Evaluation of Aluminum after One-Year Deep Sea Exposure

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Evaluation of 17 typical aluminum alloys exposed for over 13 months at a depth of 2370 ft in the Pacific Ocean confirm earlier 6-month tests. The aluminum-magnesium alloy systems continue to show excellent seawater resistance, and the claddings on X7002 and 7079 high-strength alloys completely protect the core metal. Pit depth and weight loss data from replicate panels exposed 1 year near the surface at Harbor Island, N.C., indicate that the corrosion resistance at test depth generally is roughly comparable to that for surface exposures. Exceptions appear to be alloy 3003 and the high-purity aluminum, which had considerably deeper pitting and higher corrosion rates at the deep-sea location. Results point to the desirability of keeping the copper content below 0.06% for aluminum alloys in deep-sea applications. As anticipated, high-strength aluminum alloys with substantial zinc or copper content must be protected, and a higher potential cladding or external anodes proved effective. This test showed that the cladding alloy may be used up at a faster rate in the deep sea than near the surface.

Introduction

THE background and development of studies of materials for deep-sea applications were discussed earlier[1] and only subsequent work and recent reports are discussed here. Drisko and Brouillette[2] report results of shallow and deep-sea studies on steels with nine organic and one inorganic systems tested. They note that a good protection at great depths may require minimum dry film thickness of 13 mils.

A Naval Research Laboratory report[3] indicates the effectiveness of aluminum galvanic anodes in protecting couples of aluminum alloy 5086 and dissimilar metals in surface seawater and shows the desirability of tribulyltin oxide (TBTO) as an antifoulant for aluminum, compared with cuprous oxide. The authors state that the "combination of the TBTO type antifouling paint in conjunction with the Navy's anticorrosive vinyl and cathodic protection from aluminum anodes should be a satisfactory method to prevent fouling and corrosion of 5086-H32 and 6061-T6 aluminum." Fouling normally occurs within the first few hundred feet below the surface and is not a problem at great depths.

Reinhart[4] discusses comprehensive deep-ocean studies off Port Hueneme, Calif. He summarizes data from exposures up to 1064 days at depths from 2340 ft to 5640 ft. Detailed results on corrosion rates, pitting depths, and losses of mechanical properties are reported for steels, aluminum, copper, nickel, and titanium alloys. The author also discusses the need to consider sizes of test panels and makes interesting comparisons of exposures in the Atlantic Ocean with the Naval Civil Engineering Laboratory (NCEL) tests.

As part of a continuing program to evaluate aluminum alloys in deep-sea environments, the 17 alloys reported in this paper were exposed on the NCEL submersible testing unit (STU) II-2 at 2370 ft for 402 days. For reference and comparison, replicate panels of many of these alloys were fully immersed near the surface in seawater at Harbor Island, N.C. for 1 year.

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Procedure

Single 6- × 12-in. panels of 17 different aluminum alloys were cleaned in acetone, measured, and weighed prior to exposure. The longer length of each panel is in the sheet rolling direction. The panels, whose gages varied from 0.040 to 0.250 in., were exposed April 13, 1965, on STU II-2.

Samples were photographed as removed. They were then cleaned for 10 minutes in an ultrasonically agitated solution of 2% chromic acid and 5% phosphoric acid (by weight) at 180°F, followed by a 3-min dip in 70% nitric acid. They were then rephotographed and weighed, and pit-depth measurements were made with a calibrated focus microscope. Mechanical properties were determined by American Society for Testing Materials (ASTM) Method E-8 from tensile strips cut from the test panels. Corrosion rates were calculated from weight losses for the 402-day exposure period.

Chemical analyses of the test alloys are given in Table 1. Original and after-exposure mechanical properties are given in Table 2. Solution potentials for the test alloys are given in Table 3, as measured in a 1 normal sodium chloride solution containing 0.3% hydrogen peroxide vs an 0.1 normal calomel electrode, and also with a synthetic seawater prepared according to ASTM Method D 1141-52, specification for substitute seawater vs the calomel electrode.

For the surface exposures, triplicate 4- × 12-in. panels of certain alloys were prepared as noted previously and exposed in full-immersion conditions at the International Nickel Company test station at Harbor Island, N.C. After exposure for 1 year, the panels were removed, cleaned, weighed, and the pit depths were measured. Mechanical properties were determined by testing tensile specimens cut from the exposed panels.

In the case of both the deep-sea and surface tests, mechanical properties also were measured for unexposed control panels for each alloy. Corrosion products from selected deep-sea panels were analyzed by x-ray diffraction and by x-ray fluorescent quantometer technique. Metallographic sections of some panels were made to evaluate the corrosion.

Exposure Conditions

The test structure (STU II-2) was exposed on the floor of the Pacific Ocean 2370 feet below the surface on April 13, 1965, about 75 naut miles west of Port Hueneme, Calif., at latitude 34°06' North, longitude 120°42' West. The structure was retrieved on May 20, 1966, after 402 days exposure.

Table 1 Chemical compositions

Alloy	Gage, in.	Values in percent (balance is aluminum)								
		Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti
1180-H14[a]	0.050	0.06	0.08	0.002	0.002	...	...	...	...	...
2014-T6	0.050	0.91	0.53	4.23	0.80	0.32	0.03	0.01	0.08	0.02
2219-T87	0.040	0.08	0.12	6.54	0.26	<0.02	<0.02	<0.02	0.03	0.02[g]
3003-H14	0.063	0.20	0.58	0.13	1.05	<0.01	<0.01	<0.01	<0.01	...
5050-H34	0.050	0.18	0.64	0.04	...	1.19	...	...	...	...
5052-H34	0.050	0.13	0.30	0.02	...	2.31	0.22	...	...	...
5086-H32	0.064	0.15	0.25	0.05	0.32	3.75	0.12	...	0.12	0.01
5154-H38	0.050	0.13	0.17	0.02	<0.02	3.48	0.24	<0.02	0.02	<0.02
5257-H25	0.045	0.04	0.07	<0.02	<0.02	0.52	<0.02	<0.02	<0.02	<0.02
5456-H321	0.258	0.14	0.24	0.06	0.68	5.25	0.09	<0.02	0.04	0.03
5356-H323[b]	0.050	0.18	0.32	0.036	0.26	5.08	<0.02	<0.02	0.05	...
6061-T4	0.050	0.70	0.48	0.33	...	0.85	0.20	...	...	...
X7002-T6	0.063	0.11	0.17	0.78	0.17	2.73	0.19	<0.02	3.76	0.04
Alc X7002-T6	0.063	...	...	...	...	...	...	...	...	...
core (X7002)[c]	...	...	...	0.75	0.18	2.5	0.20	...	3.5	...
cladding (7072)[d]	[e]	...	...	...	...	...	...	...	1.0	...
Alc 7079-T6	0.063	...	...	...	...	...	...	...	...	...
core (7079)[c]	...	...	...	0.6	0.2	3.3	1.17	...	4.3	...
cladding (7072)[d]	[f]	...	...	...	...	...	...	...	1.0	...
7178-T6	0.050	0.12	0.25	1.75	0.02	2.44	0.25	...	6.69	0.06
X7002-T6	0.250	0.09	0.16	0.72	0.15	2.75	0.17	<0.02	3.81	0.03

