

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20375		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE THE EFFECT OF MERCURY AND TIN FROM ALUMINUM GALVANIC ANODES ON THE CORROSION CHARACTERISTICS OF 5086-H34 AND 6061-T6 ALUMINUM ALLOYS IN SEAWATER		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final report on one phase of an NRL Problem; work is continuing on other phases.		
5. AUTHOR(S) (First name, middle initial, last name) T. J. Lennox, Jr., R. E. Groover, and M. H. Peterson		
6. REPORT DATE November 16, 1973	7a. TOTAL NO. OF PAGES 30	7b. NO. OF REFS 3
8a. CONTRACT OR GRANT NO. NRL Problem M04-02	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 7648	
b. PROJECT NO. SF 51-542-602-12431		
c. RR 007-08-44-5510	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy Naval Ship Systems Command Washington, D.C. 20362	
13. ABSTRACT <p>The corrosion behavior of 5086-H34 and 6061-T6 structural aluminum alloys has been studied under specific conditions selected to determine if corrosion products from aluminum galvanic anodes containing mercury or tin would accelerate the corrosion of the structural alloys. These studies were conducted in seawater for 696 days.</p> <p>There were no indications that corrosion products from either the Al-Hg-Zn or the Al-Sn-Zn galvanic anodes caused increased corrosion. Neither Hg nor Sn was found, by electron microprobe analysis, at corroded areas. The electron microprobe did reveal that the most severe localized corrosion occurred where copper, the source of which was unknown, had redeposited on the structural aluminum specimens.</p> <p>Cathodic protection from either the Al-Hg-Zn or the Al-Sn-Zn anodes virtually eliminated corrosion on the 5086-H34 and 6061-T6 aluminum specimens that were either continuously or alternately immersed in seawater, except for slight corrosion under some of the anodes. As expected, cathodic protection was only partially effective when it was provided for only the first 186 days of the 696 days of exposure.</p>		

(continues)

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Al-Hg-Zn galvanic anodes Al-Sn-Zn galvanic anodes Corrosion behavior 5086-H34 aluminum Corrosion behavior 6061-T6 aluminum Sea water Electron microprobe analysis Cathodic protection Continuous immersion Alternate immersion Bulky corrosion products Zinc oxide barrier						

Abstract continued

The slight corrosion and the buildup of bulky corrosion products between the anodes and the specimens confirmed the advisability of using some type of a barrier, such as zinc oxide paste or an organic coating, between aluminum anodes and the structure on which they are mounted.

CONTENTS

Abstract	ii
INTRODUCTION	1
EXPERIMENTAL PROCEDURES	1
DATA AND DISCUSSION	4
Corrosion Under Various Conditions	4
Metallographic Study	16
Electron Microprobe and X-Ray Diffraction Analyses	16
Corrosion (Open Circuit) Potentials	18
pH in Crevices	24
SUMMARY AND CONCLUSIONS	24
ACKNOWLEDGMENTS	25
REFERENCES	25

ABSTRACT

The corrosion behavior of 5086-H34 and 6061-T6 structural aluminum alloys has been studied under specific conditions selected to determine if corrosion products from aluminum galvanic anodes containing mercury or tin would accelerate the corrosion of the structural alloys. These studies were conducted in seawater for 696 days.

There were no indications that corrosion products from either the Al-Hg-Zn or the Al-Sn-Zn galvanic anodes caused increased corrosion. Neither Hg nor Sn was found, by electron microprobe analysis, at corroded areas. The electron microprobe did reveal that the most severe localized corrosion occurred where copper, the source of which was unknown, had redeposited on the structural aluminum specimens.

Cathodic protection from either the Al-Hg-Zn or the Al-Sn-Zn anodes virtually eliminated corrosion on the 5086-H34 and 6061-T6 aluminum specimens that were either continuously or alternately immersed in seawater, except for slight corrosion under some of the anodes. As expected, cathodic protection was only partially effective when it was provided for only the first 186 days of the 696 days of exposure.

The slight corrosion and the buildup of bulky corrosion products between the anodes and the specimens confirmed the advisability of using some type of a barrier, such as zinc oxide paste or an organic coating, between aluminum anodes and the structure on which they are mounted.

Manuscript submitted August 23, 1973.

THE EFFECT OF MERCURY AND TIN FROM ALUMINUM GALVANIC ANODES ON THE CORROSION CHARACTERISTICS OF 5086-H34 AND 6061-T6 ALUMINUM ALLOYS IN SEAWATER

INTRODUCTION

Commercially available aluminum galvanic anodes containing mercury and zinc have consistently shown electrochemical characteristics superior to those of aluminum anodes of other compositions in studies conducted by the Naval Research Laboratory and others [1-3]. In seawater the Al-Hg-Zn anodes have a minimum current capacity of 1250 ampere-hours per pound. The closed-circuit potential and current-output characteristics for this type anode are similar to those for the zinc anodes conforming to specification MIL-A-18001H. Since the Al-Hg-Zn anodes have a current capacity of 1250 ampere-hours per pound, they will cost less per ampere-hour than military-specification zinc anodes for use in equivalent systems. Aluminum anodes also are considerably lighter than zinc anodes, a fact that is important in the design of ocean structures with weight limitations.

A question persisted, however, concerning the effect of mercury from an anode on the corrosion of other metals in the same system.

This report discusses the data obtained in experiments conducted at NRL's Marine Corrosion Research Laboratory, Key West, Florida, concerning the effect of mercury and tin from the aluminum anodes on the corrosion behavior of 5086-H34 and 6061-T6 structural aluminum alloys.

EXPERIMENTAL PROCEDURES

These studies were continued for 696 days and included the following conditions of exposure to marine corrosion: continuous immersion in seawater with and without cathodic protection from Al-Hg-Zn and Al-Sn-Zn anodes, alternate immersion (weekly) in seawater and a humid marine atmosphere with and without cathodic protection from Al-Hg-Zn and Al-Sn-Zn anodes, and semicontinuous immersion in seawater with cathodic protection from Al-Hg-Zn and Al-Sn-Zn anodes for the first 186 days. The anodes were removed from the specimens after 186 days, but the corrosion products from the anodes were not removed from the specimens prior to reimmersing them in seawater for an additional 510 days.

Duplicate specimens of 5086-H34 and 6061-T6 aluminum were included in each experimental condition. The specimens, sheared from larger sheets, were 6 in. × 12 in. × 1/16 in., and each had two holes drilled for mounting on the exposure racks. Additional holes were punched in the specimens for attaching the anodes used for cathodic protection and the electrical leads for monitoring the potentials.

The anodes measured 1/2 in. by 1-1/4 in. by 6 in. and were sections taken from commercial anodes of the two nominal compositions shown in Table 1. The cathode-to-anode-area ratio was approximately 9:1. Each anode was drilled, tapped, cleaned with solvent, and weighed to the nearest 0.1 gram prior to exposure. Anodes were attached directly to the specimens with a metal-to-metal contact. The insulated electrical leads for the potential measurements were attached to selected specimens with stainless steel machine screws and bolts. All electrical connections and the anode mounting screws were sealed with epoxy resin to avoid the introduction of extraneous effects from undesired galvanic couples.

Table 1
Aluminum Anodes: Nominal Chemical Composition

Anode Type	Element (%)				
	Hg	Sn	Zn	Fe	Al
Al-Hg-Zn	0.05	—	0.5	0.04	Balance
Al-Sn-Zn	—	0.12	7.0	0.02	Balance

The polyurethane laboratory cell complete with specimens is shown in Fig. 1. For the experiment without cathodic protection, two specimens each of 5086-H34 and 6061-T6 aluminum were exposed in each cell as shown. Because of the greater bulk of the cathodically protected specimens, only two were exposed in each cell (Fig.2). In this case one specimen of 5086-H34 and one of 6061-T6 aluminum were exposed together and were provided with either an Al-Hg-Zn or an Al-Sn-Zn anode. All cells were covered with polyurethane covers. The specimens were mounted on 3/8-in.-diameter threaded nylon rod; the washers for spacing and the nuts holding the specimens in place also were nylon. The assemblies were suspended in the cell with glass hooks attached to the nylon support rods and to the ends of the cells.

For the continuous-immersion experiment, clean seawater flowed through the cells at a rate sufficient to provide a complete change of water every 30 minutes. For the alternate-immersion experiment, the exposure cycle was one week of continuous immersion followed by one week of exposure to a humid marine atmosphere. The latter conditions was obtained by allowing seawater to remain on the bottom of the covered cell. For the experiments in which cathodic protection was provided for only the first 186 days, the cells were drained at the end of this time and the anodes, but not the anode corrosion products, were removed from the specimens. The cells were then refilled, and the experiment continued for another 510 days under continuous-immersion conditions. Throughout this report this condition is referred to as semicontinuous immersion.

The corrosion (open circuit) potentials of selected unprotected specimens in the continuously immersed condition were measured periodically (about once a week) relative to a saturated calomel electrode (SCE). Potentials were also measured on the specimens which were protected for only part of the exposure period. The measurements were made prior to the removal of the anodes and for up to 178 days afterward.



Fig. 2 — A typical arrangement for specimens with cathodic protection from attached anodes installed in a polyurethane cell.

