig. 6 - Polished and etched end sections of naval brass continuously immersed in tropical sea water showing progression of dezincification and the sharp line of demarcation between sound and dezincified metal (4X)

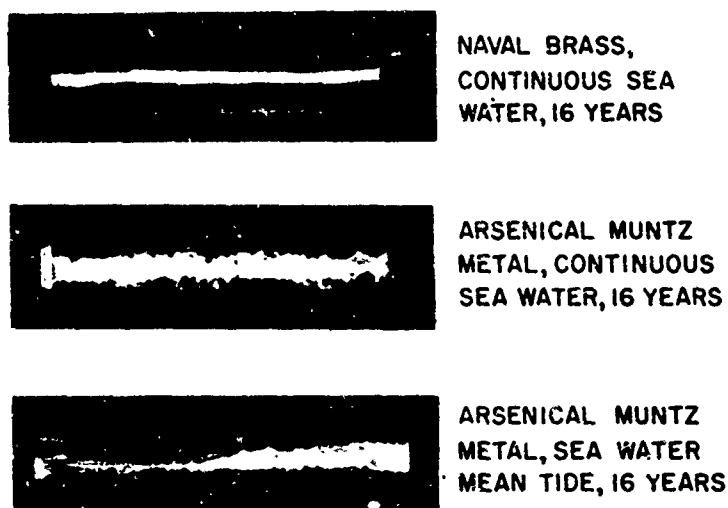


Fig. 7 - Cross-sectioned view of broken 2-inch-wide tensile sample showing variation in uniformity of dezincification

The second photograph (Fig. 7) shows cross sections of broken tensile samples from the 16-year plates. The nonuniform dezincification sustained by the arsenical 60-40 brass compared to the uniform attack on naval brass is revealed by these views. In single-phase brass, arsenic is known to be a very effective inhibitor of dezincification. Rogers (15) reports practically 100% inhibition for 0.02% to 0.05% additions to α brasses. But considerable controversy exists concerning the effectiveness of arsenic in two-phase brasses. These photographs and the previous weight loss data reveal how the differences in opinion might arise. If evaluation is based solely on weight losses, and especially if the short-term 1 and 2 year losses are the criteria, the arsenic additive appears to be beneficial. On the other hand, the nonuniformity and increased maximum depth of attack revealed by the cross-section photographs indicate that the arsenical brass, while having less total dezincification, was subject to deeper penetration. Thus, an evaluation based entirely on service life to perforation, as probable with many types of operating equipment, would condemn this additive for 60-40 brasses as not only ineffective but even harmful.

During dezincification, the porous copper residue remains firmly attached to the unattacked base metal, and the actual depth of corrosion cannot be ascertained either by surface measurements or by weight loss. Thus, with metals subject to this selective attack, we must rely on tensile values for reasonable quantitative information. However, the need for both methods of evaluation is apparent when it is considered that the weight loss gives much more precise results than the tensile tests, especially for unevenly corroded samples, and thus greater reliability is provided by the weight loss in establishing the pattern of corrosion penetration or for comparing alloys of equal zinc content. In addition, most published corrosion data is based on weight loss results, so this type of evaluation is necessary if comparisons are desired.

Tensile losses compared with weight losses for all the metals are summarized in Fig. 8. For the metals with 80% or more copper, dezincification or selective corrosion did not develop; and tensile losses generally agree with weight losses. Thus, the 5% Al bronze (metal D) again appears to be the most corrosion resistant of the metals in marine environments, and dealumination, while unlikely at this low Al content, is shown definitely not to have occurred. The variable differences of 1% to 3% between tensile and weight losses shown for the other high-copper metals are considered to be within the limits of experimental error and of no real significance. On the other hand, the large

