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Effects of Alloy Chemistry Changes
on Sacrificial Aluminum Anode Performance

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ABSTRACT

The set of aluminum alloy sacrificial anodes taken from the upper starboard stern array from a Navy submarine was evaluated at CDNSWC to determine the cause of non-uniform utilization during the approximately 30 month anode service period. Physical data from the used anodes as well as electrochemical characterizations were determined. The evidence indicated that the three distinct levels of anode weight change (and estimated discharge current) could be attributed to distinct levels of mercury contamination in the three heats of alloy from which these particular anodes were taken. The experience shows that reasonable vendor care in alloy preparation and anode casting must be taken for uniform anode performance to be achieved in multi-anode array applications.

INTRODUCTION

A US Navy submarine was outfitted with a ship set of Galvalum III, indium activated, aluminum alloy sacrificial anodes during the February 1990 post shakedown availability. The anodes had been procured by the Electric Boat (EB) Division of General Dynamics using an EB purchase specification. The EB purchase specification was modeled on a CDNSWC draft version of a military specification (Draft MIL-SPEC), "Anodes, sacrificial, aluminum alloy". Anodes from essentially all heats of the procurement were selected by the EB inspectors, shipped to CDNSWC and subjected to the QA/QC procedures by CDNSWC as outlined in the EB purchase specification. In general, the electrochemical performance of the anode heats was found to be acceptable. However, Heat 3069 was

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The anode installations and various outfitted tanks and spaces were reinspected in early October 1992. In general, the anode consumption rates were found to be as expected for the approximately 30 months of service exposure. The tanks and voids were also found to be protected with little paint deterioration or metal corrosion which might be attributed to improper anode installation or inadequate anode performance. However, there was a rather marked non-uniform anode consumption which was observed on each of the four stern array anode strings. A typical view of the first 11 of the 21 AHC-10 anodes from the upper starboard array is shown as Figure 1. Counting from forward to aft, anodes 2, 3, 7 and 11 appeared to be essentially unused. On-site visual estimates of 40-60% alloy consumption of the majority of the anodes were made. Simple on-site checks of the mounting-bolt-to-alloy-body electrical continuity showed all anodes of the upper string were electrically connected to the hull. Although there were only 17 of 84 anodes on the stern which had this "unused" appearance, the behavior was of sufficient concern to warrant a low level investigation as to cause. It should be noted that the 67 "good" anodes would be sufficient for cathodic protection of the stern. One possible assumption of cause of anode non-use was that these 17 anodes were "dead", that is, the surface oxide coating which had formed during the 6 months following fabrication and before wetting in the estuary waters was sufficiently tenacious that the pieces were completely passivated, i.e., inactive.

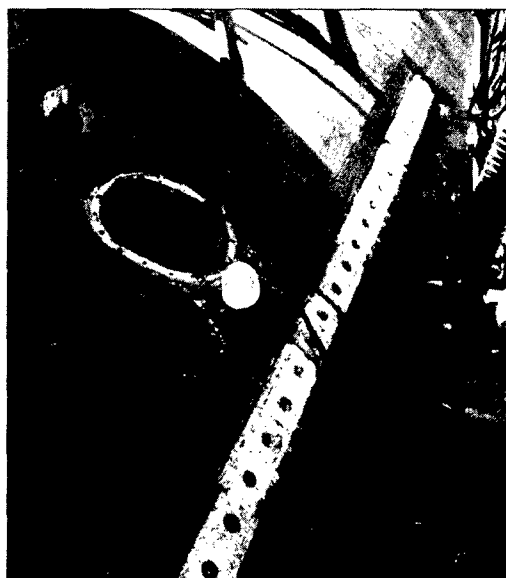


Figure 1. Upper stern aluminum alloy array, 688 Class, 30 months service.

If one makes that assumption, then removing and evaluating the anodes from the array after they became exposed in the dry dock environment carries the risk of different reactivations in the subsequent laboratory test environment. This might suggest the laboratory test results would not relate to the anode status just prior to drydocking. In addition, the submarine sat pierside for an undisclosed period prior to drydocking, during which time metal ion impurities (such as copper from the anti-fouling coating system) could have electrodeposited on the sacrificial anode surfaces affecting the general electrochemical performance characteristics. With at least these two caveats, as the stern arrays were to be replaced with new aluminum anodes, a decision was made to mark and return the upper stern array to CDNSWC for further analysis. The initial effort was to be limited to weighing the anodes and simple electrochemical testing.

Therefore, the overall objective of this effort was to attempt to determine if the cause of non-uniform anode consumption could be identified. This paper summarizes the effort and findings of the study.