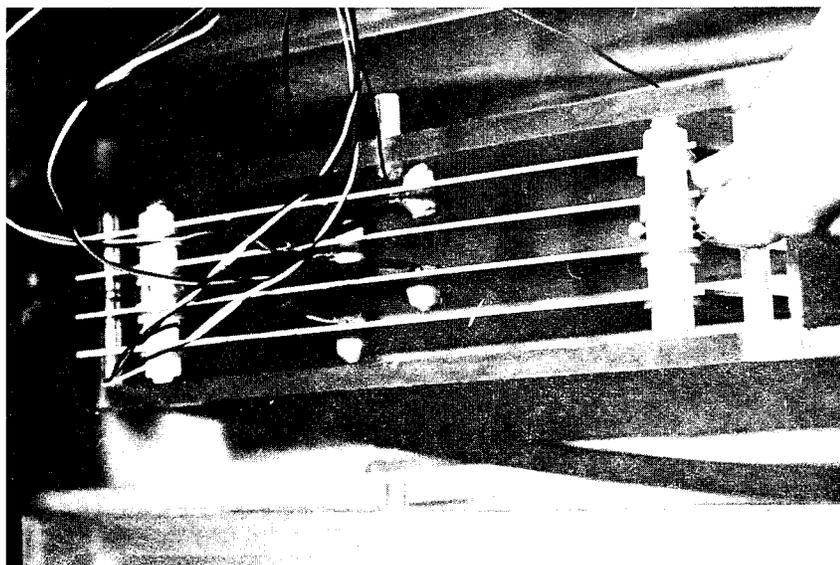


Fig. 1 — The polyurethane cell used for the exposure of the unprotected specimens. The support rods were nylon, the suspension hooks were glass, the test leads for monitoring the potentials were insulated, and the connections to the specimens were sealed with epoxy.

At the termination of the experiment, after 696 days, indicator papers were used to measure the pH in the crevices formed by the nylon spacers. The specimens and anodes were then cleaned with a high-pressure fresh-water jet, chemically cleaned in a 2% chromic acid-5% phosphoric acid solution at 80°-85°C (176°-185°F), rinsed in fresh water, and air dried. Each specimen and anode was then weighed to the nearest 0.1 gram.

The cleaned specimens were examined visually under a stereo microscope at 15X magnification, and the depth of corrosion was measured with a dial micrometer. Metallographic studies were made on some of the specimens to determine whether intergranular corrosion had occurred.

Electron microprobe analysis of corroded areas and x-ray diffraction analysis of corrosion products were conducted on selected specimens to investigate the possibility of redeposition of either Hg or Sn from the anode corrosion products and to gain insight into the cause of the unexpectedly severe corrosion on one of the unprotected specimens of 5086-H34 aluminum.

DATA AND DISCUSSION

The experimental data, with the exception of weight loss, which will be discussed later, are summarized in Table 2. These data are the measured depth of corrosion and the pH observed in the crevice areas at the end of the exposure period. For the open surface of the specimens and the large crevice under the anode, both the deepest corrosion and the average of the ten deepest corroded areas are reported. However, because of the limited area under the nylon spacer, only the deepest corrosion is reported under the heading "Other Crevices." A number of the figures show the depth of corrosion data in graphical form.

The maximum specimen weight loss of 2 grams occurred on one of the unprotected specimens of 6061-T6 aluminum continuously immersed in seawater for 696 days. A 2-gram weight loss is equivalent to an average corrosion rate of 0.16 mil per year. The weight loss on all other specimens was less than 1 gram. Because of these low weight losses and the highly localized corrosion observed on the aluminum specimens, average corrosion rates are not valid criteria for the assessment of this corrosion.

Corrosion Under Various Conditions

Continuous Immersion for 696 Days With and Without Cathodic Protection

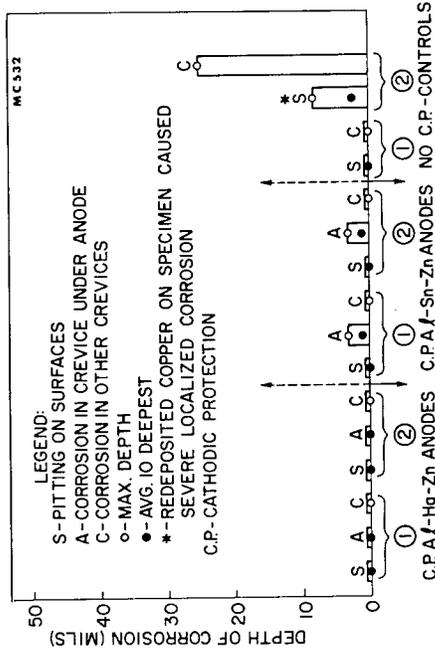
5086-H34 Aluminum — The essential absence of corrosion on the cathodically protected 5086-H34 aluminum specimens is shown by the data of Fig. 3. The maximum depth of corrosion was less than 1 mil (0.001 in.) on the specimens protected with the Al-Hg-Zn anode and was only 3 mils on the specimens protected with the Al-Sn-Zn anodes. The deepest corrosion occurred at the faying surface with the anode. These data indicate that the Hg from the galvanic aluminum anode did not cause accelerated corrosion on continuously immersed 5086-H34 aluminum when the cathodic protection was uninterrupted. Figures 4a and 4b show the excellent surface appearance and absence of corrosion on these 5086-H34 aluminum specimens.

Table 2
Corrosion and pH Data for 5086-H34 and 6061-T6 Aluminum Alloys.
Specimens Immersed in Seawater at Key West, Florida, With and Without
Cathodic Protection from Al-Hg-Zn or Al-Sn-Zn Anodes

Type of Immersion in Seawater	Aluminum Alloy	Type of Anode for Cathodic Protection	Depth of Corrosion (Mils)						pH Range in Four Crevices Between Nylon Washers and Specimen	
			On Surfaces		In Crevices		Other Crevices			
			Average of Ten Deepest	Deepest	Under Anode	Deepest				
Continuous for 696 days	5086-H34	Al-Hg-Zn	<1	<1	<1	<1	<1	<1	7.6-8.2	
	5086-H34	Al-Hg-Zn	<1	<1	<1	<1	<1	<1	8.2-8.5	
	5086-H34	Al-Sn-Zn	<1	<1	1	3	<1	<1	8.0-8.5	
	5086-H34	Al-Sn-Zn	<1	<1	1	3	<1	<1	7.9-8.8	
	5086-H34	None	0	0	—	—	0	0	7.3-8.2	
	5086-H34	None	2	8*	—	—	25*	25*	5.3-7.7	
	6061-T6	Al-Hg-Zn	<1	<1	1	1	<1	<1	7.1-8.2	
	6061-T6	Al-Hg-Zn	<1	<1	1	2	<1	<1	7.4-8.2	
	6061-T6	Al-Sn-Zn	<1	<1	2	3	<1	<1	8.2	
	6061-T6	Al-Sn-Zn	<1	<1	1	2	<1	<1	8.2-8.8	
	6061-T6	None	26	32	—	—	31	31	3.5	
	6061-T6	None	22	29	—	—	54	54	3.5-3.8	
	Semicontinuous for 696 days; anodes were removed after 186 days; specimens were reimmersed for 510 days without cathodic protection.	5086-H34	Al-Hg-Zn	<1	<1	2	2	<1	<1	7.4
		5086-H34	Al-Hg-Zn	0	0	<1	<1	<1	<1	7.6
		5086-H34	Al-Sn-Zn	<1	<1	<1	1	<1	<1	6.8-7.1
		5086-H34	Al-Sn-Zn	<1	<1	<1	1	<1	<1	6.8
6061-T6		Al-Hg-Zn	<1	<1	6	18	24	24	3.5-7.4	
6061-T6		Al-Hg-Zn	8	23	8	18	2	2	6.2	
Alternate for 696 days; one week in seawater and one week in humid marine atmosphere	6061-T6	Al-Sn-Zn	<1	<1	<1	<1	19	19	3.8-6.8	
	6061-T6	Al-Sn-Zn	6	23	1	2	34	34	3.8-6.8	
	5086-H34	Al-Hg-Zn	<1	<1	4	6†	<1	<1	8.2-8.5	
	5086-H34	Al-Hg-Zn	<1	<1	<1	<1	<1	<1	7.1-8.5	
	5086-H34	Al-Sn-Zn	<1	<1	1	2	<1	<1	6.8	
	5086-H34	Al-Sn-Zn	<1	<1	<1	1	<1	<1	7.1-7.4	
	5086-H34	None	1	6	—	—	0	0	7.1-7.4	
	5086-H34	None	0	0	—	—	0	0	6.8-7.1	
	6061-T6	Al-Hg-Zn	<1	<1	2	3†	<1	<1	7.9-8.2	
	6061-T6	Al-Hg-Zn	<1	<1	2	4†	<1	<1	8.2-9.1	
6061-T6	Al-Sn-Zn	<1	<1	1	2	<1	<1	7.9-8.2		
	Al-Sn-Zn	<1	<1	1	2	<1	<1	6.8-7.9		
	None	12	18	—	—	10	10	6.5-7.4		
	None	20	27	—	—	21	21	3.8-9.4		

*Redeposited copper caused the unusually severe corrosion on this specimen.
†Bulky corrosion products from crevice corrosion of the Al-Hg-Zn anodes were present under the anodes on these specimens.