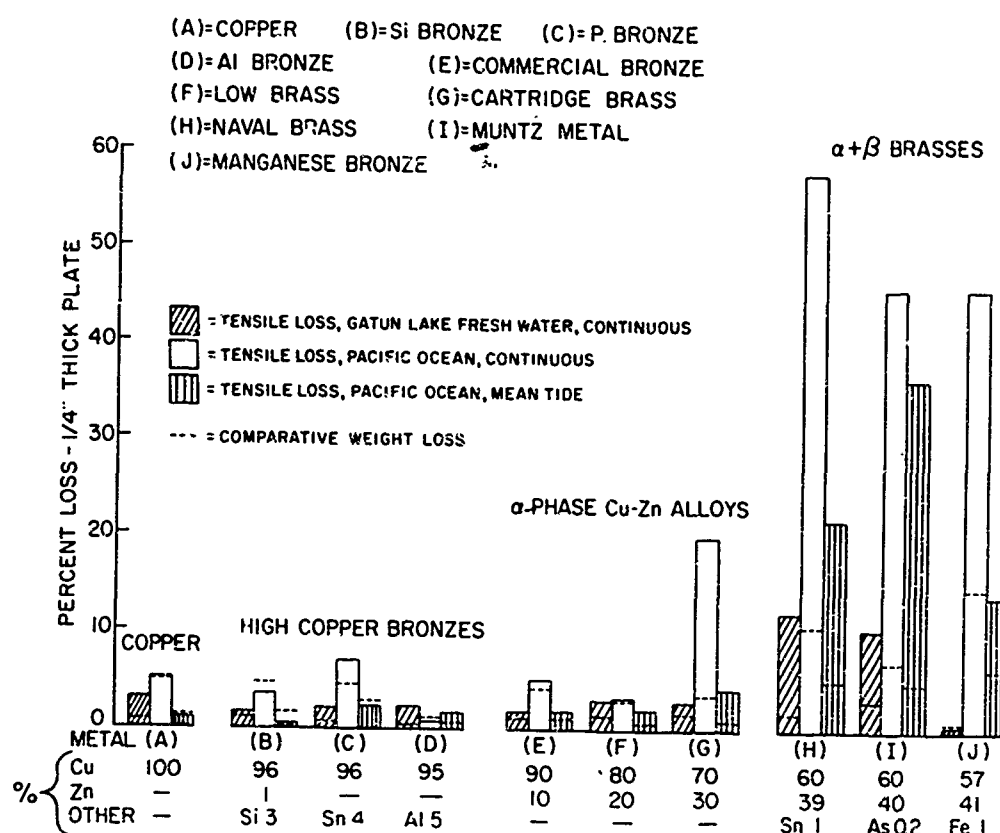


Fig. 8 - Tensile strength losses compared with weight losses for sixteen years' exposure in tropical waters

differences between tensile losses and weight losses for most of the two-phase brasses and for the 70-30 α brass in sea water indicate that heavy dezincification has developed in these metals.

For all the dezincified brasses, the penetrations indicated by tensile losses were 2.2 to 5.5 times the average penetrations calculated from weight loss. In the case of the uninhibited 70-30 α brass (metal G), weight loss from continuous sea-water immersion indicated no appreciable dezincification, but the high tensile loss reveals that by 16 years there was actually penetration to an average depth of 25 mils. The tensile data in this figure also suggest that some dezincification had occurred in two of the 60-40 brasses in fresh water. Naval brass (metal H) and Muntz metal (metal I) were penetrated to an average depth of 16 and 13 miles respectively after 16 years' immersion in Gatun Lake. However, the mild corrosion of manganese bronze in fresh water shown by weight loss was confirmed by equally low tensile loss. With the exception of this alloy-environment combination, all the 60-40 brasses showed some measurable dezincification in all environments and all alloying additions were ineffective in inhibiting dezincification of high-zinc brass.

Galvanic Effects

A large number of bimetallic couples were exposed in this 16-year investigation in both underwater and atmospheric environments. Underwater couples were made up of a 2 in. $\times$ 9 in. strip of one metal bolted to a 9 in. $\times$ 9 in. plate of a dissimilar metal. The area relation is 1 to 6.9. The undersea bimetallic couples containing a copper alloy as one

component of the couple were: copper < carbon steel,* naval brass < C steel, low brass < C steel, Al bronze < C steel, P bronze < Monel, P bronze < Cu-Ni, P bronze < 14 different ferrous metals, stainless 316 < naval brass, stainless 316 > P bronze, and C steel < each of the 10 copper-base metals. The complete results of all these combinations are much too detailed to present here but will be included in a subsequent report on bimetallic couples.

A few of the galvanic results of specific interest to this copper alloy report will be presented in the next two figures.

In Fig. 9 curves show the results for phosphor bronze and naval brass plates coupled to strips of 316 stainless steel. In both of these couples, the copper-alloy plates acted as anodes and their corrosion was galvanically accelerated by the more noble stainless. Normal corrosion of the copper alloy is shown by dashed lines so the galvanic effect can be assessed by comparison of the two. From this it can be seen that copper-alloy corrosion in tropical sea water will be accelerated by coupling with a metal only slightly more noble. Although this was only a 1 to 6.9 stainless steel to copper alloy area ratio, the weight loss corrosion of the copper-base metal plates was increased 42% for the bronze and 24% for the brass at 16 years. Had the area ratios favored the stainless steel, a highly accelerated attack on the copper alloys would probably have developed. In fact, when the area ratio was reversed with the phosphor bronze strip and stainless steel plate combination, the bronze strip corroded at about 24 times its normal rate. From these data it is apparent that under certain coupling conditions, copper alloys usually considered to be on the safe end of the galvanic series, can be susceptible to destructive galvanic attack in warm tropical sea water.