[a] BA 99.8% ½H.
[b] Similar but not identical (BA 28 − ¼H).
[c] Nominal values.
[d] Clad both sides.
[e] Average cladding thickness, 0.0028 in.
[f] Average cladding thickness, 0.0025 in.
[g] 0.10% V and 0.15% Zr.

Environmental characteristics include 1) green mud and silt; 2) current, 0.15 fps (mean); 3) pressure, 1043 psi; 4) temperature, 3.0°C (37.5°F); 5) oxygen, 0.40 ml/l of seawater (0.57 ppm); 6) pH, 7.40–7.66; 7) salinity, 34.36 parts per thousand; 8) alkalinity, 2.36 milliequivalents per liter of seawater; 9) oxidation-reduction potential +190 mv. Other gases, such as carbon dioxide and hydrogen sulfide, were not determined. In the general area of the test site, the pressure is 1030 psi greater than at the surface; the temperature is approximately 9.5°C lower; the oxygen content is much lower, 0.40 ml/l compared with 5.6 ml/l; the pH is 7.53 vs 7.87; and the salinity is 34.4 vs 33.6 parts per thousand.

Table 2 Mechanical property changes due to corrosion[a]

Alloy	Maximum pit depth, mils	Tensile strength[b]		Yield strength[b]		Elongation[b] in 2 in.	
		1000 psi	% change	1000 psi	% change	%	% change
BA 99.80	p[c]	14.7		13.7		10.0	
		13.5	−5.4	12.7	−7.3	3.7	−63.0
2014-T6	17.0	67.5		61.2		9.2	
		35.2	−48.2	...	...	0.8	−91.3
2219-T87	p[c]	70.8		56.0		10.3	
		26.0	−63.2	43.4	−22.5	0.8	−92.2
3003-H14	42.0	22.2		20.4		7.8	
		22.2	0	20.5	+0.5	7.2	−7.8
5050-H34	19.5	27.5		24.0		7.4	
		28.1	+2.2	23.9	−0.4	7.1	−4.1
5052-H34	12.0	37.3		31.3		8.8	
		38.4	+3.0	31.1	−0.6	8.8	0
5086-H32	12.0	44.3		31.4		12.1	
		44.5	+0.5	30.8	−1.9	13.0	+9.1
5154-H38	17.5	48.7		39.3		9.2	
		45.2	−7.2	38.2	−2.8	6.6	−28.3
5257-H25	4.0	20.5		15.5		13.3	
		20.3	−1.0	16.1	+3.9	13.2	−0.7
5456-H321	18.0	54.6[d]		34.4[c]		17.8[c]	
		53.5	−2.0	34.3	−0.3	15.2	−14.6
BA 28-1/4H	3.5	46.9		42.1		10.4	
		53.1	+13.2	41.3	−1.9	10.5	+1.0
6061-T4	18.0	44.0		28.2		21.0	
		41.6	−5.5	28.1	−0.4	12.7	−39.6
X7002-T6 (sheet)	40.0	69.0		59.4		12.0	
		53.4	−22.6	55.7	−6.2	4.3	−64.2
X7002-T6 (plate)	60.0	67.5		58.8		13.1	
		64.1	−5.0	56.2	−4.4	10.5	−19.9
AlcX 7002-T6	3.2	63.0		54.2		12.0	
		62.9	−1.6	54.1	−1.8	11.5	−4.2
Alc 7079-T6	3.0	75.0		69.6		11.0	
		76.1	+1.5	70.3	+1.0	10.4	−5.5
7178-T6	p[c]	87.6		82.3		11.3	
		42.6	−51.4	...	...	1.0	−91.1

[a] Exposure for 402 days at 2370 ft depth.
[b] Original properties listed first, after exposure values below for each alloy.
[c] Panel penetrated.
[d] Long transverse properties, all other longitudinal.

Table 3 Solution potentials, v

Alloy	Salt-peroxide[a]	Synthetic seawater[b]
BA 99.80	−0.84	−0.87
2014-T6	−0.81	−0.80
2219-T87	−0.79	−0.79
3003-H14	−0.84	−0.85
5050-H34	−0.86	−0.87
5052-H34	−0.85	−0.85
5086-H32	−0.87	−0.88
5154-H38	−0.79	−0.88
5257-H25	−0.78	−0.87
5456-H321	−0.88	−0.88
BA 28-¼H	−0.87	−0.90
6061-T4	−0.76	−0.77
X7002-T6 (sheet)	−0.85	−0.87
X7002-T6 (plate)	−0.86	
Alc X7002-T6		
core	−0.84	−0.86
cladding	−0.92	−0.94
Alc 7079-T6		
core	−0.87	−0.88
cladding	−0.95	−0.97
7178-T6	−0.83	−0.86

[a] 1N NaCl + 0.3% H_2O_2 vs 0.1N calomel electrode; value given is after 2 hr in solution at 30.0°C ± 0.5°.
[b] "Sea-salt" (ASTM Spec. D141-52) dissolved in deionized water (41.953 g/l). Value given is average of five determinations made on each of five consecutive days (4th–8th day) at 30.0°C ± 0.5°.

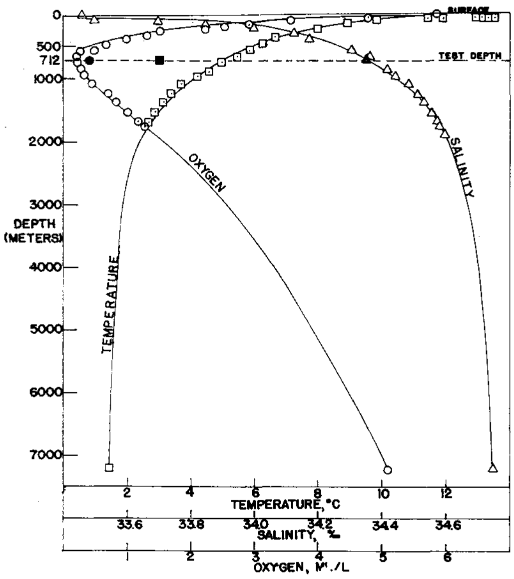


Fig. 1 Ocean profile (based on data measured 5 miles from test site by Scripps Institution of Oceanography on January 12, 1962).