EXPERIMENTAL

The anodes were purchased by EB in accordance with the EB material specification. Material chemistry and electrochemical performance data of samples taken from unused anodes from all of the heats were determined previously and selected values are included later in the Results and Discussion section.

The tagged, 6 x 12 x 1.25", AHC-10 anodes from the upper starboard stern array were received at CDNSWC, weighed in the as-received condition, nylon brush cleaned under flowing water, dried overnight at ambient conditions and reweighed. The heat numbers of many of the anodes were still legible on the "backside" of the anodes and these were noted. Physical dimensions of each anode were also recorded.

Two types of electrochemical tests were performed. The full sized, cleaned anodes were positioned vertically in a 12" x 12" x 12" polyethylene tank. A carbon steel plate counterelectrode was positioned approximately 7 inches from and parallel with the test anode. The electrochemical reactivating characteristics were determined by monitoring the anode potential for roughly a one day period while discharging the test anode at a constant current of 288 mA. This current was selected as approximating the discharge current density of 4 mA/in² used in the previous smaller sample QA/QC test effort. The 288 mA current assumes only the alloy surface facing the counterelectrode contributed appreciably to the discharge process.

All testing was performed at laboratory ambient temperature (20-23°C, 68-75°F) using aerated ASTM-D-1141, substitute ocean water. The electrolyte bath was not changed until after testing three anodes, as the small amount of accumulated anode reaction products was judged not to be affecting the electrochemical performance.

Three anodes, selected as typical for each observed type of repassivation behavior, were tested further. Two preselected pairs from these three anodes were subjected to an overnight galvanic couple experiment, followed by full potentiodynamic scans in the range of - 1200 to - 700 mV. vs. saturated calomel reference electrode (SCE). Several additional runs were made with new zinc and new Galvalum III anodes as well as used zinc and estuary-exposed Galvalum III pieces. After the test electrolyte was contaminated with zinc anode reaction products, another zinc anode was tested or the test cell was replenished with fresh test solution.

RESULTS AND DISCUSSION

The weights of the cleaned anodes are summarized in Table 1 by tag number which should correspond to the linear position coming aft in the upper starboard stern array. The anode tag numbers of the four anodes which showed little consumption do not quite agree with the photographic data and notes from the inspection but the tag numbers will be utilized throughout the rest of this report. Subtracting the used anode weight from the 3951 gram alloy average initial weight as well as the 272 gram steel strap weight determined previously for the AHC-10 anodes (and correcting for the machined leading and lagging taper of the two end anodes), results in the approximate weight change values shown in Table 1 for the anodes during the approximately 30 month exposure. The weight change values were converted to averaged anode currents utilizing 90% averaged Faradaic efficiencies determined previously. The calculated current data are then summarized as Figure 2. A column of percentage used (or percentage consumed) is included in Table 1. As the actual values of the "active" anodes ranged from 15 to 35%, the availability of a set of comparative visual standards would probably have resulted in better estimates than the 40-60% range made during the drydock inspection.

Table 1
Anode Weights Calculated Weight Changes and Anode Currents

Anode Number	Cleaned Weight (g)	Calculated Weight loss (g)	Percent Used	Calculated (mA) Anode Current	Heat Number
1	3061.1	1095	28	134	*3160
2	2924.9	1298	32	159	3070
3	4042.0	181	5	22	3069
4	4122.0	101	3	12	- -69
5	2811.5	1418	36	174	3130
6	3145.9	1077	27	132	-130
7	2955.2	1267	32	155	3130
8	4225.4	0	0	0	3069
9	3290.8	932	24	114	3070
10	3126.9	1096	28	134	3130
11	4215.7	7	0	1	3069
12	3108.2	1093	28	134	3130
13	3251.9	971	25	118	3130
14	3469.6	753	19	92	3070
15	3414.6	808	20	99	-070
16	3212.1	1011	26	124	3130
17	3623.8	599	15	73	3070
18	3066.1	1157	29	142	3130
19	3519.6	703	18	86	3070
20	3019.5	1204	30	147	3130
21	2437.7	1719	44	211	3130