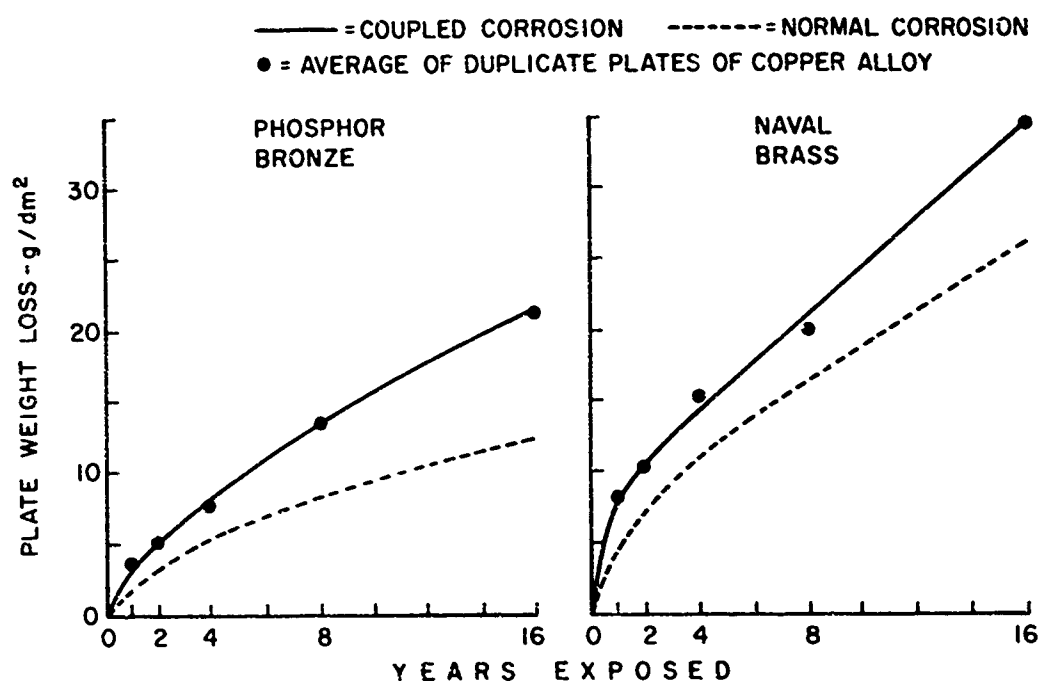


Fig. 9 - Galvanic corrosion for coupling with 1/7-area 316 stainless steel

*The "less than" sign (<) is used to indicate the metal having the lesser area.

In Fig. 10 the copper-alloy plates act as cathodes and are being protected by carbon steel strips with the 1 to 6.9 area ratio. Prolonged and efficient protection of the brass and bronze with mild carbon steel is indicated by these two curves. They show that the strip anodes lasted over 8 years for the brass plates and over 12 years for the bronze plates. In both cases, almost complete protection was afforded during the life of the anode.

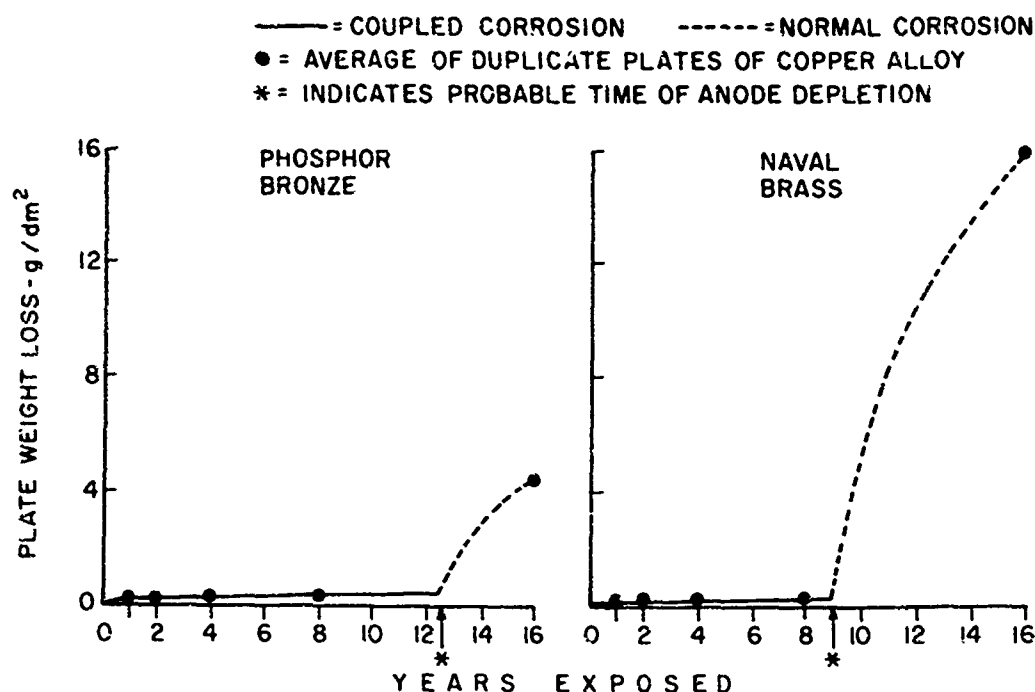


Fig. 10 - Cathodic protection of copper alloys under tropical sea water showing effectiveness and duration of protection with 1/7-area carbon steel strips

Biofouling of Copper Base Metals

Inspections and photographs of the marine fouling attachment on the sea water exposure panels were made at 9 months, 2 years, and 16 years. Normal fouling growth in both continuous and mean-tide immersion was very heavy at the Amador site. At the lower rack elevation, the attachment consisted of a multitude of organisms, with bryozoa, tunicates, mollusks, tubeworms, and barnacles among the more prevalent. At the mean tide location, the heavy coverage consisted almost entirely of barnacles, with some tubeworms.

Simple plates of copper had no fouling in 9 months and were fairly clear of fouling at the 2-year period but were moderately to heavily covered by 16 years. This loss in antifouling property was a result of the decreasing rate of corrosion of copper in sea water. LaQue and Clapp (16) have reported a copper solution rate of 5 mdd necessary for effective antifouling. With the empirical relation $1.5t^{1/2}$ found for copper in tropical sea water, 5 mdd loss would be exceeded for only the first 0.9 years (determined from the first derivative of the function with respect to time). At two years, the rate of copper solution has decreased to 3.4 mdd and by 16 years was only 1.2 mdd. All of the high-copper alloys showed decreased antifouling effectiveness with time of exposure. All had slight to no fouling at 9 months and 2 years but were moderately to heavily fouled at 16 years.