The relationship of temperature, oxygen content, and salinity to depth is shown in Fig. 1, based on measurements by the Scripps Institution of Oceanography about 5 miles from the location of this test, except for values at 7200 m, which are from the bottom of the Romanche Deep in the Atlantic Ocean. Measured values at the 2370-ft level are superimposed on Fig. 1 and, in general, agree with the profile curves. The oxygen content at the test depth is in the region of minimal values.

Discussion

Corrosion Effects on Mechanical Properties

The aging effects on the mechanical properties of the test alloys were neglected since experience has shown 1-year aging to have negligible effect. The temperature of 3°C at depth should tend to improve both tensile strength and elongation.

As shown in Fig. 2, the aluminum-magnesium alloys (5050, 5052, 5086, and BA 28) did not lose tensile strength within the 1-year exposure at 2370 ft. This was also the case for the high-purity 1180 alloy, the aluminum-manganese alloy 3003, and the clad X7002 and 7079 alloys. The high-strength, aluminum-copper alloys 2014 and 2219 suffered up to 60% loss in tensile strength. The aluminum-zinc-magnesium-copper alloy 7178, which lost 50% of its ultimate tensile strength after 6 months exposure, showed no further loss after 1 year. Bare X7002 sheet lost 22.6% of the initial tensile strength.

The initial elongations of the test alloys are compared with the 6-month and 1-year values in Fig. 3. Essentially no change was noted for the aluminum-magnesium alloys 5050, 5052, and BA 28 or for 3003 and alclad X7002 and 7079 alloys. The high-purity 1180 and aluminum-copper alloys 2014 and 2219 lost at least half of their original elongations after 1-year deep-sea exposure. The 2014, 2219, and 7178 alloys showed little residual elongation after this period.

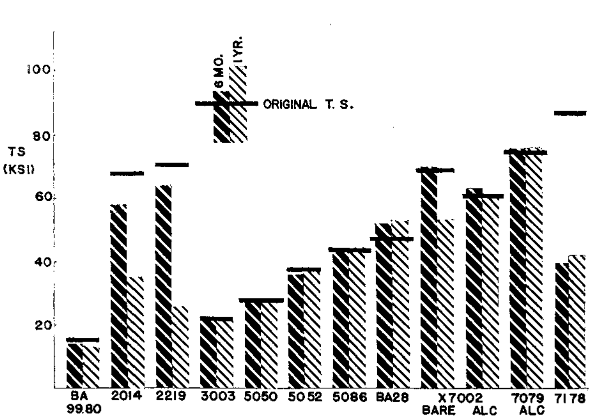


Fig. 2 Tensile strengths of test alloys.

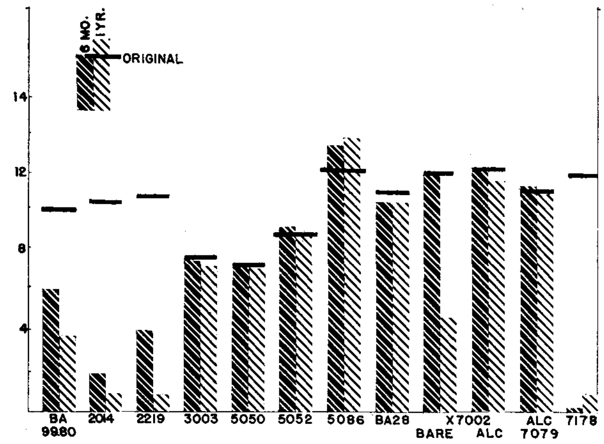


Fig. 3 Elongation of test alloys (% in 2 in.).

Depth Effects on Mechanical Properties

Figure 4 compares the percent changes in ultimate tensile strength for alloys exposed 1 year in seawater at shallow and deep locations. The general pattern indicates a similar effect for both surface and deep-sea exposures. Slightly greater losses for alloys 6061 and X7002 can be noted for deep-sea specimens. For comparison with the 1180 alloy, surface exposure data from tests on 1199 high-purity alloy were graphed in Fig. 4. Alloy 5456 data were compared with that of the nearly comparable BA 28.

Changes in elongation properties for a number of aluminum alloys are shown in Fig. 5. The effect of the deep-sea exposure was essentially comparable to that of the surface immersion for alloys 2219, 3003, 5086, 5257, 5456, and the alclad X7002 and 7079. Loss of elongation on deep-sea exposure was greater for 1180, 5154, 6061, and X7002.

Corrosion Rates

Weight losses of exposed panels were used to calculate corrosion rates in milligrams per square decimeter per day

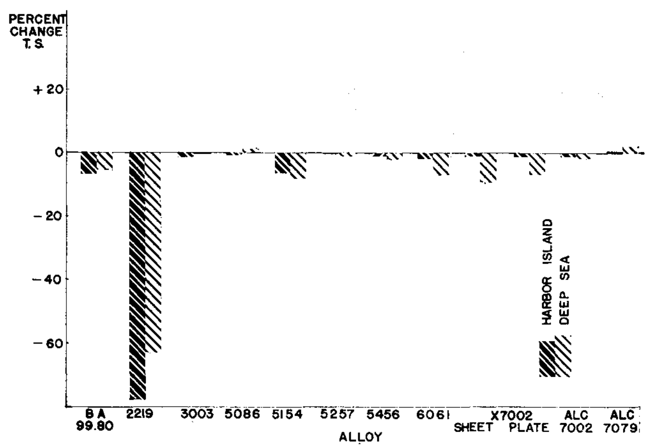


Fig. 4 Changes in tensile strengths for surface and deep-sea exposures for 1 year.

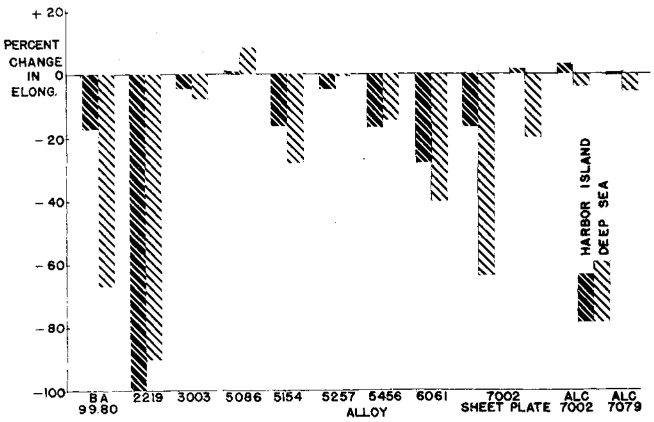


Fig. 5 Changes in elongation for surface and deep-sea exposures for 1 year.