* = incorrect heat number

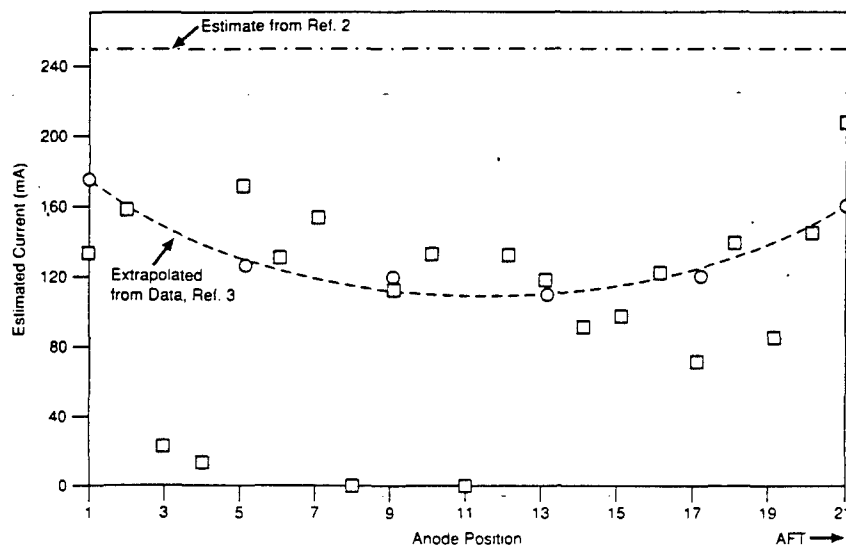


Figure 2. Calculated anode currents by anode position in stem array.

Two reference lines are included in Figure 2. The upper horizontal line represents the average anode current expected using the formula published by Waldon and Peterson². The lower curved line is an estimated current distribution derived from experimental data from a six anode array which showed the end anodes to contribute more current than the inner anodes in a linear array³. Although there is considerable scatter and associated risk in drawing conclusions with these estimated weight loss data, the calculated currents tend to indicate the first ten anodes in the array contributed somewhat more protection current than the anodes further aft excluding the last two anodes. The electrical and mechanical linkage of the propeller through the shaft to the hull does occur forward of the array and the potential drop through the hull may account for the apparent maldistribution. An equivalent argument could be made regarding the distribution of ionic currents which would allow the greater consumption at the aft end of the string. Unfortunately, the computer program BEASY cannot be used to model this problem as electrical current through the metallic elements is assumed to be uniform⁴.

The four under-utilized anodes at positions 3, 4, 8 and 11 obviously would not be explained by the current distribution considerations. However, as one

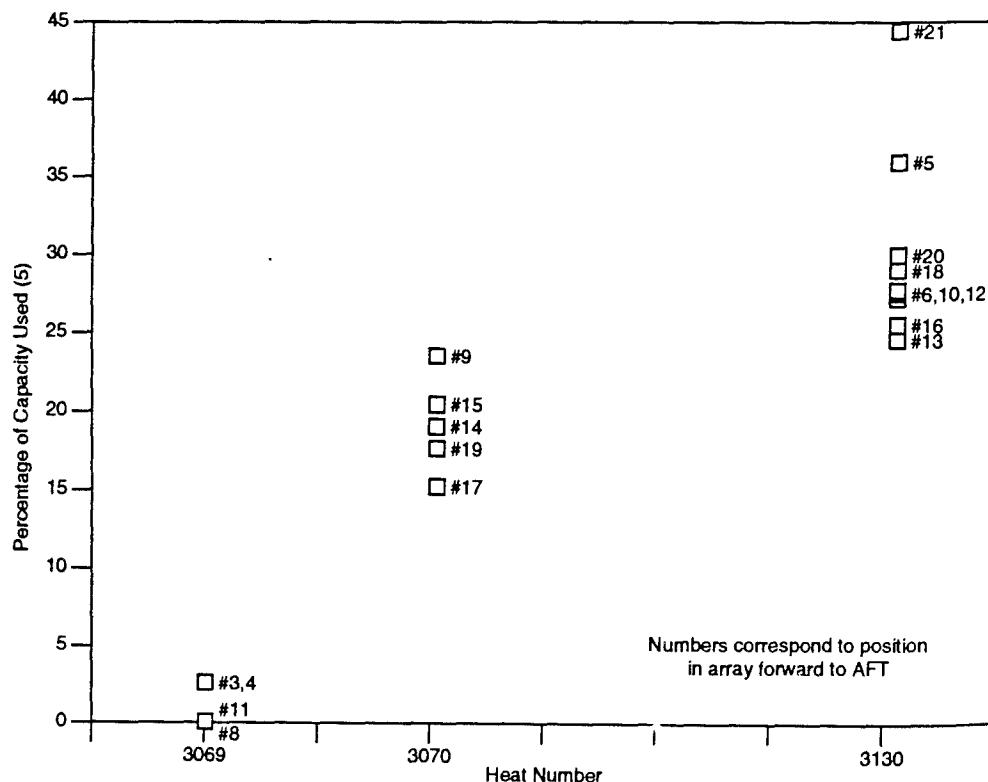


Figure 3. Percentage of alloy contained in 30 months vs. heat number.

might have observed in the Table 1 data, the four anodes in question were the only anodes associated with fabrication Heat 3069. Anode consumption is plotted against the heat number as Figure 3. Interestingly, the amounts of alloy consumed fell into three groups which then were associated with three particular heats.