Fig. 3 — Depth of corrosion on 5086-H34 aluminum after immersion in seawater for 696 days with and without protection from Al-Hg-Zn or Al-Sn-Zn anodes



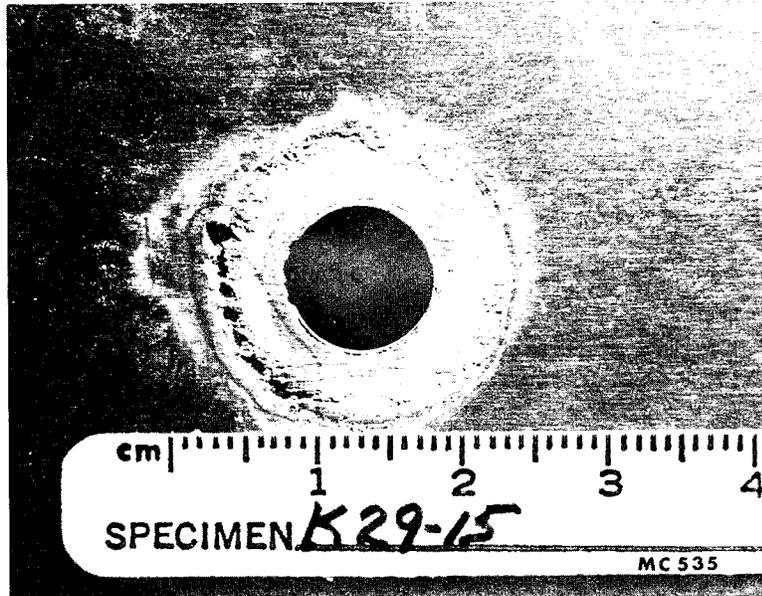
(a) Cathodic protection from Al-Hg-Zn anode

Fig. 4 — 5086-H34 aluminum after continuous immersion in seawater for 696 days with cathodic protection: area under anode, after cleaning

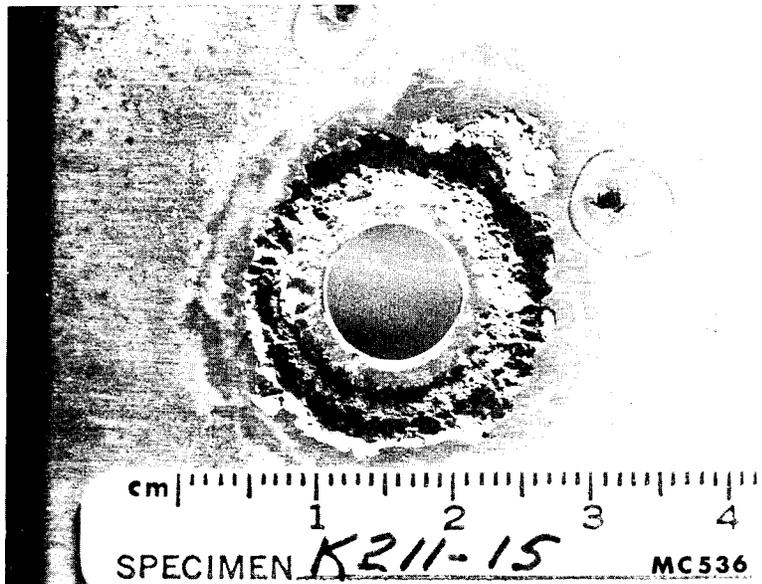


(b) Cathodic protection from Al-Sn-Zn anode

An unusual amount of corrosion occurred on one of the unprotected specimens of 5086-H34 aluminum. This specimen pitted to a depth of 8 mils on the flat surfaces and corroded to a depth of 25 mils in the crevice (Figs. 5a and 5b). In contrast, the duplicate specimen was essentially corrosion-free. The relatively severe corrosion on only one of the unprotected specimens of 5086-H34 aluminum cannot be completely explained, but as discussed later, was related to the redeposition of copper from an unknown source.



(a) Crevice corrosion on 5086-H34 aluminum, under a nylon washer, caused by deposited copper



(b) Crevice corrosion under a nylon washer and pitting on 6061-T6 aluminum.

Fig. 5 — Corrosion on continuous immersion specimens after 696 days in seawater without cathodic protection

6061-T6 Aluminum — The depth of corrosion observed on the cathodically protected specimens of 6061-T6 aluminum (Fig. 6) was similar to that on the 5086-H34 aluminum. The essential absence of corrosion on the continuously immersed 6061-T6 aluminum specimens protected with either Al-Hg-Zn or Al-Sn-Zn anodes is shown in Fig. 7. These data also indicate that Hg from the galvanic aluminum anode did not cause any accelerated corrosion under the continuous immersion condition when cathodic protection was provided for the full exposure period.

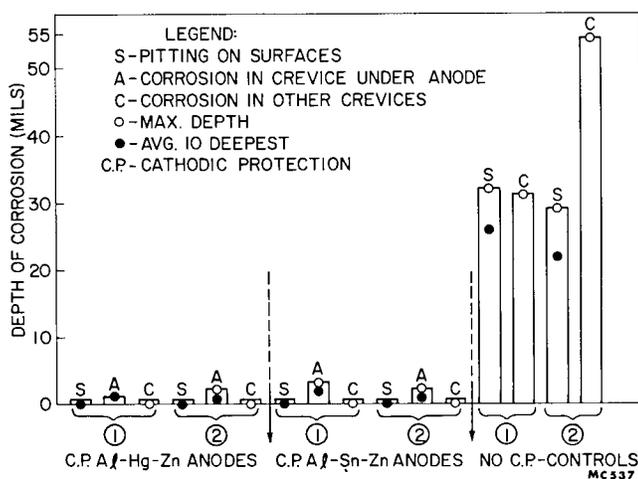


Fig. 6 — Depth of corrosion on 6061-T6 aluminum after continuous immersion in seawater for 696 days with and without cathodic protection from Al-Hg-Zn or Al-Sn-Zn anodes

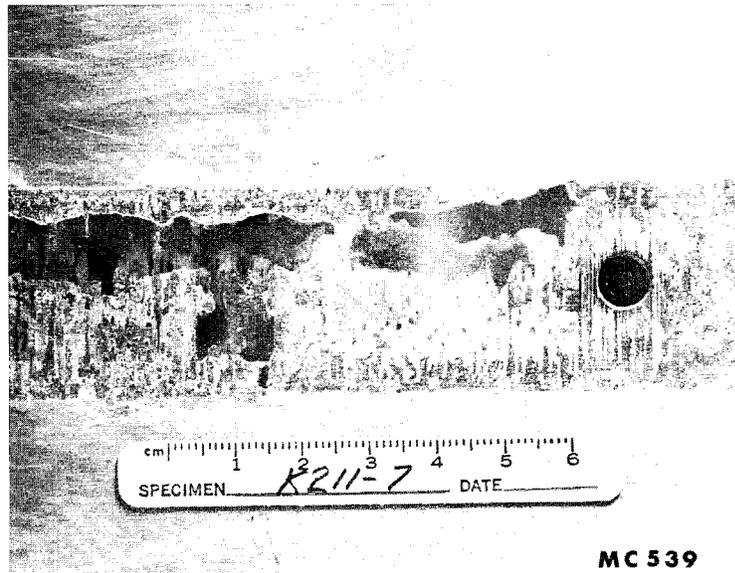
Corrosion on the unprotected specimens of 6061-T6 aluminum was characterized by numerous pits to a maximum depth of 32 mils on the flat surfaces and by severe crevice corrosion to a depth of 54 mils. The severe crevice corrosion and pitting observed on one of the unprotected 6061-T6 aluminum specimens is shown in Fig. 5b.

*Semicontinuous Immersion for 696 Days —
Cathodic Protection Removed After 186 Days*

5086-H34 Aluminum — Figure 8 shows the corrosion depth data for cathodically protected 5086-H34 aluminum semicontinuously immersed in seawater for 696 days. The Al-Hg-Zn and the Al-Sn-Zn anodes (but not the anode corrosion products) were removed after 186 days. These data show that if any residual Hg from the corrosion products of the anodes existed on these specimens, it had no deleterious effect on the depth of corrosion.



(a) Cathodic protection from Al-Hg-Zn anode



(b) Cathodic protection from Al-Sn-Zn anode

Fig. 7 — 6061-T6 aluminum after continuous immersion in seawater for 696 days with cathodic protection: area under anode, after cleaning

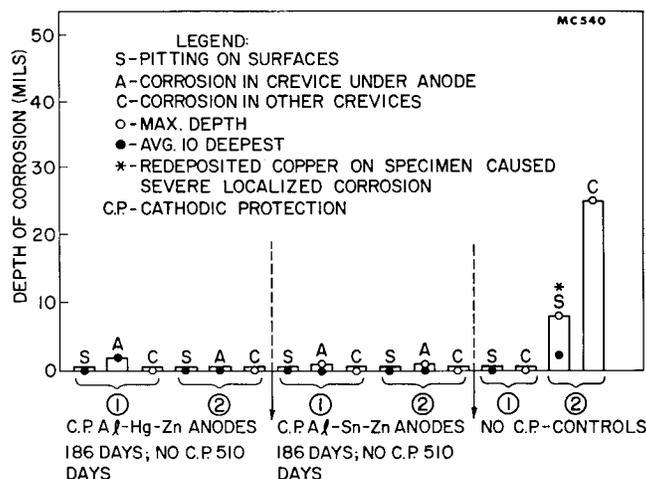


Fig. 8 — Depth of corrosion on 5086-H34 aluminum after semicontinuous immersion in seawater for 696 days, with cathodic protection from Al-Hg-Zn or Al-Sn-Zn anodes for 186 days, and without cathodic protection for 510 days.

Although the depth of corrosion was not generally affected by the Al-Hg-Zn anodes, some corrosion was observed under the anodes. A comparison of the corrosion observed at areas of the specimens under the Al-Hg-Zn and Al-Sn-Zn anodes is shown in Figs. 9a and 9b respectively.