(mg/dm²/day) and mils/year penetration. These values are recorded in Table 4 and plotted in the bar graph in Fig. 6.

The 6-month-exposure results[1] previously reported showed the aluminum-magnesium alloys had the lowest corrosion rates in deep-sea exposure. The 1-year tests confirm the good general corrosion resistance of these alloy systems. The BA 28 (5356 type) had a rate of 0.065 mg/dm²/day after one year at 2370 ft and the 5257 had a rate of 0.071 mg/dm²/day. For comparison, the aluminum-zinc-magnesium-copper alloy 7178 corrosion rate was 4.65 mg/dm²/day. For service usage, the 5000 series may usually be left bare, whereas the 7000 series must be protected. The high-strength, high-copper alloy 2014 had a rate of 2.71 mg/dm²/day and the 2219 alloy had 2.26 mg/dm²/day. Neither of these alloys should be used in marine exposures without protection.

The low corrosion rates for clad X7002 and 7079 showed the effectiveness of a high electrical potential cladding (7072) in protecting a vulnerable core metal. Aluminum-magnesium silicide alloy 6061 exhibited good seawater resistance with a 1-year rate of 0.77 mg/dm²/day. The rate for the aluminum-manganese 3003 was 1.60 mg/dm²/day.

A comparison of 1 year and 6-month rates at 2370 ft is shown in Fig. 7. As is true for surface exposures, the corrosion rates are, in all cases, higher for the longer time period. However, surface examination indicated the probability of a leveling off of these rates after the first year.

The corrosion rates in mils per year penetration based on weight losses are compared with the average depths of the 20 deepest pits in Fig. 8. For all alloys except the clad materials, these calculated mils/year penetrations are of lesser magnitude than the averages of the measured pits by a factor of at least 10.

Table 4 Corrosion evaluation of panels exposed 1 year

Alloy	Gage	Corrosion rates mg/dm²/day	Corrosion rates mils/year	Average pit depth, (20 pits), mils	Maximum pit depth, mils
Alc 7079-T6	0.062	0.786	0.412	2.1	3.0[a]
Alc 7002-T6	0.063	1.036	0.540	3.0	3.2[b,h]
BA 28-¼H	0.048	0.065	0.035	2.3	3.5
5257-H25	0.045	0.071	0.038	2.2	4.0
2014-T6	0.051	2.707	1.389	13.9	17.0[i]
5052-H34	0.049	0.238	0.128	6.8	12.0
5086-H32	0.065	0.580	0.313	5.3	12.0[g,i]
5154-H38	0.050	0.325	0.176	10.8	17.5
5456-H321	0.258	0.331	0.179	15.5	18.0
6061-T4	0.052	0.767	0.413	11.3	18.0[f,g]
5050-H34	0.050	0.195	0.104	5.6	19.5
X7002-T6	0.065	2.082	1.084	26.2	40.0[f,g]
3003-H14	0.064	1.602	0.843	14.5	42.0[g]
X7002-T6	0.258	0.990	0.516	23.6	60.0[f]
2219-T87	0.040	2.261	1.156	14.7[c]	p[c,i]
BA 99.80	0.050	1.265	0.673	30.8[d]	p[d,g]
7178-T6	0.051	4.654	2.380	45.2[e]	p[e,f,g]

[a] Cladding thickness, 2.6 mils max.
[b] Cladding thickness: 3.0 mils max.
[c] Perforation at 1 location.
[d] Perforation at 5 locations.
[e] Perforation at 17 locations.
[f] Exfoliation at edges.
[g] Edge corrosion.
[h] Blistering.
[i] Intergranular attack.

The importance of copper content in the corrosion behavior of aluminum in seawater is indicated in Fig. 9. Even with widely varying magnesium percentages, a low copper percentage (less than 0.06) correlates with good corrosion resistance. In alloys with large amounts of zinc (7000 series), the corrosion rates increase with increasing copper content. For essentially magnesium-free alloys (1180, 3003, 2219, and 2014) the corrosion rates show a trend of increasing severity with copper content.

Corrosion Effects—Pitting

The maximum measured, deepest pits after 1-year exposure at 2370 ft are recorded in Table 4, along with the average depth for the 20 deepest pits found on each panel. These data are graphically displayed in Fig. 10.

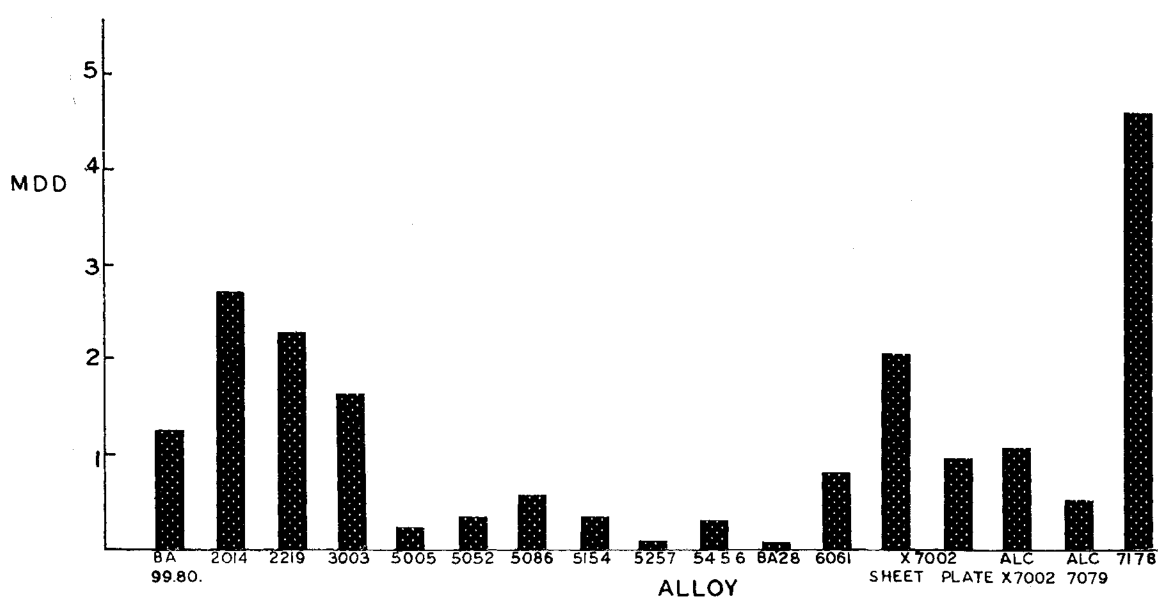


Fig. 6 Corrosion rates (mg/dm²/day) of test alloys, 1-year exposure.