As would be expected, these same metals were very heavily fouled when galvanically protected, as the corrosion rate of copper was then much lower than required for effective

prevention. The dezincification of $\alpha + \beta$ brasses also presented a copper surface to which marine organisms attached readily. After two years of continuous immersion in sea water, the uniformly dezincified naval brass was covered completely by marine fouling, principally encrusting bryozoa. For the same exposure, the nonuniformly attacked arsenical Muntz brass had spots of fouling over darkened areas of the metal, which appeared to be the first areas of dezincification. At 16 years all the duplex brasses were completely covered with heavy biofouling attachment.

Atmospheric Corrosion of Copper Alloys

The effects of sixteen years' exposure in marine and inland tropical atmospheres is shown by weight-loss time curves in Fig. 11. These graphs are somewhat similar to the underwater curves in that the variety of patterns obtained for the different metal-environment combinations preclude the possibility of establishing a single empirical relation for the copper alloys in tropical atmospheres. However, there is considerably more similarity of curve patterns among the atmospheric results than among the underwater exposures. The six alloys containing zinc and the aluminum bronze produced weight-loss time relations sufficiently similar in magnitude and shape to fit into the bands shown by the crosshatched areas in this figure. The only significant difference for the metals contained in the band was in the first 1 to 2 years, after which all corroded at almost constant and equal rates. The median rates for the bands are $0.05 \text{ g/dm}^2 - \text{yr}$ for marine atmosphere and $0.04 \text{ g/dm}^2 - \text{yr}$ for the inland site.

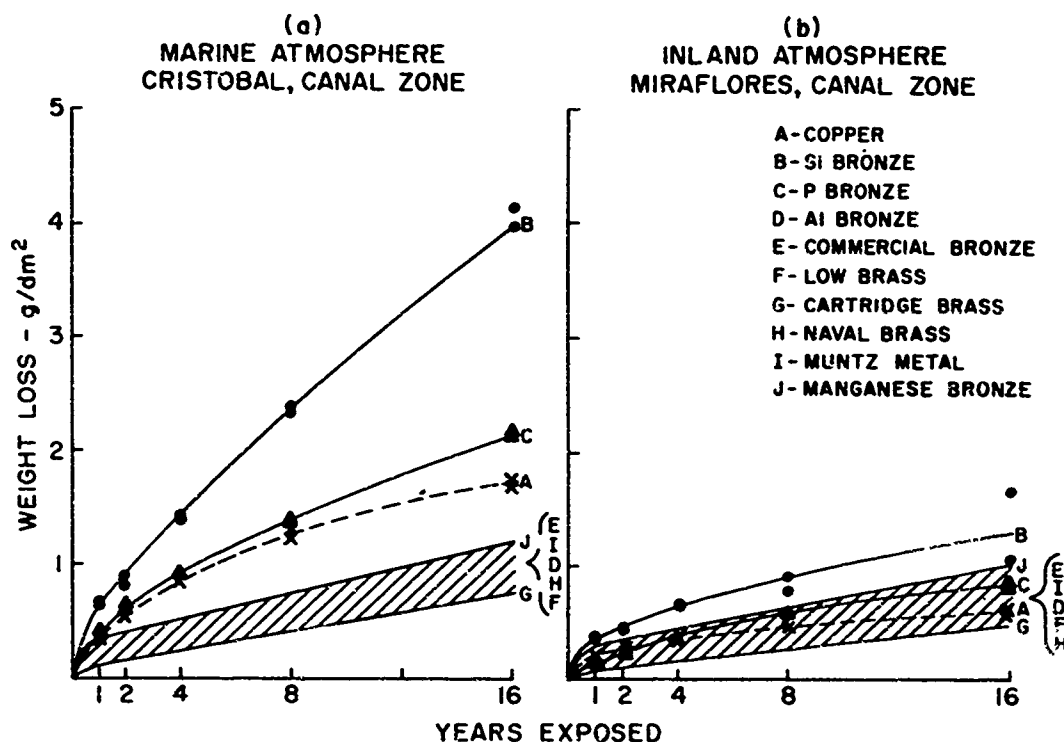


Fig. 11 - Corrosion weight loss as a function of time for copper-base metals exposed to tropical atmospheres

Percent tensile losses for the ten cupreous metals in the two atmospheres are included in Table 1. The data are based on percent loss of the 62.5-mil-thick atmospheric sheets. When converted to one average surface penetration, the 16-year values range from 0.75

mil for Al bronze to 2.6 mils for arsenical 60-40 brass. Compared to weight losses, tensile results show that some dezincification was sustained by the 60-40 $\alpha + \beta$ brasses and a slight amount by the 70-30 α brass. After 16 years' exposure, penetrations indicated by tensile loss averaged 4.8 times the penetrations from weight loss for the duplex brasses, and 3.3 times for the 70-30 brass.

