

CORROSION

in Natural Waters

C. H. Baloun, editor



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The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution of time and effort on behalf of ASTM.

Foreword

The symposium on Corrosion in Natural Waters was held in Atlanta, Georgia, 8 Nov. 1988. The symposium was sponsored by ASTM Committee G01 on the Corrosion of Metals. Calvin H. Baloun, Ohio University, presided as symposium chairman and is editor of this publication. W. W. Kirk, LaQue Center for Corrosion Technology Inc., presided as symposium cochairman.

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Overview

The origin of the symposium on Corrosion in Natural Waters occurred with the need for a vehicle to present the three-year interim results of the World-Wide Variability of Seawaters study.

Over the past decade or more many papers have been presented concerning degradation of metallic materials in natural or nearly natural waters. Symposia have been sponsored by groups involved in Off Shore Technology, Pipelines, Petroleum and Natural Gas, Waterworks Associations, Nuclear Waste Storage, and other specialized interest areas. Unfortunately, some worthwhile research tends to slip through the cracks between these areas and not be presented.

This symposium has offered a receptacle for a varied collection of research presentations in a timely fashion and should thus be of value to the corrosion community.

Well deserved thanks go to W. W. Kirk as cochairman of this symposium and one of the presenters, to the other authors and presenters, and to the reviewers who devoted much time and effort to these thankless tasks.

Calvin H. Baloun

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symposium chairman and editor.

Seawater Corrosivity Around the World: Results from Three Years of Testing

REFERENCE: Kirk, W. W. and Pikul, S. J., "Seawater Corrosivity Around the World: Results from Three Years of Testing," *Corrosion in Natural Waters, ASTM STP 1086*, C. H. Baloun, Ed., American Society for Testing and Materials, Philadelphia, 1990, pp. 2-36.

ABSTRACT: A world-wide test program was undertaken by Task Group G1.09.02.03 to assess the relative corrosivity of seawater at 14 test sites. Aluminum alloy A95086, copper-nickel alloy C70600, and carbon steel alloy K01501 specimens were prepared at one location, shipped to the various sites, and returned to the original site for final evaluations. Results obtained through three years of testing indicate that average corrosion behavior was generally within limits of previously published results. Individual site characteristics have been identified, however, that can have a profound effect on test results. Even when the ASTM standard test method was prescribed, variations affecting corrosion results became evident. In reality there is no natural seawater environment, as identified to date, in which to test materials. The final five year results are yet to be collected, but the cooperation of all program participants has contributed much toward accomplishment of the objectives. Still, more frequent and broader monitoring of seawater variables at the exposure sites would assist in interpreting corrosion results.

KEY WORDS: seawater, world-wide, aluminum, copper-nickel, steel, localized corrosion, fretting, velocity, biofouling

Within ASTM Subcommittee G1.09 on Corrosion in Natural Waters, a task group (G1.09.02.03) was appointed in 1980 to organize a world-wide series of seawater corrosion evaluations. The objective of the task group was to apply existing standards for conducting corrosion tests in natural waters to compare the relative corrosivities of natural coastal sites around the world. This was to be accomplished via the exposure of aluminum alloy A95086, copper-nickel alloy C70600, and K01501 steel specimens at the 14 test sites listed in Table 1 and shown on a world map (Fig. 1). A five-year exposure program was initiated with duplicate removals scheduled for 0.5, 1, 3, and 5 year durations. The LaQue Center for Corrosion Technology, Inc. agreed to handle the initiation of the program as well as the final evaluations. This report covers results through three years of testing.

Experimental Procedure

Test Method

The test program was conducted according to the guidelines provided in ASTM Recommended Practice for Conducting Surface Seawater Exposure Tests on Metals and Alloys (G 52). One exception occurred at the Hawaii site where test panels were exposed horizontally

¹ President and senior technical supervisor, LaQue Center for Corrosion Technology, Inc., Post Office Box 656, Wrightsville Beach, NC 28480.