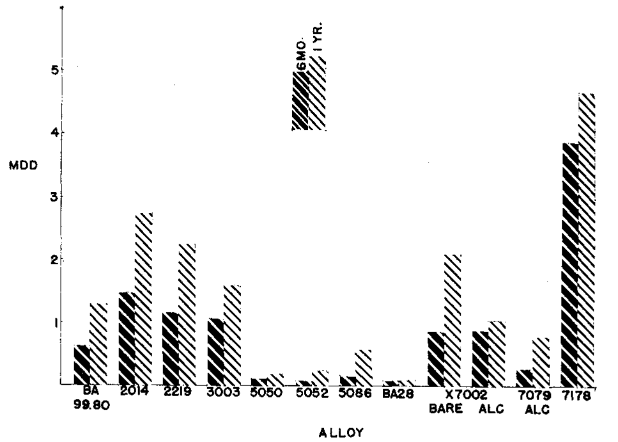


Fig. 7 Corrosion rate ($mg/dm^2/day$) at 2370-ft exposure.

Consistent with earlier 6-month tests, the 1180 alloy had deep pits, averaging 30.8 mils for the 20 deepest. These included five pits that perforated the 0.050-in.-gage sheet. The aluminum-copper alloy 2219 and aluminum-zinc-magnesium-copper 7178 also had pitting penetration through their panels. Although the X7002 plate had a maximum pit of 60.0 mils, compared to 40.0 mils for sheet material of the same alloy, the average depths were quite similar, being 26.2 mils for the sheet and 23.6 mils for the plate.

The shallowest pits were found in the clad alloys X7002 and 7079 and the aluminum alloys 5257 and BA 28. In the case of the clad materials, pits were confined almost completely to the thickness of the 7072 cladding and did not exceed 3.2 mils for either X7002 or 7079. A significant build-up of corrosion products on the clad sheets, plus corrosion rates greater than 0.79 $mg/dm^2/day$, indicated that this protection of the core metal was obtained through the sacrificial anodic action of the 7072 cladding.

The BA 28 (5356 type) had maximum pits of 3.5 mils with an average of 2.3 mils. The 5257 alloy had pits as deep as 4.0 mils, but averaged only 2.2 mils for the 20 deepest. Deeper pits occurred on the other aluminum-magnesium alloys tested. Maximum pits measured included 19.5 mils for 5050, 12.0 mils for 5052 and 5086, 17.5 mils for 5154, and 18.0 mils for 5456.

The 6061-T4 alloy had a maximum depth of attack of 18.0 mils and showed exfoliation at the panel edges. Aluminum-manganese alloy 3003-H14 had pits as deep as 42.0 mils with an average value of 14.5 mils. The aluminum-copper alloy 2014-T6 showed pitting (maximum depth 17.0 mils) with general corrosion and intergranular-type attack.

Figure 11 on maximum pit depth demonstrates that pits generally were growing during the second half of the 1-year exposure. Exceptions were the clad alloys, and the 2014 alloy and alloys 5052 and BA 28 appear to be slowing in this growth rate at the end of the year. The bar graph on Fig. 12 compares averages of the 20 deepest pits for several alloys for the two time periods of 6 months and 1 year. Although the average is greater for all unclad alloys, they are approaching the maximum values for the 5052 and BA 28 alloys.

Corrosion Effects as Related to Depths of Exposure

Corrosion Rates

Figure 13 relates the 1-year corrosion rates determined from weight losses for surface exposure to similar rates for exposures at 2370 ft. The surface tests were all conducted at Harbor Island, N.C., at the International Nickel Company exposure station. The BA 99.80 aluminum was compared with the high-purity 1199 exposed on the surface, and the BA 28 alloy was considered equivalent to the 5456 alloy tested on the surface.

In the case of the aluminum-copper 2219-T87, the surface rate was 2.29 mils/year compared with 1.16 mils/year for the deep-sea test. The corrosion rates for 5457, 5456, 6061, and X7002 plate were also less after 1 year for the deep-sea than for the surface exposure. Alloy 5154 showed essentially the same corrosion rate (about 0.17 mil/year) for both locations. These data are shown in Table 5.

The clad alloys X7002 and 7079 had somewhat greater corrosion rates for the deep exposure than for the surface tests. This reflected a larger amount of cladding used to protect the core metal anodically.

The deep-sea corrosion rates after 1 year were higher for alloys 3003, 5086, and X7002 sheet. The higher value for the BA 99.80 alloy could be a measure of the differences in purity of this 99.80% aluminum compared with the 99.99% aluminum exposed on the surface.

Pit Depths

Maximum measured pit depths for surface and deep exposures are shown in Fig. 14. The depth of pitting for clad