On a practical basis, all of the copper metals were very resistant to tropical atmospheres, and can be considered excellent for long-term exposure in this environment. There are, however, relative differences between some of the metals which, when extrapolated to long exposure periods, are revealed to be of some significance. This can be seen in the probable 50-year corrosion penetrations shown in Table 3 for a representative number of the copper alloys.

Table 3
Probable Corrosion Penetrations at 50 Years

Metal	Probable Penetration at 50 years (mils*)	
	Marine Atmosphere	Inland Atmosphere
Copper (A)	1.45	0.54
Si bronze (B)	5.06	1.66
P bronze (C)	3.17	0.84
Al bronze (D)	1.26	0.99
80-20 Brass (F)	1.21	0.94
Naval brass (H) 60-39-1 Sn	32.4†	4.95†

*Obtained by extrapolation of 16-year weight loss curves.

†Includes tensile correction.

All of these values are much lower than results determined with the commonly used one-period secant rates. For example, the one-year rate for the low brass in this marine atmosphere is 0.19 mpy and the rate based solely on the 8-year samples is 0.11 mpy. With these rates, 50-year penetration predictions would be 9.50 mils or 5.50 mils respectively, which is appreciably higher than the 1.21 mils predicted from the 16-year curves.

Industrial contamination, or excessively high salt content in the air, such as would occur near a surf beach, will cause higher corrosion rates of copper alloys than the losses reported here. But excluding such specific contaminated conditions, these tropical losses are probably near the upper limit of the corrosion range of copper-base metals in natural atmospheres and should be useful as a safe estimate of the atmospheric corrosion of copper alloys in any latitude.

CONCLUSIONS

Copper and copper alloys exposed to tropical sea water had corrosion weight losses 1.4 to 2 times higher than losses in temperate sea water on the east and west coasts of the United States. Tropical marine atmospheres also caused higher weight losses to cupreous metals. Mean tide exposure at Fort Amador, C.Z., generally was less aggressive than temperate climate mean tide exposures.

Because of distinctly different patterns for the corrosion-time curve, a general empirical equation for the copper-base metals was not feasible, but the corrosion of commercially pure copper in sea water during 16 years was found to be approximately

proportional to $Ct^{1/2}$. Corrosion-time functions for the other high-copper and α phase copper-zinc alloys were generally curvilinear for the first 4 to 8 years' exposures. Extrapolation of the curves emphasize the unreliability of the normally used short-term secant rates for predicting long-term corrosion of the copper metals. Errors as much as one order of magnitude are probable in estimating loss over 50 years' exposure.

In the different tropical environments 5% Al bronze had the best overall corrosion resistance. Sixteen years' loss was 1/2 that of copper in fresh-water immersion, 1/3 at mean-tide immersion, and 1/5 in continuous sea-water immersion. In the tropical atmospheres, the Al bronze was also excellent, having 1/2 the sixteen-year loss of copper at the marine site and very low corrosion, equal to copper in the inland atmosphere.

Alpha-phase copper-zincs had slightly higher losses than copper in fresh water and equal to or somewhat lower than copper in the two sea-water and two atmospheric exposures.

The 60-40 $\alpha + \beta$ brasses had considerably higher weight losses than copper in all underwater exposures, except manganese bronze in fresh water, where the results approximated the copper losses.

Heavy dezincification occurred on all the $\alpha + \beta$ brasses in the two sea-water exposures and a moderate amount was revealed for these duplex brasses in fresh water and marine atmospheric exposures. The small additives of arsenic, tin, and manganese were ineffective in inhibiting marine dezincification of high brasses.

Tensile tests generally confirmed weight losses for the high-copper alloys but revealed heavy dezincification in the duplex brasses with penetrations 2.2 to 5.5 times that shown by weight loss for the sea-water exposures.

Galvanic effects of bimetallic coupling were pronounced under tropical sea water. Corrosion of plates of P bronze and naval brass was anodically accelerated 42% and 24% by weight loss when coupled with 1/7-area strips of type 316 stainless steel. Coupling plates of the same copper alloys with strips of carbon steel provided efficient cathodic protection of the bronze and brass and the 1/7-area carbon steel anodes lasted 8 to 12 years.

Copper and copper alloys showed varying degrees of fouling resistance in the bioactive tropical waters. Marine fouling collected directly on copper panels when the corrosion rate of the copper was too low to provide an effective concentration of copper ions. Thus, galvanically protected copper metals, including dezincified surfaces, were moderately to heavily covered at the 2-year inspection. Simple plates of copper and high-copper alloys showed decreasing fouling resistance with time of exposure. The loss in antifouling was proportional to the decreasing corrosion rates of the metals. Panels that rated trace to slight fouling at 2 years with corrosion rates of 3 to 4 mdd were moderately to heavily covered at 16 years, when rates were down to 1 to 2 mdd.

Corrosion of all the cupreous metals in the tropical atmospheres was very low, and they can be considered excellent for long-term service in this environment. Al bronze and copper zinc alloys corroded linearly with time after 1 or 2 years' exposure in the atmospheres at approximate rates of 0.05 g/dm²-yr at the marine site and 0.04 g/dm²-yr at the inland location.