TABLE 1—*Test sites for world seawater corrosivity evaluations.*

Site	Contact
Ocean City, New Jersey Bar Graph Code: NJ	G. A. Gehring, Jr. Ocean City Research Corporation
Wrightsville Beach, North Carolina Bar Graph Code: NC	S. J. Pikul LaQue Center for Corrosion Technology, Inc.
Key West, Florida Bar Graph Code: FL	M. H. Peterson U.S. Naval Research Laboratory
Freeport, Texas Bar Graph Code: TX	C. Arnold The Dow Chemical Company
Port Hueneme, California Bar Graph Code: CA	J. F. Jenkins U.S. Naval Civil Engineering Laboratory
Talara, Peru Bar Graph Code: PE	K. D. Efrid Occidental Oil and Gas Company
KeAhole, Kona, Hawaii Bar Graph Code: HI	J. Larsen-Basse/T. Daniel University of Hawaii at Manoa
Australia, North Barnard Islands Bar Graph Code: AU	J. J. Batten Materials Research Laboratories
Sakata Harbor, Japan Bar Graph Code: JA	S. Sato Sumitomo Light Metal Industries, Inc.
Genoa, Italy Bar Graph Code: IT	E. Mor Istituto per la Corrosione Marina dei Metalli-del C.N.R.
Sjælland, Denmark Bar Graph Code: DE	H. Arup Korrosionscentralen, ATV
Studsvik, Sweden Bar Code: ST	S. Henrikson/E. Mattsson Swedish Corrosion Institute
Bohus-Malmon, Sweden Bar Code: BM	S. Henrikson/E. Mattsson Swedish Corrosion Institute
Isle of Wight, England Bar Code: EN	P. E. Francis National Physical Laboratory

rather than vertically, affixed to a nonmetallic pipe resting on the seabed. Environmental characteristics provided by the participants at all sites are summarized in Table 2. Initial exposure times and average seawater temperatures for each test period are given in Table 3.

Test Materials

The materials used in the tests are listed in Table 4 with their compositions. Specimens (6 by 100 by 300 mm) of each material were supplied as-sheared to size and were notch coded for identification (Fig. 2). Table 5 outlines the cleaning procedures used for each material. Following cleaning, specimens were weighed to the nearest 0.1 g.

Test Racks

Specimens were mounted on metallic test racks using nylon bolts and washers for electrical isolation (Fig. 3). The bolts were tightened to a torque of 1.7 nm. Eight specimens of each material were affixed to three individual racks for exposure at each site. The A95086 aluminum specimens were mounted on a 1.3-m-long aluminum alloy test rack. Two Ni-Cu

TABLE 2—Worldwide seawater exposure site characteristics.

Site	Rack Location	Range of Environmental Constituents ^a			
		Dissolved Oxygen, ppm	Salinity, ppt	Temperature, °C	pH
Ocean City, NJ	from raft .3 m below surface	5.2 to 11.7	31 to 34	1 to 29	7.5 to 8.2
Wrightsville Beach, NC	from wharf in channel	5.0 to 9.6	31.8 to 37.6	7 to 30	7.9 to 8.2
Banks Channel					
Key West, FL	under pier	4 to 8	33 to 39	16 to 31	8.0 to 8.2
Fleming Key					
Freeport, TX	intake flume	1.5 to 6.0	11.7 to 19.4 ^b	15 to 27	7.5 to 8.6
Port Hueneme, CA	from bulkhead	3.6 to 5.3	33	14 to 21	7.9 to 8.1
Port Hueneme Harbor					
Talara, Peru	from pier 180 m from shore	5 to 6	19.8 ^b	18 to 22	8.2
Keahole, Kona, Hawaii	45 m from shore on pipe	6 to 14	34.6 to 35	24 to 28	8 to 8.3
Australia	from raft	5.1 to 6.5	31.7 to 37.2	23 to 30	8 to 8.5
North Barnard Islands					
Japan	off docking pier	7.1 to 13	16.8 to 18.3 ^b	2 to 28	8.4
Sakata Harbor					
Italy	from raft	4.5 to 6.0	35	11 to 25	8.1
Genoa Harbor					
Denmark	from raft in Fjord	NA ^c	18 to 28	0 to 18	7.5 to 8.0
Kyndby Isefjord					
Sweden					
Studsvik (Baltic Sea)	from wooden bulkhead	6 to 10	7.8 to 8.1	2 to 20	7.4 to 7.6
Bohus-Malmon (North Sea)	from raft	6 to 10	21 to 28	2 to 20	8.0 to 8.2
England	from raft	88 to 118 ^d	34 to 34.6	5 to 22	7.8 to 8.4
Langstone Harbour					

^a compiled from information provided by participants.^b Chlorinity, g/L.^c NA = not available.^d % saturation.