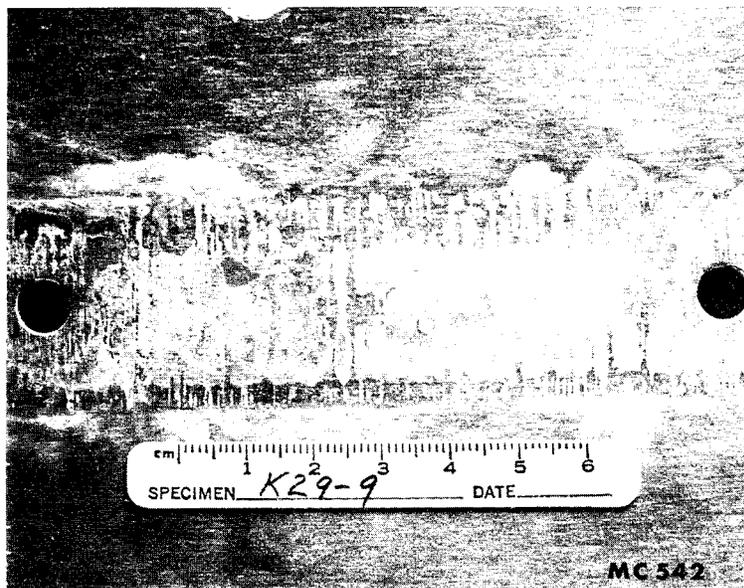
6061-T6 Aluminum — Figure 10 shows the corrosion depth data for 6061-T6 aluminum specimens that were cathodically protected for 186 days before removal of the anodes, but not of the anode corrosion products. These data, when compared to the data for the specimens that received no cathodic protection, show that the Al-Hg-Zn anodes, as expected, reduced the depth of corrosion. Figures 11a and 11b show the extent of corrosion on 6061-T6 aluminum specimens that were protected for the first 186 days of the experiment with Al-Hg-Zn and Al-Sn-Zn anodes respectively. Comparison of Figs. 11a and 11b to Fig. 5b shows also that the corrosion products from neither the Al-Hg-Zn nor the Al-Sn-Zn anodes had any deleterious effect on the corrosion of 6061-T6 aluminum.

Alternate Immersion Cycle for 696 Days With and Without Cathodic Protection

5086-H34 Aluminum — The corrosion depth data for 5086-H34 aluminum alternately immersed in seawater with and without cathodic protection are shown in Fig. 12. These data again indicate that the depth of corrosion was no greater for the specimen protected by the Al-Hg-Zn anodes than for the unprotected specimens. The corrosion observed in the crevice directly under the Al-Hg-Zn anode, however, was greater than observed on any of the other specimens of 5086-H34 aluminum that were cathodically protected (compare Figs. 13a and 9a). The corrosion products which developed from the Al-Hg-Zn anode at the faying surface between the anode and the specimen may have contributed in part to the corrosion observed on this specimen. Of interest is that the same area on a duplicate specimen of 5086-H34 aluminum protected with Al-Hg-Zn anode did not corrode at the faying surface.



(a) Cathodic protection from Al-Hg-Zn anode



(b) Cathodic protection from Al-Sn-Zn anode

Fig. 9 — 5086-H34 aluminum after semicontinuous immersion in seawater for 696 days; with cathodic protection for 186 days, and without cathodic protection for 510 days: area under anode, after cleaning

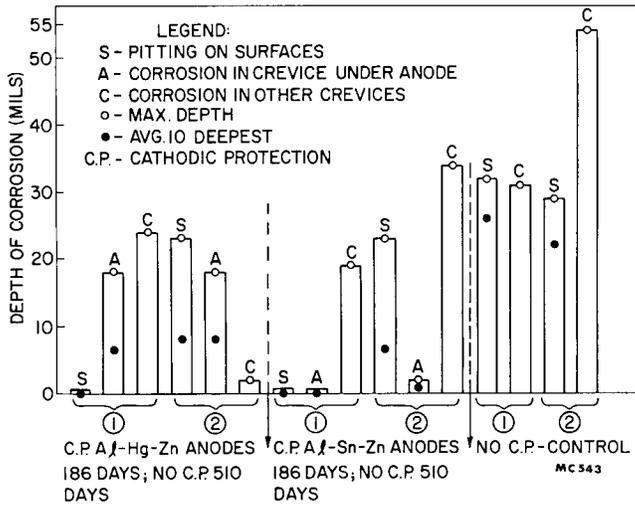
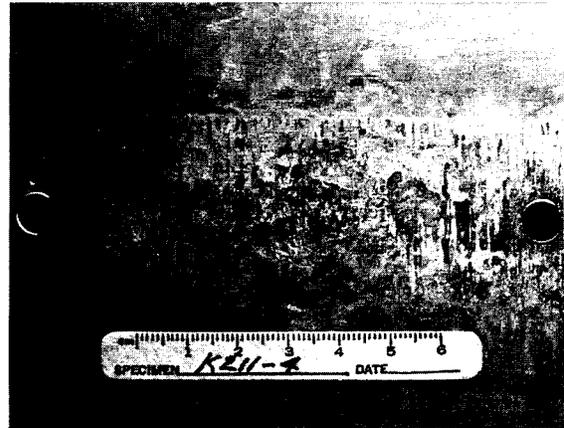


Fig. 10 — Depth of corrosion on 6061-T6 aluminum after semicontinuous immersion in seawater for 696 days, with cathodic protection from Al-Hg-Zn or Al-Sn-Zn anodes for 186 days, and without cathodic protection for 510 days.

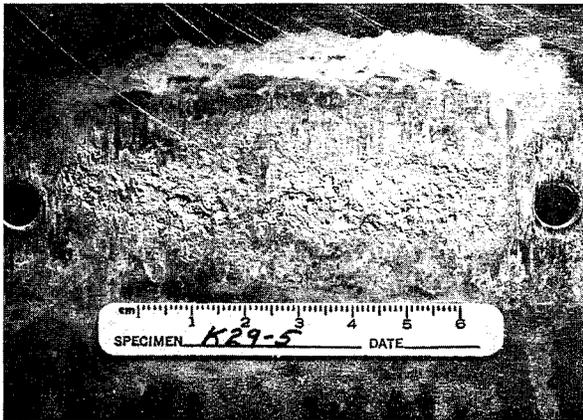
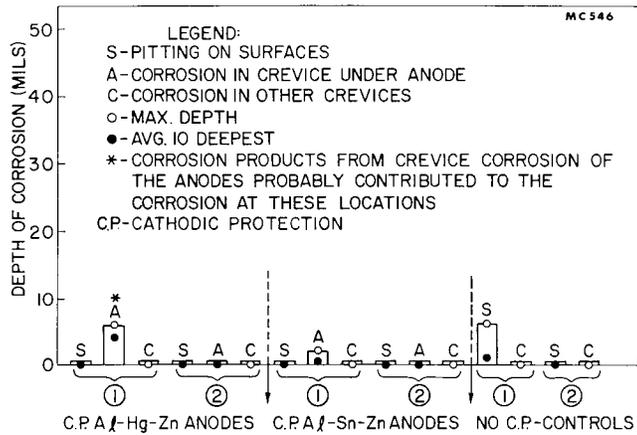
(a) Cathodic protection from Al-Hg-Zn anode



(b) Cathodic protection from Al-Sn-Zn anode

Fig. 11 — 6061-T6 aluminum after semicontinuous immersion in seawater for 686 days, with cathodic protection for 186 days and without cathodic protection for 510 days: area under anode, after cleaning

Fig. 12 -- Depth of corrosion on 5086-H34 aluminum after alternate immersion in seawater for 696 days (one week in seawater and one week in humid marine atmosphere), with and without cathodic protection from Al-Hg-Zn or Al-Sn-Zn anodes



(a) Cathodic protection from Al-Hg-Zn anode

(b) Cathodic protection from Al-Sn-Zn anode

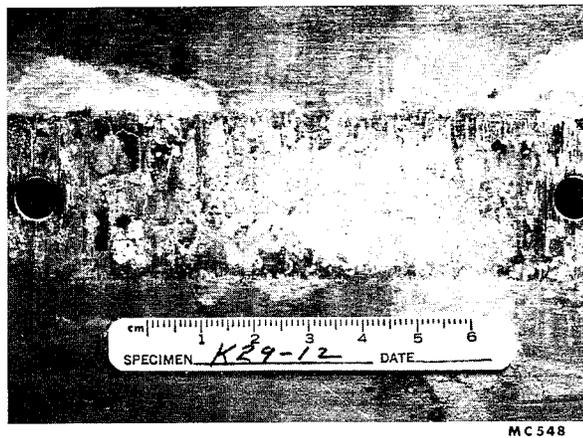


Fig. 13 -- 5086-H34 aluminum after alternate immersion in seawater for 696 days (one week in seawater and one week in humid marine atmosphere): area under anode, after cleaning

The only corrosion noted on the two 5086-H34 aluminum specimens alternately immersed in seawater without cathodic protection was an isolated pit 6 mils deep on a flat surface of one specimen.

6061-T6 Aluminum — The corrosion depth data for 6061-T6 aluminum alternately immersed in seawater with and without cathodic protection are shown in Fig. 14. These data also show that the Al-Hg-Zn anodes led to a marked decrease in the depth of corrosion. The incidence of corrosion, however, was somewhat greater for the specimens protected with the Al-Hg-Zn anode. Figures 15a and 15b show the extent of corrosion at areas under the two types of anodes used for cathodic protection in the alternate immersion condition.