ACKNOWLEDGMENTS

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REFERENCES

1. Alexander, A.L., Forgeson, B.W., Mundt, H.W., Southwell, C.R., and Thompson, L.J., "Corrosion of Metals in Tropical Environments, Part 1 - Test Methods Used and Results Obtained for Pure Metals and a Structural Steel," NRL Report 4929, June 1957; Corrosion 14:73t (1958)
2. Southwell, C.R., Forgeson, B.W., and Alexander, A.L., "Corrosion of Metals in Tropical Environments, Part 2 - Atmospheric Corrosion of Ten Structural Steels," NRL Report 5002, Dec. 1957; Corrosion 14:435t (1958)
3. Forgeson, B.W., Southwell, C.R., and Alexander, A.L., "Corrosion of Metals in Tropical Environments, Part 3 - Underwater Corrosion of Ten Structural Steels," NRL Report 5153, Aug. 1958; Corrosion 16:105t (1960)
4. Southwell, C.R., Forgeson, B.W., and Alexander, A.L., "Corrosion of Metals in Tropical Environments, Part 4 - Wrought Iron," NRL Report 5370, Oct. 1959; Corrosion 16:512t (1960)
5. Alexander, A.L., Southwell, C.R., and Forgeson, B.W., "Corrosion of Metals in Tropical Environments, Part 5 - Stainless Steels," NRL Report 5517, Sept. 1960; Corrosion 17:345t (1961)
6. Southwell, C.R., Hummer, C.W., and Alexander, A.L., "Corrosion of Metals in Tropical Environments, Part 6 - Aluminum and Magnesium," NRL Report 6105, Dec. 1964; Materials Protection 4(No. 12):30-35 (1965)
7. Materials Corrosion Investigation at Eastport, Maine, Fifth Interim Report, U.S. Engineer Office, Boston, Mass. (1946)
8. LaQue, F.L., "Behavior of Metals and Alloys in Sea Water," Corrosion Handbook, New York, Wiley, pp. 383-430, 1948
9. Brouillette, C.V., "Corrosion Rates in Sea Water at Port Hueneme, Calif.," Project NY 450-004-1, Technical Note 194, Oct. 5, 1954
10. "Symposium on Atmospheric Corrosion of Non-Ferrous Metals," Am. Soc. Testing Mater., Spec. Tech. Publ., No. 175, 1955
11. Ambler, H.R., and Bain, A.A.J., "Corrosion of Metals in the Tropics," J. of Appl. Chem. 5:437-467 (1955)
12. May, T.P., personal correspondence
13. A. S. M. Committee on Corrosion of Copper "Corrosion of Wrought Copper and Copper Alloys," Metals Handbook, Vol. 1, 8th ed. Novelty, Ohio American Society for Metals, p. 986, 1961

14. Bulow, C.L., "Use of Copper Base Alloys in Marine Service," Naval Engineers Journal 77:470-482 (June 1965)
15. Rogers, T.H., "The Marine Corrosion Handbook," New York, McGraw-Hill, p. 135, 1960
16. LaQue, F.L. and Clapp, W.F., "Relationships Between Corrosion and Fouling of Copper-Nickel Alloys in Sea Water," Trans. Electrochemical Society pp. 87, 103 (1945)

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 - A4 and Fig. 1 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.