FIG. 1—Approximate location of exposure sites.

TABLE 3—Summary of average seawater temperatures at test sites.

Test Site	Initial Exposure Date	Average Seawater Temperatures, °C		
		0.5 year Exposure	1.0 year Exposure	3.0 year Exposure
Ocean City, NJ	July 1983	15 ^a	15.2	14.7
Wrightsville, Beach, NC	May 1983	25.2	19.5	20.1
Key West, FL	May 1983	28	22 ^a	22 ^a
Freeport, TX	Oct. 1983	16 ^a	22 ^a	22 ^a
Port Hueneme, CA	May 1983	17.4	16 ^a	16 ^a
Talara, Peru	March 1984	NA ^b	NA ^b	20
KeAhole, Kona, Hawaii	July 1983	NA ^b	NA ^b	26 ^a
Australia	July 1986	...	26 ^a	...
Sakata Harbor, Japan	Aug. 1983	5 ^a	18 ^a	18 ^a
Genoa, Italy	Sept. 1983	17.1	17.7	17.7
Sjælland, Denmark	Oct. 1983	5 ^a	9 ^a	9 ^a
Studs vik, Sweden	Aug. 1983	5 ^a	10 ^a	10 ^a
Bohus-Malmon, Sweden	Aug. 1983	5 ^a	10 ^a	10 ^a
Isle of Wight, England	Aug. 1983	10 ^a	14 ^a	14 ^a

^a Estimated based on general environmental characteristics provided about test site.^b NA = no information available.

TABLE 4—*Test materials chemical analyses.*

Alloy	Composition, weight %		Supplier
A95086 (H116 temper)	0.14 Si		Kaiser Aluminum and Chemical Corporation (T. J. Summerson)
	0.33 Fe		
	0.030 Cu		
	0.57 Mn		
	3.89 Mg		
	0.13 Cr		
C70600 (hard)	BAL Al		Revere Copper Products, Inc. (B. S. Vagnoni)
	9.44 Ni		
	1.40 Fe		
	0.29 Mn		
	0.008 P		
	0.007 S		
K01501 (copper-bearing carbon steel)	BAL Cu		Armco, Incorporated (H. H. Lawson)
	0.046 C	<0.006 Ti	
	0.32 Mn	0.008 Al	
	0.006 P	<0.002 Cb	
	0.009 S	<0.0001 B	
	0.003 Si	<0.002 Zr	
	0.19 Cu	0.004 Co	
	0.019 Ni	<0.006 Pb	
	0.020 Cr	<0.004 Te	
	<0.002 Sn	<0.004 Ce	
	<0.004 V	0.0004 As	
	0.011 Mo		