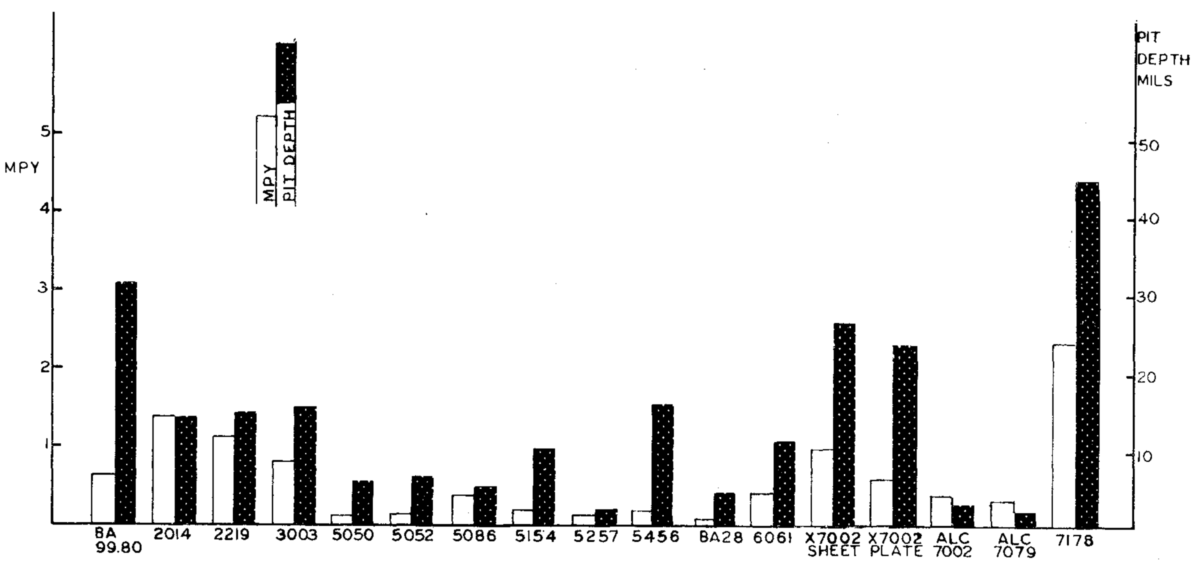


Fig. 8 Corrosion rates (mils/year) compared with averages of 20 deepest pits, 1-year exposure.

Table 5 Comparison of pitting and corrosion rates[a]

Alloy	Gage	Corrosion rate, mils/year		Average of 20 deepest pits, mils		Max pit depth, mils	
		Harbor I.	Deep sea	Harbor I.	Deep sea	Harbor I.	Deep sea
Alc 7079-T6	0.063	0.283	0.412	1.7	2.1	3.0	3.0
Alc X7002-T6	0.063	0.217	0.540	1.7	3.0	3.1	3.2
5257-H25	0.050	0.190	0.038	4.2	2.2	7.3	4.0
5086-H32	0.064	0.212[b]	0.313	10.0[b]	5.3	13.2[b]	12.0
5154-H38	0.050	0.169	0.176	8.8	10.8	15.2	17.5
5456-H321	0.250	0.217	0.179	17.8	15.5	28.8	18.0
6061-T4	0.050	0.493[d]	0.413	26.5[d]	11.3	41.0[d]	18.0
X7002-T6	0.063	0.848	1.084	20.6	26.2	33.0	40.0
3003-H14	0.063	0.317	0.843	1.0	14.5	2.0	42.0
X7002-T6	0.250	0.776	0.516	12.2	23.6	15.6	60.0
BA 99.80	0.050	0.118[c]	0.673	7.8[c]	30.8	12.7[c]	p[e]
2219-T87	0.040	2.287	1.156	p[e]	14.7	p[e]	p[f]

[a] For surface exposure and same alloys at 2370-ft, 1-year immersion.
[b] 5086-H112.
[c] BA 99.99.
[d] 6061-T6.
[e] Perforation at 5 locations.
[f] Perforation at 1 location.

alloys X7002 and 7079 was confined to the thickness of the cladding for both test depths. Alloys 5086, 5227, 5456, and 6061 had shallower pitting at depth than at Harbor Island. The 5257 was the best bare alloy at both locations from the point of view of pit resistance, the maximum depth being 7.3 mils at the surface and 4.0 mils at 2370 ft.

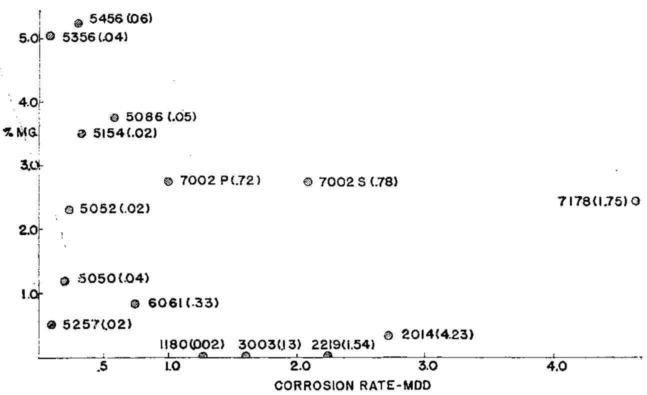


Fig. 9 Corrosion rate vs magnesium content (percent copper in parentheses).

The higher-purity aluminum, the 3003 alloy and the X7002 sheet and plate all had deeper pits at the deep exposure. The 5154 alloy had nearly comparable pitting depths for both sites—15.2 mils at Harbor Island and 17.5 mils at the deep-sea location. Alloy 2219 and the 99.80 aluminum perforated at both depths after 1 year.

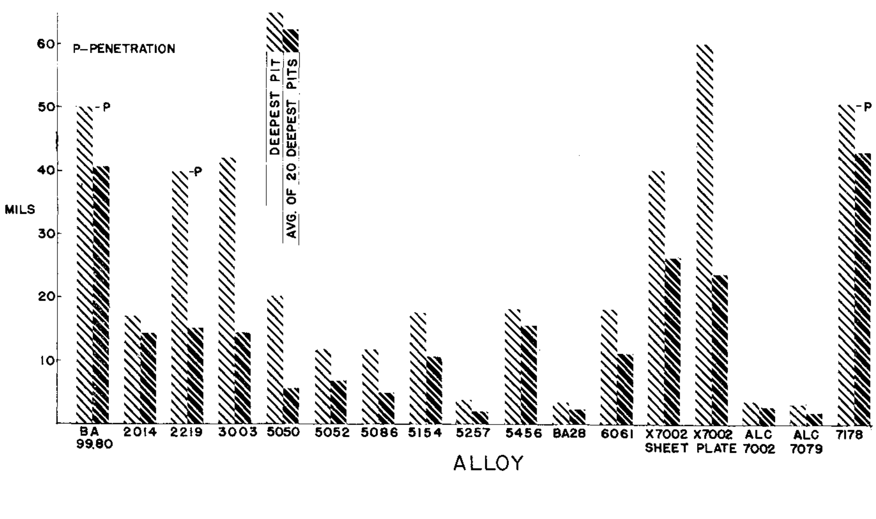
The relationship of the average of the 20 deepest pits to the exposure depth is shown by the bar graphs in Fig. 15. The aluminum-magnesium alloys 5086, 5154, and 5257 performed well for both marine exposures with the 5086 and 5257 having shallower pits at 2370 ft than at the surface. The clad alloys X7002 and 7079 reflected average pit depths at both locations which were less than their cladding thicknesses.

The average pit depths for 2219, 5456, and 6061 were less for the deep exposure than for the shallow location. The depth of pitting was adversely affected by deep-sea environment for the high-purity alloy, the 3003 material, the 5154, and the X7002 sheet and plate.