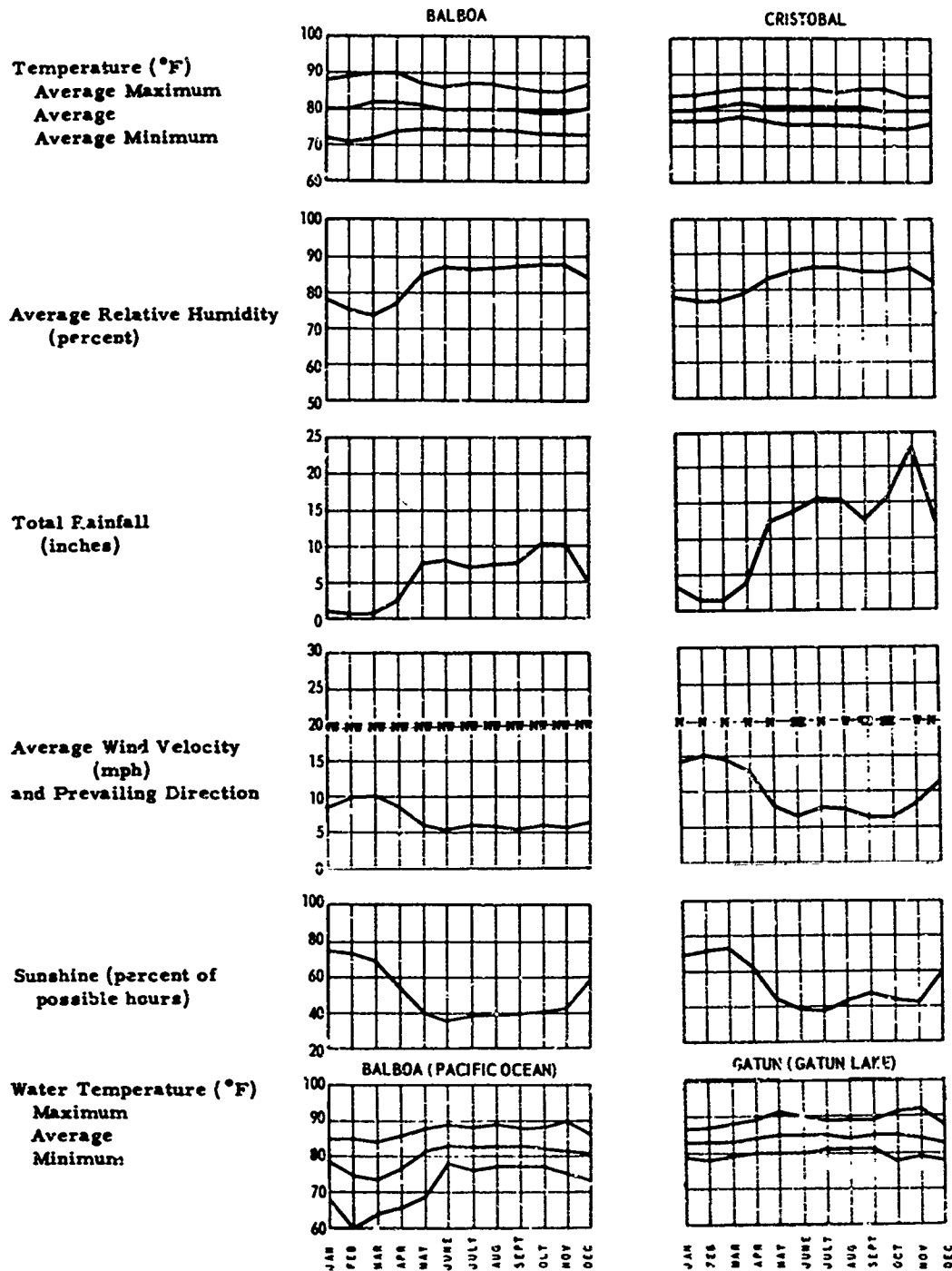


Fig. A1 - Canal Zone climatic conditions
(average records, 20 years minimum)

Table A1
Chemical Composition of Test Metals

Metal Code	Type	Specification	Proximate Chemical Composition (wt.-%)											
			Cu	Zn	Mn	P	S	Si	As	Fe	Al	Sn	Pb	Ni
Submerged Metals														
A	Copper	QQ-C-501a, Class A, Soft	99.92	-	-	-	0.001	-	-	0.002	-	-	-	-
B	Silicon bronze	QQ-C-591a, Class A, 1/2 Hard	96.30	-	None	-	-	2.64	-	0.04	-	-	Trace	None
C	Phosphor bronze	QQ-B-746, IV, Grade A, 1/2 Hard	95.54	0.30	-	0.25	-	-	-	0.01	-	4.21	0.048	-
D	Aluminum bronze	QQ-B-666, IV, Grade A, 1/2 Hard	94.84	0.01	-	-	-	-	-	0.08	5.07*	-	-	-
E	Commercial bronze	ASTM B-36-41T, No. 2, 1/2 Hard	90.50	9.46*	-	-	-	-	-	0.007	-	-	0.030	-
F	Low brass	ASTM B-30-43T, No. 4, 1/2 Hard	80.00	19.96*	-	-	-	-	-	0.04	-	-	0.049	-
G	Cartridge brass	QQ-B-611a, Comp. E., 1/2 Hard	70.07	29.89*	-	-	-	-	-	0.04	-	-	None	-
H	Naval brass	QQ-B-636, Class A, 1/2 Hard	59.87	39.41*	-	-	-	-	-	0.05	-	0.58	0.09	-
I	Muntz metal	ASTM B-171-42, (0.2% As)	59.98	39.35*	-	-	-	-	0.19	0.048	-	0.022	0.41	-
J	Manganese bronze	QQ-B-721a, Class A, 1/2 Hard	57.32	40.77*	0.09	-	-	-	-	1.12	0.10	0.50	0.10	-
Atmospheric Metals														
a	Copper	QQ-C-501A, Class A, soft	99.94	-	-	-	-	-	-	-	-	-	-	-
b	Silicon bronze	QQ-C-591A, Class A, 1/2 hard	96.14	0.54	0.08	-	-	2.90	-	0.05	-	None	None	None
c	Phosphor bronze	QQ-B-746, Type V, Grade A, S.T.	95.10	None	0.07	0.36	-	-	-	0.04	-	4.38	None	-
d	Aluminum bronze	QQ-B-666, Grade A, Type V	95.68	-	-	-	-	-	-	0.03	3.77	-	0.01	0.050
e	Commercial bronze	ASTM B-36-41T, No. 2, 1/2 hard	80.68	10.31*	-	-	-	-	-	0.007	-	-	0.004	-
f	Low brass	ASTM B-30-43T, No. 4, 1/2 hard	80.06	19.90*	-	-	-	-	-	0.03	-	-	0.016	-
g	Cartridge brass	QQ-B-611A, Comp E, 1/2 hard	70.00	29.96*	-	-	-	-	-	0.02	-	-	0.024	-
h	Naval brass	QQ-B-636, Class A, 1/2 hard	60.08	39.02*	-	-	-	-	-	0.04	-	0.84	0.02	-
i	Muntz metal	ASTM B-171-42 (0.2% As)	59.95	38.87*	-	-	-	-	0.19	0.01	-	0.022	0.76	-
j	Manganese bronze	QQ-B-721A, Class A, 1/2 hard	57.86	40.25*	-	-	-	-	-	1.04	0.12	0.65	0.02	-