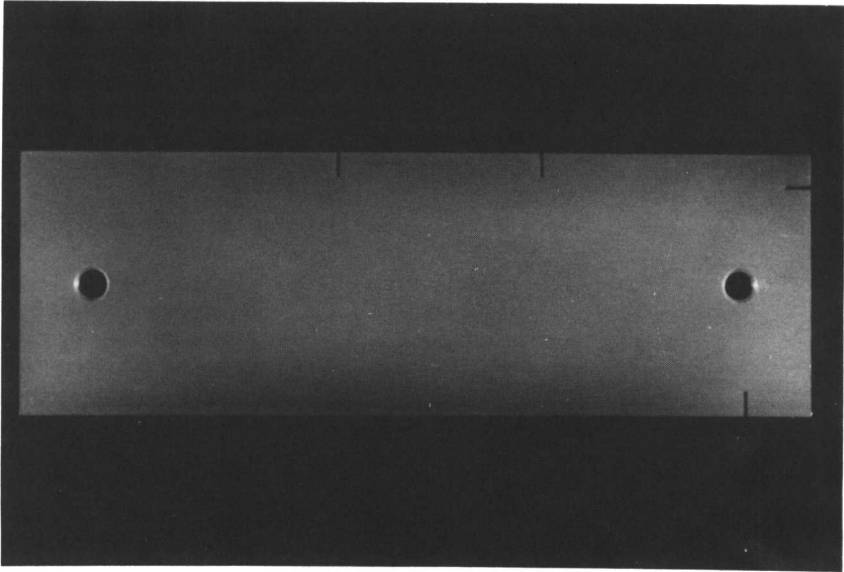


FIG. 2—*Appearance of aluminum alloy A95086 prior to exposure.*

TABLE 5—*Cleaning procedures for test specimens.^a*

A95086
Acetone degrease 30% HNO ₃ pickle (3 min) Water rinse Pumice scrub ^b Water rinse Alcohol rinse Dry with towel Forced hot air dry Oven dry at 120°C
C70600
Acetone degrease Water rinse Pumice scrub (light) ^b Water rinse 10% H ₂ SO ₄ pickle (3 to 5 min) Water rinse Pumice scrub Water rinse Alcohol rinse Dry with towel Forced hot air dry Oven dry at 120°C
K01501
Sand blasted 100% HCl pickle (15 to 45 min) Water rinse Pumice scrub ^b Water rinse Alcohol rinse Acetone rinse Dry with towel Forced hot air dry Oven dry at 120°C

^a All specimens were lightly scraped to remove marine biofouling and loose corrosion products. This was followed in each case by pickling, pumice and detergent scrubbing and the remainder of the cleaning procedure. No detectable mass loss was noted on control specimens in any pickling treatment.

^b Prior to exposure.

alloy 400 test racks (1.3 m long) were used to separately accommodate the C70600 copper-nickel and K01501 steel specimens.

Eyebolts were affixed to the racks to allow rope support from a fixed structure at each site. The test racks with specimens already mounted were wrapped in plastic with two enclosed cotton bags of desiccant, crated, and shipped to each test site.

Exposures

At each of the 14 test sites, test racks were to be retrieved for removal of two specimens of each alloy after 0.5, 1, 3, and 5 years. Upon removal, specimens were lightly brushed/scraped

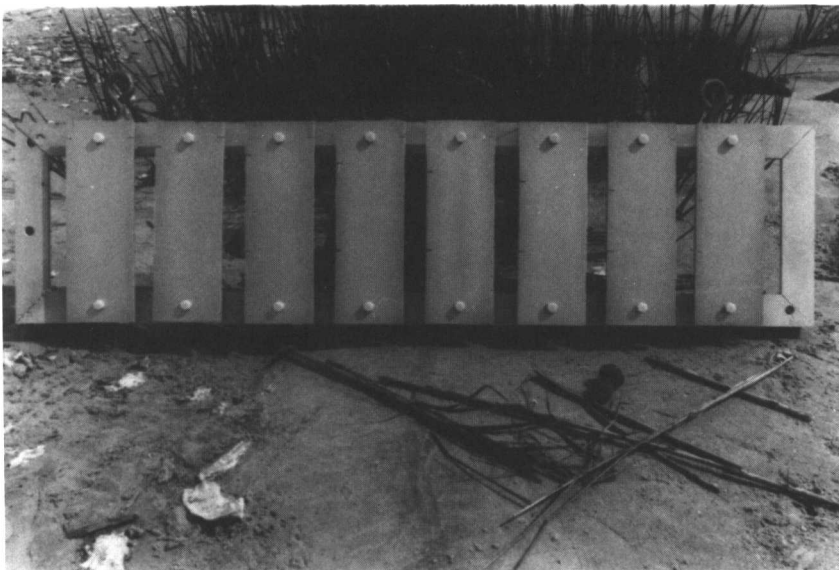


FIG. 3—Assembled test rack prior to exposure.

to remove excessive biofouling, packaged, and returned to the LaQue Center for evaluation. Photographic documentation of specimens and environmental monitoring were performed at those sites where feasible.