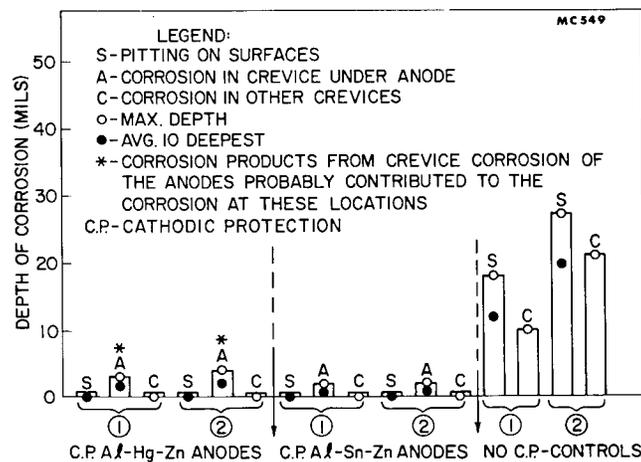


Fig. 14 — Depth of corrosion on 6061-T6 aluminum after alternate immersion in seawater for 696 days (one week in seawater and one week in humid marine atmosphere), with and without cathodic protection from Al-Hg-Zn or Al-Sn-Zn anodes

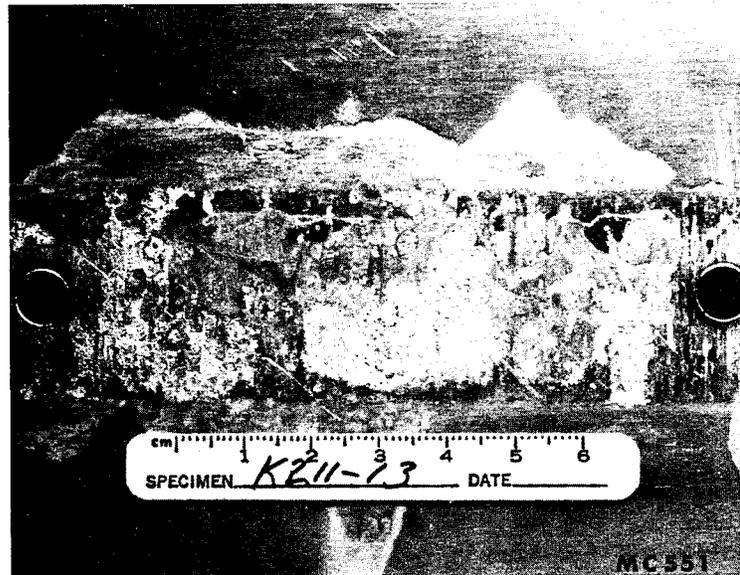
In this condition the aluminum anodes that contained Hg corroded more on the faying surface when coupled to 6061-T6 aluminum specimens than when coupled to 5086-H34 aluminum. The anode corrosion products were approximately 1/4-in. thick for the anodes that corroded significantly at the faying surfaces. Figure 16 shows a comparison of the corrosion observed on the faying surfaces of the Al-Hg-Zn anodes used for protection of the 5086-H34 and of the 6061-T6 aluminum in the alternate immersion condition.

The unprotected specimens of 6061-T6 aluminum were corroded both on the flat surfaces and in the crevices. Of considerable interest was the smaller corrosion depth in the alternate immersion condition as compared to the total immersion condition (compare Figs. 6 and 14). This is somewhat unexpected, because alternate immersion is generally considered a more severe exposure condition than total immersion.

Also of extreme interest was the apparent "carryover cathodic protection" in the alternate immersion condition. This result indicates a possibility that aluminum structures which are under cathodic protection and are removed intermittently from seawater will not corrode significantly during the nonimmersion part of the cycle.



(a) Cathodic protection from Al-Hg-Zn anode



(b) Cathodic protection from Al-Sn-Zn anode

Fig. 15 — 6061-T6 aluminum after alternate immersion in seawater for 696 days (one week in seawater and one week in humid marine atmosphere): area under anode, after cleaning. The incidence of corrosion to a depth of 2 mils or more was greater on the specimen shown in (a).



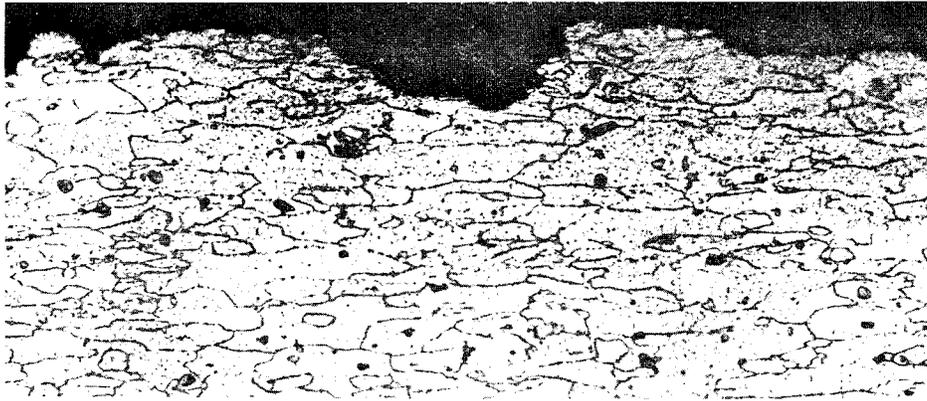
Fig. 16 — Crevice corrosion on Al-Hg-Zn anodes after alternate immersion in seawater for 696 days, photographed after cleaning. The top pair of anodes protected 5086-H34 aluminum specimens, and the lower pair of anodes protected 6061-T6 aluminum specimens. Corrosion products from the anodes, located between the anodes and the specimens, were approximately 1/4 in. thick and warped the specimens.

Metallographic Study

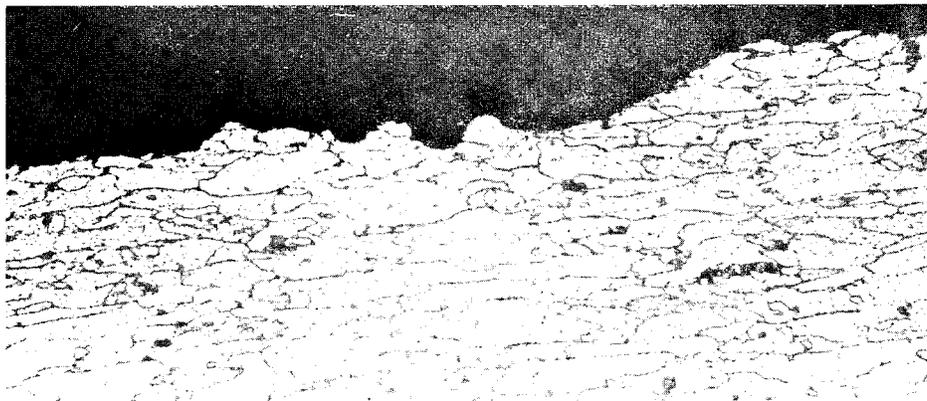
Selected specimens of the 5086-H34 aluminum alloy were examined metallographically for intergranular corrosion and other evidence of abnormal corrosion associated with Hg, Sn, or corrosion products from Al-Hg-Zn or Al-Sn-Zn anodes. No evidence of either intergranular or other abnormal corrosion was found in the following cases: on an immersion specimen protected with an Al-Hg-Zn anode for 186 days followed by an additional exposure of 510 days in contact with the corrosion products but with the anode removed (Fig. 17a), on an alternate immersion specimen protected with an Al-Hg-Zn anode (Fig. 17b), and on an alternate immersion specimen protected with an Al-Sn-Zn anode (Fig. 17c).

Electron Microprobe and X-Ray Diffraction Analyses

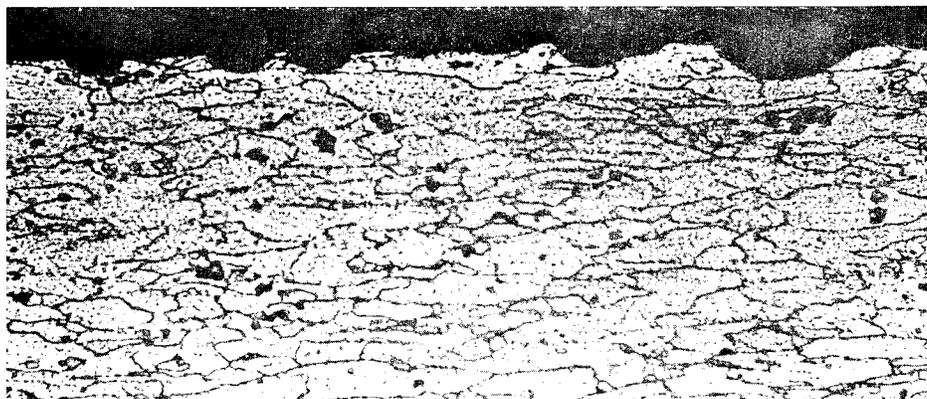
A limited amount of x-ray diffraction analysis of corrosion products and of electron microprobe analysis of corroded areas was conducted to investigate the possibility of re-deposition of mercury or tin from the anode corrosion products. These analytical methods were also used to gain insight into the cause of the unexpectedly severe corrosion observed on one specimen of 5086-H34 aluminum alloy exposed without cathodic protection.

**MC 553**

(a) Semicontinuous immersion with cathodic protection from an Al-Hg-Zn anode for 186 days, without cathodic protection for 510 days

**MC 554**

(b) Alternate immersion with cathodic protection from an Al-Hg-Zn anode: area under anode

**MC 555**

(c) Same as (b) but with cathodic protection from an Al-Sn-Zn anode

Fig. 17 — Photomicrographs at 500X magnification showing the absence of intergranular corrosion on 5086-H34 aluminum immersed in seawater for 696 days. All specimens were etched in 1% NaOH at 1.5 volts for 30 seconds.