Other Corrosion Phenomena

In addition to the usual pitting type of corrosion, some panels showed other modes of attack after 1-year, deep-sea exposure. Intergranular attack was noted for 2014-T6, 2219-T87, and 5086-H32. Bare X7002-T6 and 7178-T6 exhibited some stress corrosion cracking at the edge areas. Exfoliation-mode attack was seen on the 6061-T4 panel. The intergranular-type attack found on the 5086 sheet apparently is a function of the metal temper since no evidence of this attack on extruded 5086 is reported by Reinhart.[4]

Fig. 10 Measured pit depths, 1-year exposure.



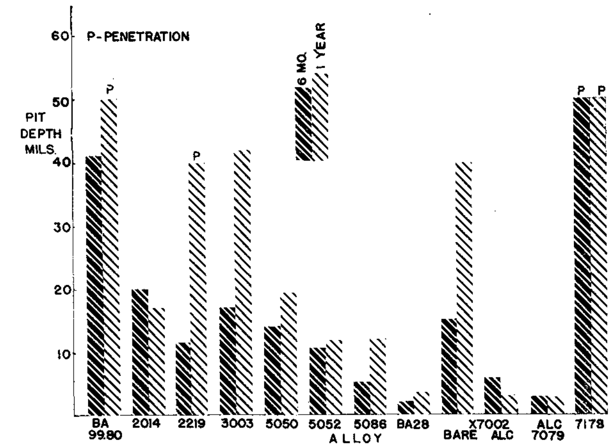


Fig. 11 Maximum pit depths, 2370-ft exposure.

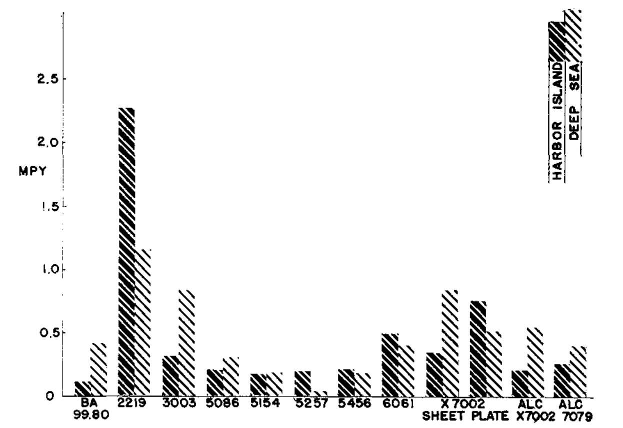


Fig. 13 Corrosion rates related to surface and deep-sea exposures, 1-year immersion.

Solution Potentials of Test Alloys

The results of laboratory determinations of solution potentials for the test alloys are shown in Table 3. These values, measured either in salt-peroxide solution or synthetic seawater, were in all cases very close, and in many instances identical, for each alloy.

The copper-bearing alloys 2014 and 2219 had potentials of −0.79 to −0.80 v in synthetic seawater while the zinc-magnesium alloys X7002 and 7178 showed values of −0.86 to −0.87 v. Cladding potentials ranging from −0.94 to −0.97 v gave nearly complete protection to the X7002 and 7079 core alloys.

The potential of an aluminum alloy is not sufficient to predict the corrosion properties of the alloy since it can be seen that the aluminum-magnesium alloy having high seawater corrosion resistance also have potentials in the order of −0.85 to −0.90 v. Cladding these alloys with higher-potential alloys further increases their corrosion resistance.

The high-purity aluminum alloy 1180 had a synthetic seawater potential of −0.87 v. Adding copper or other less negative heavy metals can lower this potential. The addition of magnesium or zinc can raise this potential. Combinations of these elements have mixed effects as in the case of the aluminum-zinc-magnesium-copper alloy X7002 whose potential is approximately the same as pure aluminum.

Conclusions

Aluminum alloys exposed for 1 year at a Pacific Ocean depth of 2730 feet showed corrosion resistance comparable to surface exposures at Harbor Island, N.C., for 5086-H32, 5154-H34, BA 28-1/4H, and 6061-T4. The deep-sea rates were less for alloys 2219-T87, 5257-H34, and X7002 plate. For alloys 1180, 3003-H14, X7002 sheet, and alclad X7002 and 7079, the corrosion rates were greater at depth.

Maximum depth of pitting reflected the following relationships: 1) deeper pits at the surface for 5086, 5257, BA 28, and 6061; 2) deeper pits at 2370 ft for 1180, 3003, and X7002 sheet and plate; 3) equivalent pit depths at surface and at depth for alloys 2219, 5154, and alclad X7002 and 7079.

The averages of the 20 deepest pits for each alloy showed the same general relationships as for the maximum pits. An exception was the 2219-T87 allow which had greater average pit depth at the surface as compared with the deep environment.

No fouling was found on any deep-sea specimen, but voluminous mounds of corrosion products developed at pitted and corroded areas. Surface samples were all heavily fouled.

Aluminum-manganese alloy 3003 and high-purity 1180 are not recommended for deep-sea applications unless clad or otherwise protected. This restriction is the result of deep pitting on the bare alloys.

Best resistance to corrosion and pitting at 2370 ft was found for aluminum-magnesium alloy 5257 with less than 0.02% copper. The cladding on alloys X7002 and 7079 gave good protection to the core metal. The importance of keeping the copper content below 0.06% for aluminum alloys in deep-sea applications was emphasized.

The corrosion in seawater generally takes the form of pitting attack. In tests at 2370 ft, intergranular attack was found on speciments of 2014-T6, 2219-T87, and 5086-H32. Some stress corrosion cracking was noted at edge areas of X7002-T6 and 7178-T6. Clad X7002-T6 showed no evidence of exfoliation or stress attack and no core attack. Exfoliation-mode attack was seen on the 6061-T4 panel.

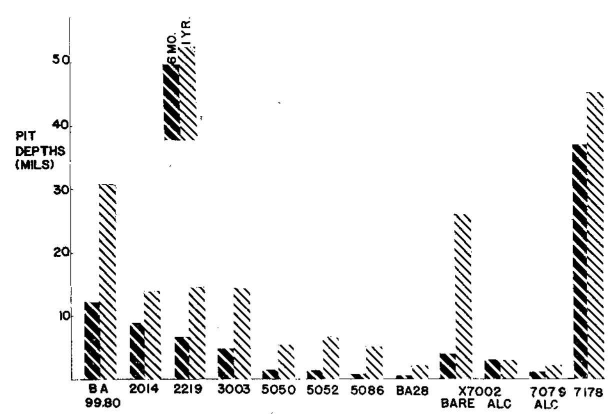


Fig. 12 Average pit depth (20 deepest pits), 2370-ft exposure.