Evaluations

Upon receipt of specimens from each site, the “before-cleaning” appearance was photographically documented. Specimens were then cleaned of corrosion products and any biofouling attachments using the following procedures according to ASTM Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens (G1-88):

- for A95086—ambient temperature, 30% nitric acid (concentrated acid is preferred, but many tests have shown no detectable mass loss on controls within three minutes immersion)
- for C70600—ambient temperature, 10% sulfuric acid
- for K01501—ambient temperature, 100% hydrochloric acid inhibited with antimony trioxide

Further details of the cleaning procedures are given in Table 5.

Weighing of specimens for mass loss determinations was then performed (± 0.1 g) and measurements of thickness loss or localized attack were obtained using a micrometer (± 0.01 mm) or depth gage (± 0.01 mm), respectively. Selected specimens were also photographed after cleaning to illustrate variations observed in the type or extent of corrosion.

Results and Discussion

Corrosion data for each material and exposure time are summarized in Table 6, indicating a rather wide range in both corrosion rates and depths of localized attack. To enable detailed examination and comparisons within and among the 14 test sites, data for each of the 240 specimens removed to date are tabulated in the Appendix, Tables 7 through 20. It should be noted that the original set of specimens sent to Australia were lost in a cyclone and a replacement set was provided. Their late entry into the program, therefore, yields only one-year results at this time.

Aluminum Alloy A95086

Aluminum-magnesium alloys (5000 series) generally have good resistance to both general and localized corrosion in seawater [1]. Some pitting or crevice corrosion, however, can be expected but the extent of such attack in surface seawater will be affected by a number of factors, including oxygen content, temperature, velocity, and crevices such as those areas shielded by the attachment of biofouling organisms or deposits of sand or silt [1,2,3]. Since the corrosion resistance depends upon the maintenance of a passive oxide film, aluminum-magnesium alloys would be expected to be most resistant in seawater that is well aerated, for example near the ocean surface. It is of interest, therefore, to note the variations in corrosion behavior from one site to another.

Mass loss data collected in this program (detailed in the Appendix) reflect the average corrosion rate for alloy A95086 decreased from 11 $\mu\text{m}/\text{year}$ after 0.5 year to 7 $\mu\text{m}/\text{year}$ after 1 year to 3 $\mu\text{m}/\text{year}$ after three years. The corrosion rates compare favorably and are within the range of published data referenced previously. The corrosion rates are calculated from mass loss and, while they are of interest to assess trends of corrosion behavior versus time, one must compare the extent of pitting or crevice corrosion from one test site to another since this is the predominant mode of attack on aluminum alloys when they corrode in seawater. Depth of attack data are summarized in Fig. 4 and show no particular trend toward increasing depth of corrosion with time, as might be expected, except at the California, Japan, and Bohus-Malmon, Sweden sites. The maximum depth of localized attack on a

TABLE 6—Summary of corrosion data for 14 worldwide seawater test sites.

Alloy	Exposure Period, year	Corrosion Rate Range, $\mu\text{m}/\text{year}$	Average Thickness Loss Range, mm	Maximum Thickness Loss Range, mm	Maximum Depth of Localized Attack Range, mm
A95086	0.5	3 to 19	0.01 to 0.32
	1.0	3 to 12	0.02 to 0.68
	3.0	1 to 12	0.03 to 0.91
C70600	0.5	6 to 374	0.03 to 0.46
	1.0 ^a	4 to 29	0.01 to 0.35
	3.0	2 to 24	0.01 to 2.68
K01501	0.5	82 to 550	0.08 to 0.59	0.16 to 0.95	...
	1.0	86 to 536	0.10 to 1.51	0.22 to 6.07	...
	3.0	62 to 224	0.72 to 2.58	0.92 to 6.07	...

^a Excludes 1.5 and 2.0 year data from Denmark and California sites, respectively.