In many instances the corrosion products gave weak or diffuse x-ray patterns, but $\beta\text{Al}(\text{OH})_3$, bayerite, was generally present. Calcite, CaCO_3 , was identified by x-ray diffraction in the corrosion products on the unprotected 5086-H34 aluminum specimen that had corroded unexpectedly at a crevice when continuously immersed in seawater. Redeposited copper was suspected as the cause of this corrosion. Electron microprobe analysis confirmed the presence of copper on this specimen concentrated at a level of 61 percent in the crevice area that had corroded. An electron microprobe x-ray display of copper at this area is shown in Fig. 18. A secondary electron topographical display of the same area is shown in Fig. 19.

In addition to bayerite, hydromagnesite $\text{Mg}_4(\text{OH})_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ was found in the corrosion products on a 5086-H34 aluminum specimen protected with an aluminum anode containing Sn and alternately immersed in seawater. Electron microprobe analysis did not detect Sn on this specimen at the location under the anode where corrosion had occurred. Copper was found on the specimen, however, at two locations beneath the anode, concentrated at levels of 12 and 31 percent. Figure 20 shows an electron microprobe x-ray display of one of the locations where copper was detected. Figure 21 shows a secondary electron topographical display of the same area.

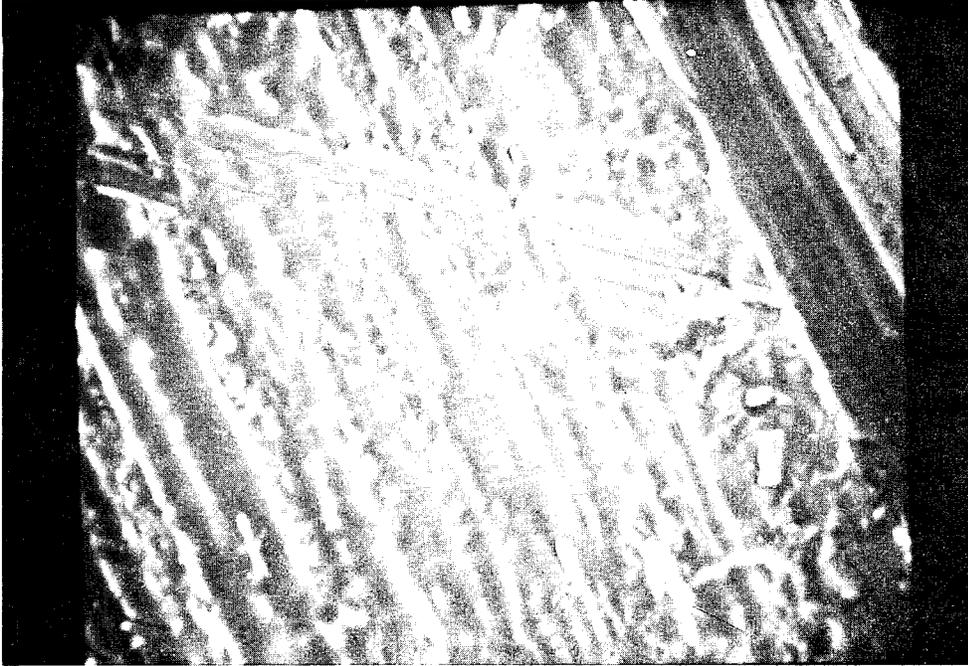
Spectrographic analysis of the corrosion products from the 5086-H34 aluminum specimen which corroded in the crevice under the Al-Hg-Zn anode when exposed in the alternate immersion condition, showed very weak lines for Hg, but electron microprobe analysis did not detect Hg at the corroded areas. Copper was found, however, by microprobe analysis at two locations beneath the anode, concentrated at levels of 1 and 6 percent. Figure 22 shows an electron microprobe x-ray display of one area that had corroded, and Fig. 23 shows a secondary electron topographical display of the same area.

The electron microprobe analyses confirmed that copper was present and undoubtedly caused the accelerated corrosion at the crevices on the unprotected 5086-H34 aluminum continuously immersed in seawater. Neither Hg nor Sn were detected by microprobe analysis on the specimens of 5086-H34 aluminum, which, in the alternate immersion condition, had corroded at the faying surface between the specimens and the aluminum anodes containing Hg or Sn. The detection of copper on both of these specimens suggests that deposited copper may also have contributed to the corrosion in these instances. The source of the copper on these specimens is not known.

Corrosion (Open Circuit) Potentials

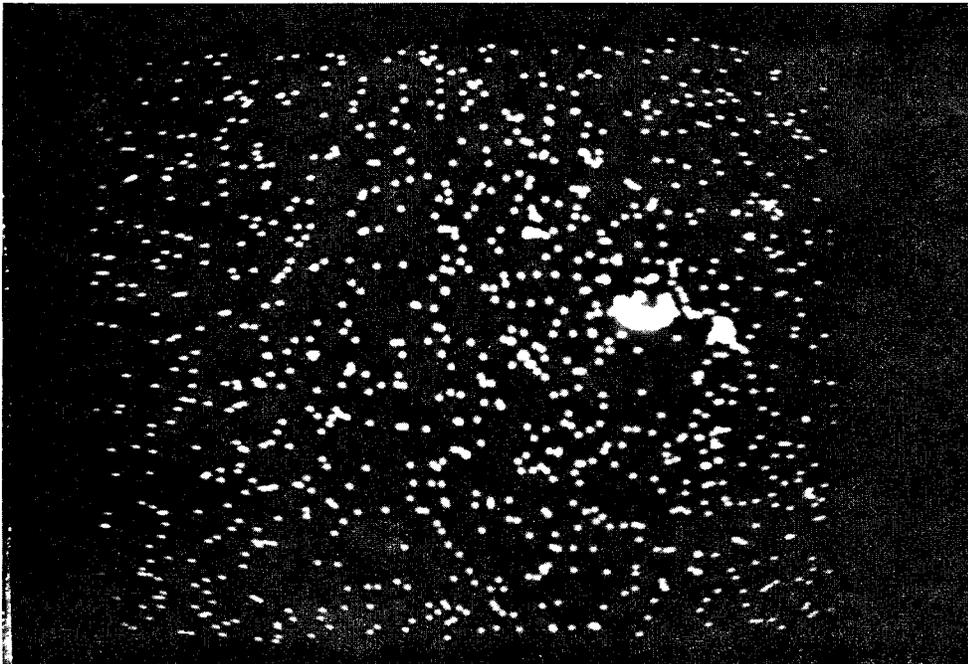
5086-H34 Aluminum — The mean corrosion potentials of unprotected specimens of 5086-H34 aluminum continuously immersed in seawater for 696 days were -0.92 volt to a saturated calomel electrode. The corrosion potential data are summarized in the histograms in Fig. 24.

The flow of seawater past the continuously immersed specimens was inadvertently intermittent rather than continuous for 9 days starting at the 405th day. During the short interval of interrupted seawater flow, the corrosion potential of one of the unprotected specimens of 5086-H34 aluminum shifted in the positive direction and remained more positive for the duration of the experiment. The change in the potential is believed to have been caused by the redeposition of copper on the surface of the specimen. As discussed earlier, copper was detected on this specimen by electron microprobe analysis and undoubtedly contributed to the unusually severe localized corrosion and the relatively positive potentials observed on this specimen after the 405th day of exposure (Fig. 24c).



MC557

Fig. 19 -- Electron microprobe analysis: secondary electron topographical display (20 $\mu/8$ mm) of the same specimen and location shown in Fig. 18.



MC556

Fig. 18 -- Electron microprobe x-ray display (20 $\mu/8$ mm) showing copper at corroded crevice area of unprotected 5086-H34 aluminum after continuous immersion in seawater for 696 days.

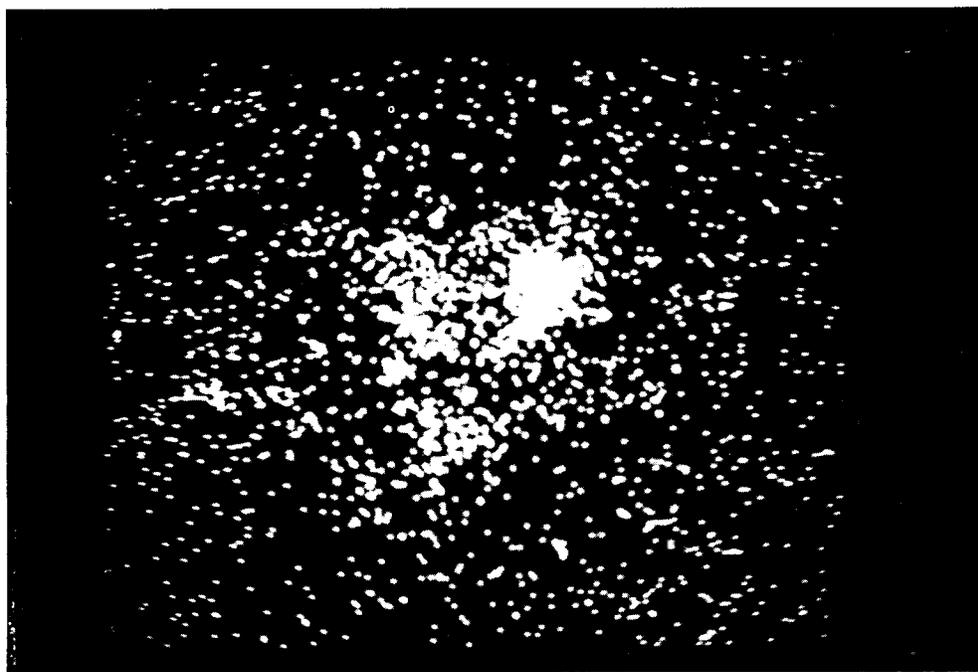
**MC 558**

Fig. 20 — Electron microprobe x-ray display (10 $\mu/8$ mm) showing copper at the location where the Al-Sr-Zn anode was attached and corrosion had occurred on 5086-H34 aluminum after alternate immersion in seawater for 696 days. Tin was not detected on this specimen by electron microprobe analysis.