Note: * Values obtained by difference

Table A2
Physical and Mechanical Properties of Test Metals

Metal Code	Material	Physical Properties			Mechanical Properties					
		Temper	Grain Size (dia. - mm)	Density (g/cc)	Ultimate Tensile Strength (psi)	Yield Strength 0.2% Offset (psi)	Elongation (% for 2 in.)	Hardness (BHN) with 500 kg	Free Bend	
									Elong. (%)	Final Cond.
Submerged Metals (nominal thickness, 1/4 in.)										
A	Copper	Soft	0.035	8.91	31,570	7,880	51	45	50	Good
B	Silicon bronze	1/2 hard	0.035	8.58	71,300	56,570	32	147	50	Checked
C	Phosphor bronze	1/2 hard	0.090	8.90	58,070	54,000	31	130	50	Checked
D	Aluminum bronze	1/2 hard	0.045	8.20	59,730	38,330	58	135	50	Good
E	Commercial bronze	1/2 hard	0.025	8.80	51,000	49,870	15	110	50	Cracked
F	Low brass	1/2 hard	0.025	8.66	63,870	59,170	17	111	50	Checked
G	Cartridge brass	1/2 hard	0.090	8.53	58,730	51,100	29	123	50	Checked
H	Naval brass	1/2 hard	0.025	8.39	69,000	43,630	35	115	33	Cracked
I	Muntz metal	1/4 hard	0.015	8.36	57,570	23,770	49	82	50	Good
J	Manganese bronze	1/2 hard	0.025	8.38	73,330	38,600	32	128	17	Cracked
Atmospheric Metals (nominal thickness, 1/16 in.)										
a	Copper	Soft	0.035	8.91	31,530	14,300	45	-	-	-
b	Silicon bronze	1/2 hard	0.035	8.56	66,030	40,230	47	-	-	-
c	Phosphor bronze	Spring	0.045	8.89	103,170	95,070	5	-	-	-
d	Aluminum bronze	1/2 hard	0.045	8.36	64,330	55,970	18	-	-	-
e	Commercial bronze	1/2 hard	0.025	8.79	46,770	43,530	16	-	-	-
f	Low brass	1/2 hard	0.065	8.65	51,000	44,000	29	-	-	-
g	Cartridge brass	1/2 hard	0.035	8.52	64,330	55,330	22	-	-	-
h	Naval brass	1/2 hard	0.045	8.41	65,900	41,400	26	-	-	-
i	Muntz metal	1/4 hard	0.015	8.40	55,070	24,000	46	-	-	-
j	Manganese bronze	1/2 hard	0.035	8.37	72,030	40,370	26	-	-	-

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
Elec. conductivity (mhos $\times 10^{-3}$ at 81°F)	0.12	0.091	0.11	51.7	21.3	42.2	51.7	35.4
Total dissolved solids (ppm)	165	69	113	42,776	22,613	35,832	41,480	26,390
Total suspended solids (ppm)	23	0.0	7.6	220	0	84	173	0
Turbidity (ppm)	<5	<5	<5	20	<5	<5	25	<5
Oxygen saturation (percent)	98	78	90	105	62	90	103	64
Oxygen consumed (ppm)	2.4	0.7	1.4	2.5	0.6	1.6	2.6	0.4
Biochemical oxygen demand (ppm)	2.2	0.1	1.0	3.4	0.2	1.6	2.3	0.0
pH (colorimetric)	8.0	6.9	7.5	8.4	7.8	8.2	8.4	7.8
Organic and volatile matter (ppm)	65	6.6	34	10,379	2,150	6,226	10,632	2,759
Sulfate (ppm)	7.2	0.0	2.6	3,240	1,590	2,431	3,177	1,637
Chloride (ppm)	12.5	0.0	7.0	20,098	11,300	17,415	19,949	10,379
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

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		2b. GROUP
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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research) and Department of the Army	
13. ABSTRACT The corrosion of copper and nine wrought copper alloys is reported for exposures in five tropical environments for one, two, four, eight, and sixteen years. Weight loss, pitting, and change in tensile strength were measured to evaluate corrosion resistance. Higher corrosion rates are shown for tropical sea water immersion and tropical marine atmosphere than similar exposures in temperate climates. Of the various alloys studied, 5% Al bronze showed the highest general corrosion resistance; its 16-year losses in sea water were only 1/5 that of copper. Copper and the high-copper alloys were resistant to all environments and generally had decreasing corrosion rates with time of exposure. Tensile tests revealed heavy dezincification in the lower-copper brasses when exposed in marine environments, and for two of the brasses in fresh water immersion. As a result of the decreasing corrosion rates or dezincification, antifouling properties of copper alloys decreased with time of exposure. All were moderately to heavily fouled after 16 years in sea water. Galvanic effects were pronounced in tropical sea water. The corrosion of copper alloys was accelerated appreciably by contact with stainless steel (316) of 1/7 their area, while similar carbon steel strips gave effective cathodic protection of plates of brass and bronze over the long term. Tropical atmospheric corrosion of cupreous metals was generally very low, but dezincification of $\alpha + \beta$ brasses caused average penetrations three to five times greater than alloys of less than 20% zinc content.		

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Copper						
Copper alloys						
Corrosion						
Sea water						
Zinc						
Brass						
Marine biology						
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