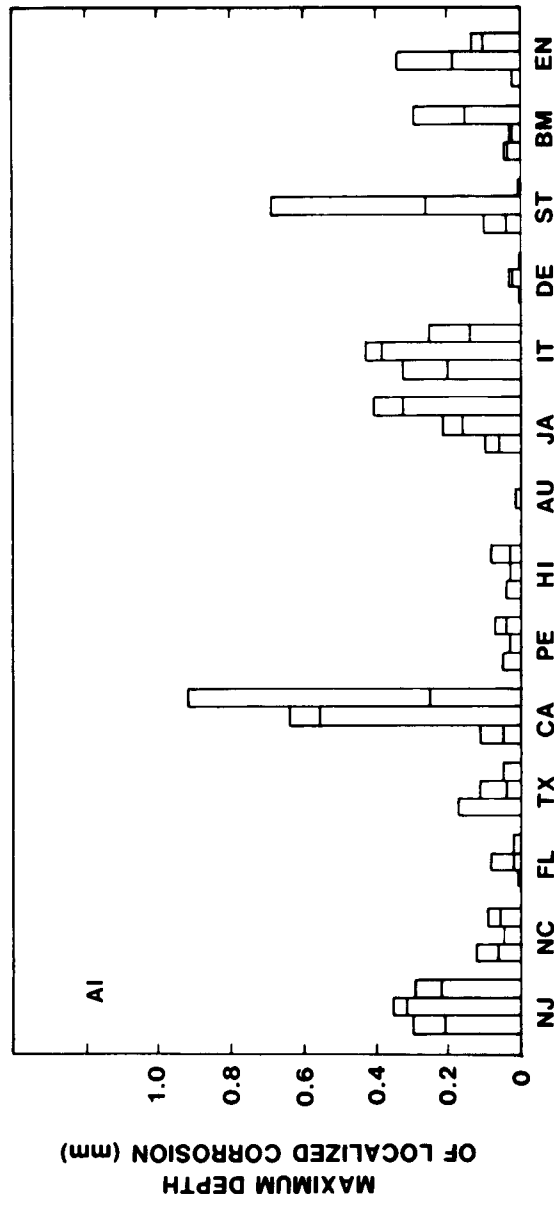


FIG. 4—Localized corrosion data for A95086 aluminum alloy after 0.5, 1.0, and 3 year exposures (bars 1–3, left to right) in seawater at various sites. (Note that the second bar for the California and Denmark sites represent exposure data for 2 and 1.5 years, respectively, and only 1.0 year results are reported for Australia.)

boldy exposed surface (0.9 mm after 3 years) occurred at Port Hueneme, California, a site where the test racks were subjected to constant wave action. This would normally bring a greater oxygen supply to the specimen surfaces leading to maintenance of the protective oxide film and rapid film repair when it is disrupted, for example by the chloride ion or by impingement. Opposing effects, however, could be also present since marine organism attachment and growth would be also encouraged. The shielding effect of the naturally created crevices, would tend to break down the passive film and lead to sites of crevice corrosion. This is the most likely mechanism leading to pitting of the aluminum alloy and was previously observed and documented by Ailor [1]. This localized corrosion mechanism, in turn, could be adversely affected by anode to cathode area ratios depending on the crevice geometry. Whether similar effects of seawater velocity were present at any other sites is not known, since complete documentation of site characteristics is difficult to obtain. The maximum pit depth reported by Brouillette [3] for alloy A95052 at the same Port Hueneme Harbor location was also 0.9 mm.

The second deepest localized attack (0.7 mm) occurred after one year at Studsvik, Sweden, a brackish water site. Even more noteworthy is the fact that no measurable localized attack was noted on the two Studsvik panels removed after three years. Since some measurable corrosion occurred on all four of the panels removed earlier, this perhaps can be attributed only to a matter of probability.

In regard to seawater temperature, there appears to be some evidence of lesser attack at the warmer sites, for instance North Carolina, Florida, Texas, Peru, Hawaii, and Australia. The very slight attack at the colder Denmark site, however, directly opposes that argument. The extent to which biofouling, silting index or any other environmental factors may affect results is impossible to assess due to insufficient documentation of such characteristics.