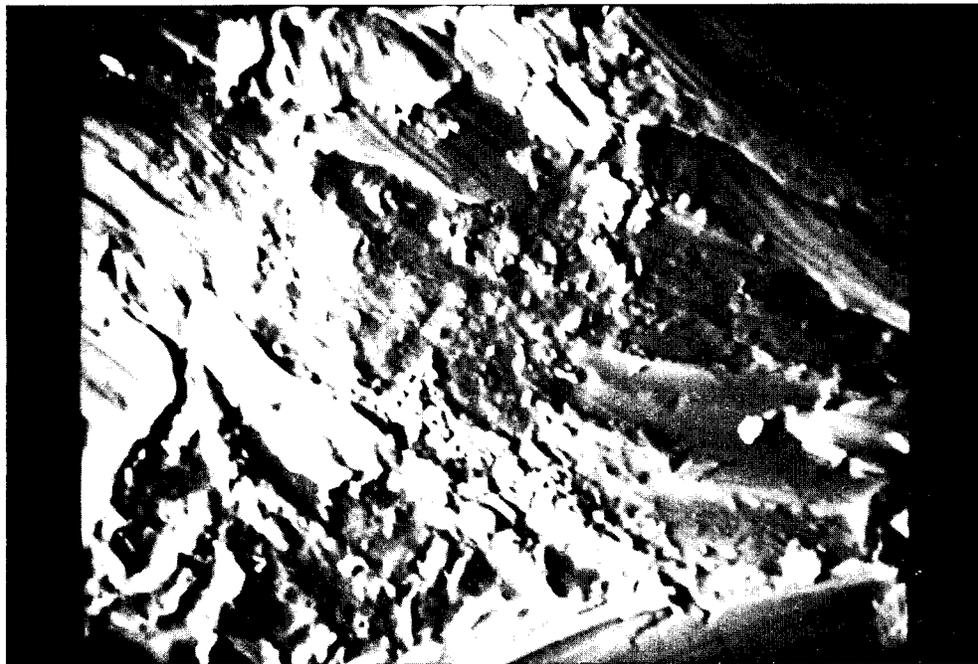
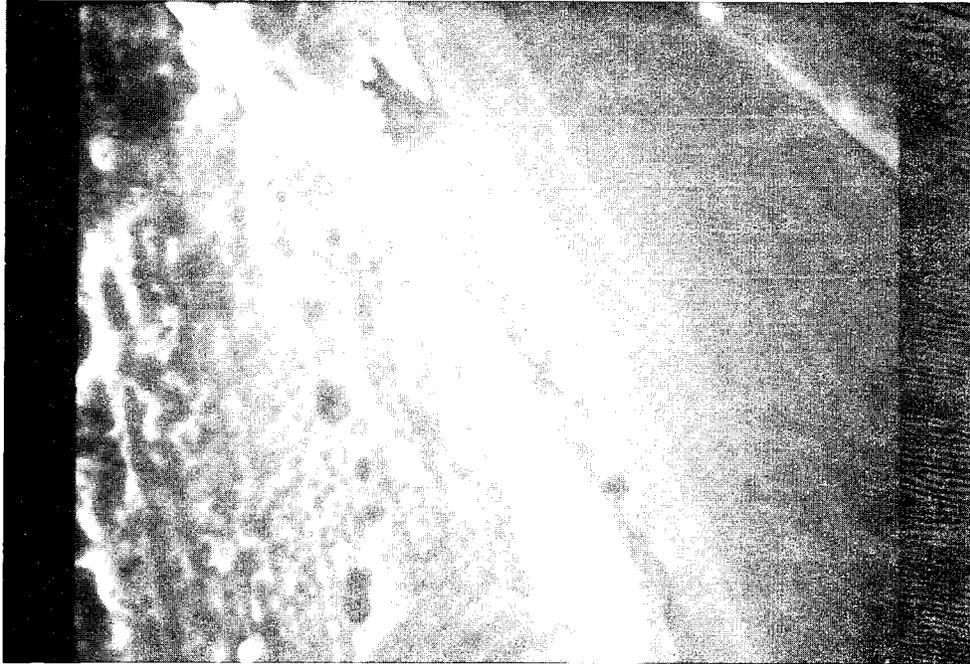
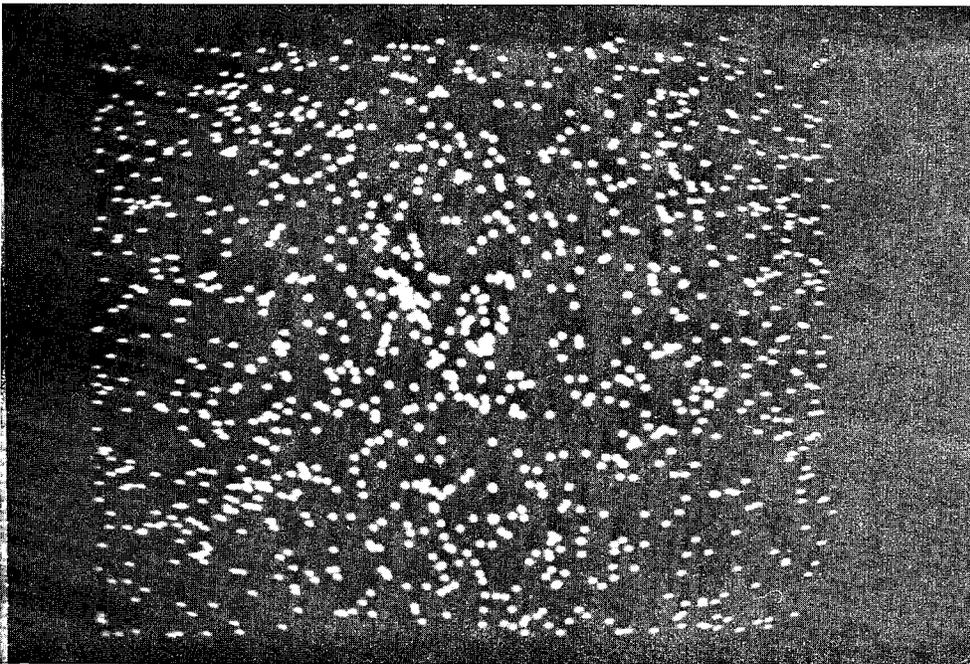
**MC 559**

Fig. 21 — Electron microprobe analysis: secondary electron topographical display (10 $\mu/8$ mm) of the same specimen and location shown in Fig. 20.



MC 561

Fig. 23 — Electron microprobe analysis: secondary electron topographical display ($10 \mu/8 \text{ mm}$) of the same specimen and location shown in Fig. 22.



MC 560

Fig. 22 — Electron microprobe x-ray display ($10 \mu/8 \text{ mm}$) showing copper at the location where the Al-Hg-Zn anode was attached and corrosion had occurred on 5086-H34 aluminum after alternate immersion in seawater for 696 days. Mercury was not detected on this specimen by electron microprobe analysis.

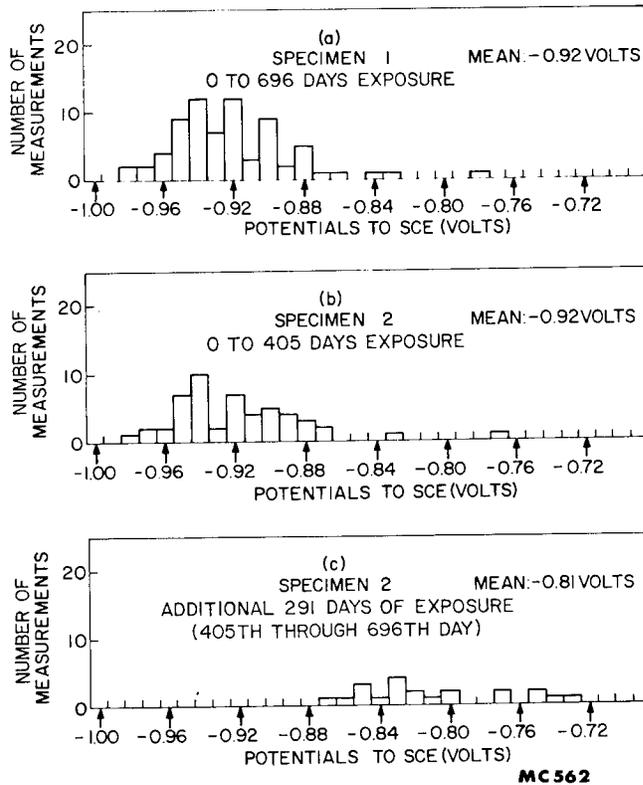
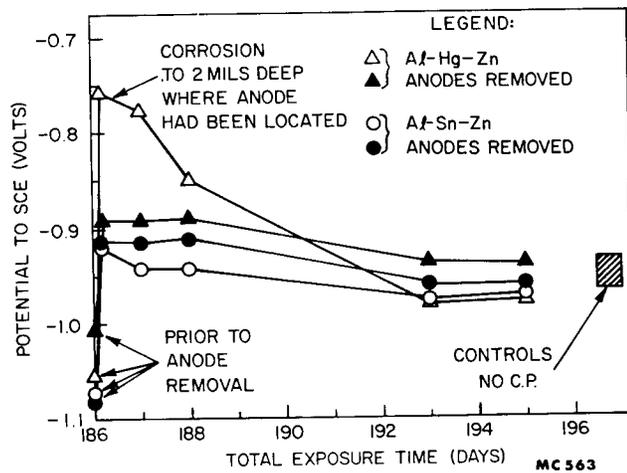


Fig. 24 — Histograms of potential data for two unprotected 5086-H34 aluminum specimens after continuous immersion in seawater for 696 days; (a) No copper contamination suspected on this specimen; (b) Potentials for second specimen for the first 405 days of exposure. Copper contamination was suspected; (c) Potentials for the second specimen during an additional 291 days of exposure. Copper contamination was confirmed by electron microprobe analysis.