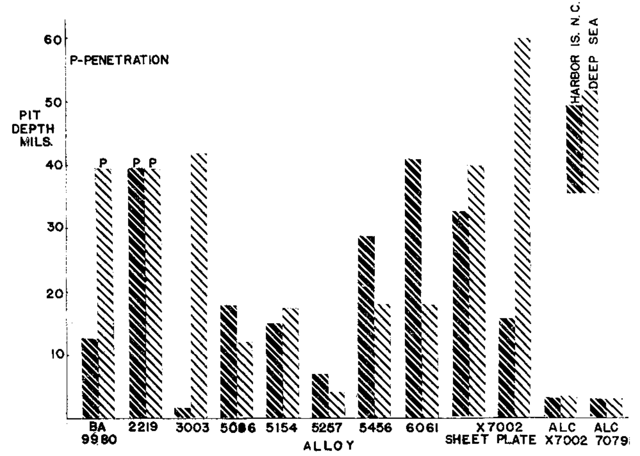


Fig. 14 Maximum pit depths related to surface and deep-sea exposures, 1-year.

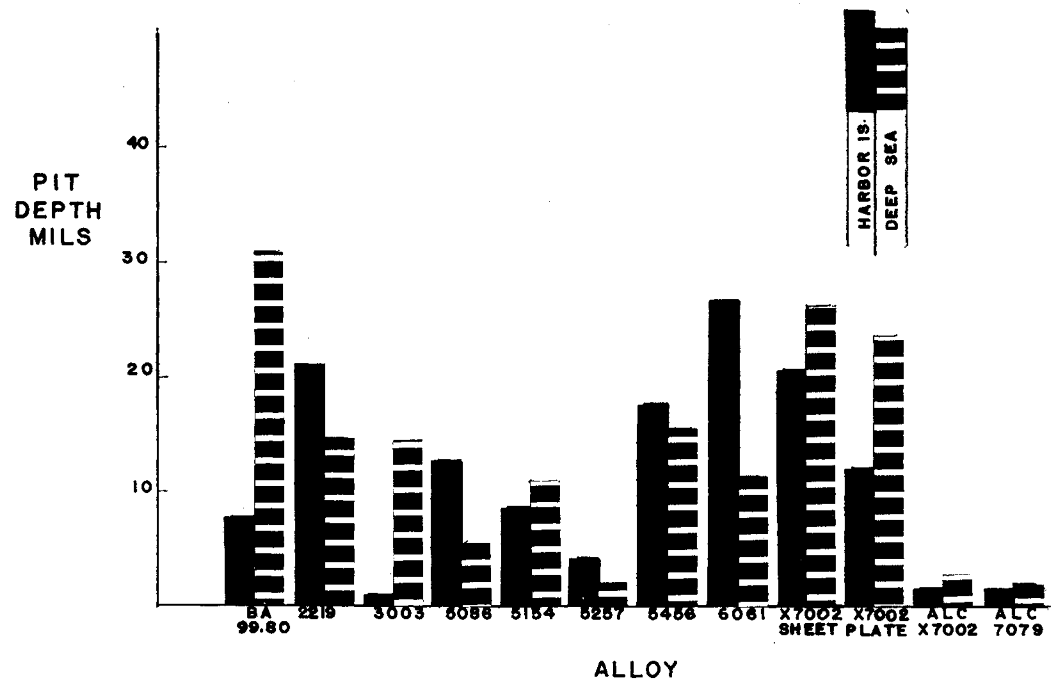


Fig. 15 Average pit depth (20 deepest pits) vs sea depth, 1-year exposure.

References

[1] Ailor, W. H., "Evaluation of Aluminum Panels Exposed in the Pacific Ocean at 2340 Feet for Six Months," *Metallurgia*, Vol. 75, March 1967, pp. 99–108.

[2] Drisko, R. W. and Brouillette, C. V., "Comparing Coatings in Deep Environments," *Materials Protection*, Vol. 5, April 1966, pp. 32–34.

[3] Lennox, T. J. et al., "Marine Corrosion Studies," NRL Memo. Rept. 1711, May 1966, Naval Research Laboratory, Washington, D.C.

[4] Reinhart, F. M., "Corrosion of Materials in Hydrospace," Technical Rept. R-504, Dec. 1966, U.S. Naval Civil Engineering Laboratory, Port Hueneme, Calif.

[5] Rush, P. J., "Preliminary Studies Concerning Structures in the Deep Ocean," Technical Rept. N-447, June 27, 1962, U.S. Naval Civil Engineering Laboratory, Port Hueneme, Calif.

[6] Thompson, J. C., Logan, R. K., and Nehrich, R. B., "A Survey of Materials Research in Ocean Environments," Rept. 1110, July 31, 1962, Navy Electronics Laboratory.

[7] Forgeson, B. W. et al., "Abyssal Corrosion and Its Mitigation. Part II. Results of a Pilot Test Exposure," NRL Memo Rept. 1383, December 1962, Naval Research Laboratory, Washington, D.C.

[8] Reinhart, F. M., "Preliminary Examination of Materials Exposed on STU 1-3 in the Deep Ocean (5,640 Feet of Depth for 123 Days)," Technical Note N-605, June 1964, Naval Civil Engineering Laboratory.

[9] Gray, K. O., "Materials Testing in the Deep Ocean," *Materials Protection*, Vol. 3, July 1964, pp. 46–53.

[10] DeLuccia, J. J. and Taylor, E., "Evaluation of Metallic Materials Exposed to the Deep Ocean Environment at 5,640 Feet for 123 Days," NAEC Rept. AML-2132, June 22, 1965, Naval Air Engineering Center.

[11] Brown, B. E. et al., "Marine Corrosion Studies. Third Interim Report of Progress," NRL Memo Rept. 1634, July 1965, U.S. Naval Research Laboratory, Port Hueneme, Calif.

[12] Reinhart, F. M., "First Results—Deep Ocean Corrosion," *Geo-Marine Technology*, Sept. 1965, pp. 15–26.

[13] Craven, J. P. and Bernstein, H., "Materials for Deep Submergence—A Development Dilemma," *Materials Research and Standards*, Vol. 5, Nov. 1965, pp. 551–556.

[14] Wheatfall, W. L., "Metal Corrosion in Deep-Ocean Environments," *Naval Engineers Journal*, Vol. 79, No. 4, Aug. 1967, pp. 611–618.