Copper-Nickel Alloy C 70600

The 90/10 Cu-Ni alloy C70600 selected for this program is known for its resistance to corrosion in seawater and to biofouling [4-10]. Its corrosion resistance is attributed to the growth of a protective corrosion product film which in the classical sense is "passive." This film growth, although initiated quickly upon exposure to seawater, may take very long times to reach steady state, eventually yielding very low corrosion rates on the order of $3 \mu\text{m}/\text{year}$ [6]. As in the case of aluminum alloys, many factors within the seawater environment can affect the corrosion behavior of this alloy. It appears obvious from the data summarized in Table 6 that a large site to site variability exists.

Corrosion rate data shown in Fig. 5 demonstrate a general trend toward decreasing corrosion rates as a function of exposure time. Maximum depths of localized corrosion shown in Fig. 6 increased with increased time, though not linearly, at most of the sites. In contrast to the very low corrosion rate mentioned previously, specimens from only half of the test sites show a rate less than $10 \mu\text{m}/\text{year}$ after three years. Reinhart [11] reported corrosion rates decreasing from 25 to $13 \mu\text{m}/\text{year}$ for 6 months to two years of exposure for this alloy at Point Mugu, California, not far from Port Hueneme. It is interesting to observe that the low rate calculated for both panels removed after three years at the North Carolina site equals that reported at the same site in long-term tests concluded eleven years earlier [6].

The highest corrosion rate was noted at Port Hueneme, California, on one panel removed after six months. The validity of the extremely high rate was questioned, but thorough review of the specimen history (original and final weights and dimensions) confirm this observation. Once again the constant wave action at this site appears to be the reason for this severe corrosion. The specimen in question was mounted on the end of the rack receiving the first full impingement from the seawater velocity. The companion specimen also exhibited a high

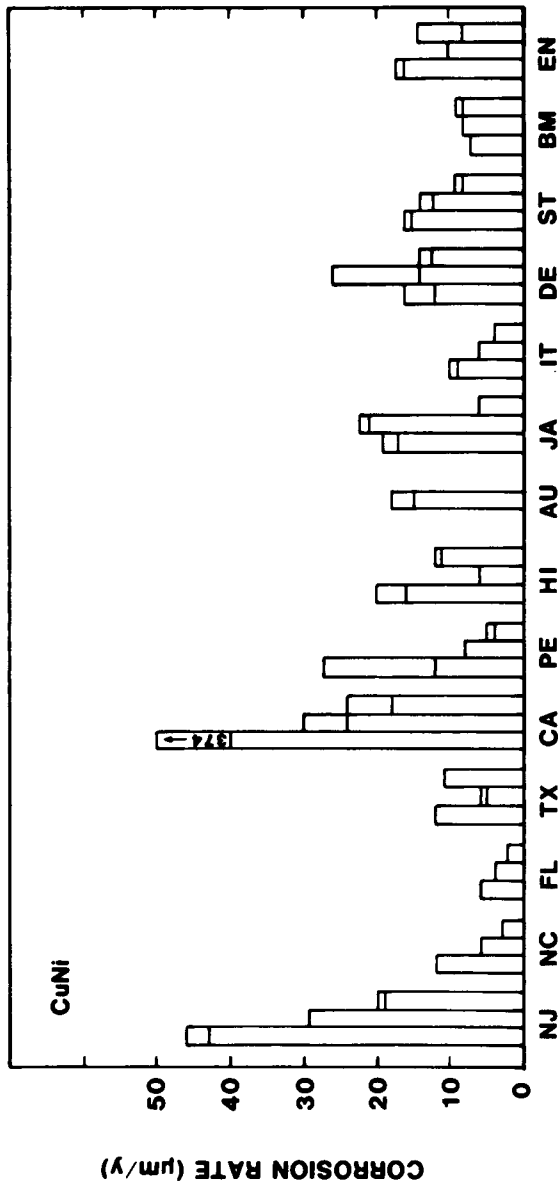


FIG. 5—Corrosion rate data for copper-nickel alloy C70600 after 0.5, 1.0, and 3 year exposures (bars 1–3, left to right) in seawater at various sites. (Note that the second bar for the California and Denmark sites represent exposure data for 2 and 1.5 years, respectively, and only 1.0 year results are reported for Australia.)