The corrosion potentials of the aluminum specimens which had the anodes removed after 186 days were measured periodically after the specimens were reimmersed in the seawater. The potential of one specimen which had been protected with an Al-Hg-Zn anode shifted rapidly to more positive values, i.e., from -1.055 to -0.76 volt, following reimmersion. Gradually the potential became more negative, reaching -0.98 volt within 7 days (Fig. 25).

Fig. 25 — Potentials of 5086-H34 aluminum specimens after removal of cathodic protection; immersion in seawater was semicontinuous for 696 days, with cathodic protection for 186 days and without cathodic protection for 510 days.



6061-T6 Aluminum — Continuously immersed unprotected specimens of 6061-T6 aluminum had mean corrosion potentials of -0.75 and -0.77 volt relative to the SCE reference electrode. The potentials recorded for these specimens are summarized in the histograms of Fig. 26.

Figure 27 shows the potential data obtained following reimmersion of the 6061-T6 aluminum specimens after the anodes were removed at 186 days. Shortly after reimmersion, the potentials shifted in the positive direction and into the range of the potential of the control specimens. Gradually the potentials become more negative, and within 7 days the potentials were approximately 0.15 volt more negative than the potentials of the unprotected control specimens. The potentials of these specimens remained more negative for up to 178 days following reimmersion.

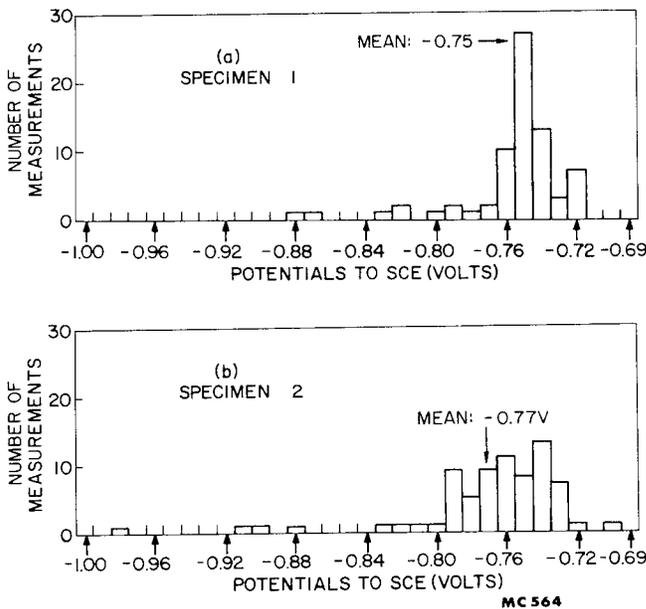
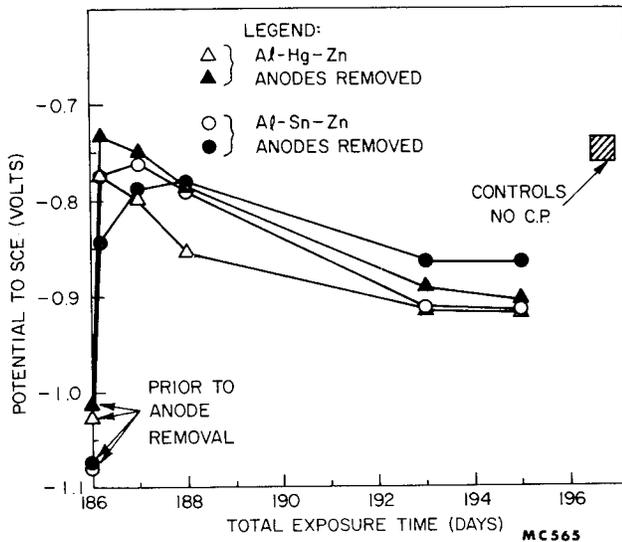


Fig. 26 — Histograms of potential data for two unprotected 6061-T6 aluminum specimens after continuous immersion in seawater for 696 days.

Fig. 27 — Potentials of 6061-T6 aluminum specimens after removal of cathodic protection; immersion in seawater was semicontinuous for 696 days, with cathodic protection for 186 days and without cathodic protection for 510 days.



pH in Crevices

The pH data for the solution in the crevices have been summarized in Table 2. In the crevices of the cathodically protected specimens of both types of aluminum in either continuous or alternate immersion in seawater for 696 days, the pH ranged from 6.8 to 9.1. The most frequently observed value was 8.2, the approximate pH of seawater.

In the case of all the unprotected specimens of 5086-H34 aluminum, the pH was generally from 6.8 to 7.4 in the crevices where corrosion did not occur. Where crevice corrosion did occur, a pH of 5.3 was observed.

In the case of unprotected and continuously immersed specimens of 6061-T6 aluminum, pH levels from 3.5 to 3.8 were measured in the crevices where corrosion had occurred. In the alternate immersion condition, a wide range of pH levels — from 3.8 up to 9.4 — was observed in the crevices of the unprotected specimens of 6061-T6 aluminum that had corroded.

SUMMARY AND CONCLUSIONS

- Galvanic anodes of the Al-Hg-Zn and Al-Sn-Zn types provided satisfactory cathodic protection to continuously immersed 5086-H34 and 6061-T6 aluminum in seawater when the cathodic protection was uninterrupted.

- In the alternate immersion condition, corrosion to a depth of 6 mils was observed at the location where the Al-Hg-Zn anodes contacted the 5086-H34 aluminum and to a depth of 4 mils at a similar location on 6061-T6 aluminum. Corrosion under the Al-Sn-Zn anodes was 2 mils or less on both aluminum alloys. Cathodic protection by either type of aluminum anode can be considered effective even in the alternate immersion condition, at least under the conditions of this experiment.

- In the semicontinuous immersion condition, where the cathodic protection was removed after 186 days and the specimens were reimmersed without cathodic protection for 510 days, the corrosion of the 6061-T6 aluminum was less than on the specimens that were unprotected for the entire period.

On the 5086-H34 aluminum under this condition, the depth of corrosion was not generally affected by the Al-Hg-Zn anode, although some corrosion was observed where the anode had been located on the specimen.

- Redeposited copper on one of the unprotected 5086-H34 aluminum specimens caused severe localized corrosion. The presence of copper on the corroded area was confirmed by electron microprobe analysis. During the experiment the potential of this specimen shifted in the positive direction, a shift which also indicated the possible presence of a more noble metal on the surface.

- In the alternate immersion condition, there were indications that corrosion products that formed at the anodes and developed between the anodes and the specimen may have contributed to the corrosion under the anodes. However, electron microprobe analysis did not detect any Hg or Sn at these locations but did detect copper. Corrosion products from the Al-Hg-Zn anode were bulky and caused warping of the specimens. These data suggest

that a barrier such as zinc oxide paste should be used between aluminum anodes and a structure being protected, especially if the structure, or parts of it, are not continuously immersed.

- The mean corrosion (open circuit) potential of unprotected and uncontaminated 5086-H34 aluminum specimens was -0.92 volt to a saturated calomel reference electrode. The mean potentials for the 6061-T6 aluminum were -0.75 to -0.77 volt.

- The solution in the crevices of cathodically protected 5086-H34 and 6061-T6 aluminum either continuously or alternately immersed, generally had a pH of 8.2, which approximates that of the seawater. Crevice corrosion of the unprotected and continuously immersed specimens resulted in a pH of 5.3 in the crevices for 5086-H34 aluminum and 3.5 to 3.8 for 6061-T6 aluminum. In the alternate immersion condition, the solution in the crevices of unprotected and corroded 6061-T6 aluminum had inconsistent pH levels ranging from 3.8 to 9.4.

- Additional studies should be conducted to determine the effect of mercury from aluminum anodes on other metals commonly used in seawater with cathodic protection. Any effects on the cracking characteristics of the metals should also be included in such a study.

ACKNOWLEDGMENTS

The authors are indebted to Mr. W. M. Lazier (retired) and Mr. C. W. Billow of the NRL Marine Corrosion Research Laboratory, Key West, Florida, for assisting in the exposure phase of this study; Mr. J. A. Smith for the x-ray diffraction data and Ms. F. W. Fraser for the electron microprobe analysis. This research was sponsored by the Naval Ship Systems Command.

REFERENCES

1. T. J. Lennox, Jr., et al., "A Study of Electrochemical Efficiencies of Aluminum Galvanic Anodes in Sea Water," *Materials Protection*, 7:2, 33, Feb. 1968.
2. J. T. Reding and J. J. Newport, "The Influence of Alloying Elements on Aluminum Anodes in Sea Water," *Materials Protection*, 5:12, 15, Dec. 1966.
3. T. J. Lennox, Jr., et al., "Electrochemical Characteristics of Six Aluminum Galvanic Anode Alloys in the Sea," *Materials Protection and Performance*, 10:9, 39, Sep. 1971.