The reactivation (constant current, voltage-time) data also tended to group within the same heat number pattern. Nearly all the 21 anodes allowed an initial on-current potential of -0.9 V vs SCE, inferior to the maximum required potential level of < -0.98 V vs. SCE. The Heat 3130 anode potentials started to decrease (become more negative) somewhat rapidly after about 3 hours exposure, still decreasing at a slower rate from the 20+ hour end-of-test exposure of approximately -1.01 V vs SCE. Heat 3069 anodes tended to stabilize at a potential of approximately -0.95 V vs SCE at 10 hours exposure whereas Heat 3070 anodes tended to stabilize at a higher potential of -0.92 V vs SCE. The general anode voltage behavior patterns are summarized in Figure 4. An examination of the short-term QA/QC electrochemical test data from these three heats also shows the same general trends but somewhat lower potentials which might be expected with fresh chemically cleaned metallic surfaces exposed only to laboratory air prior to electrochemical testing. The relevant electrochemical test data are presented in Table 2.

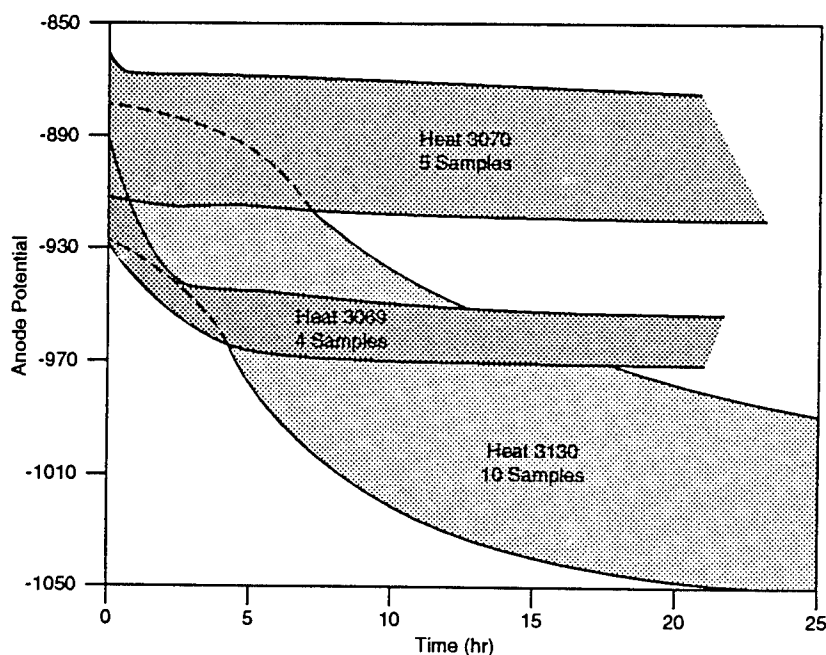


Figure 4. Summary of reactivation time characteristics, 288mA constant current, full size, used anodes.

Table 2
Anode Potential Data from QA/QC and Reactivation Tests

Heat Number	QA/QC Potentials			Reactivation Potentials		
	1 Hour	3 Hours	24 Hours	1 Hour	3 Hours	20 Hours
3069	-1.016	-1.017	-0.993	-0.930	-0.950	-0.955
3070	-0.971	-1.023	-1.070	-0.900	-0.905	-0.910
(av. 3)						
3130	-1.094	-1.101	-1.110	-0.910	-0.920	-1.005

In addition, the QA/QC test, Faradaic efficiency (η) of Heat 3069 was observed to be particularly high at 95 % (weight loss efficiency, wt η) and 97% (efficiency from evolved H_2 gas rate, H_2 η).

The QA/QC electrochemical test results were attributed to the presence of a high degree of mercury contamination which was introduced into the process in Heat 3069. The mercury contamination was diluted in Heat 3070 and subsequently found to be at very low levels by Heat 3104. The specific chemistry results for the relevant heats, the specification ranges and the averaged values for the purchase lot are represented as Table 3. As can be seen, the mercury contamination appears to be one factor of importance at these contamination levels. The mercury activated aluminum alloy composition, Galvalum I¹ corresponds to the chemistry found with this heat and previous testing had shown the mercury activated aluminum alloys were technically acceptable as sacrificial anodes.⁵ The Navy rejection of utilization of mercury activated aluminum alloy anodes was based on potential environmental (sea water) contamination considerations.

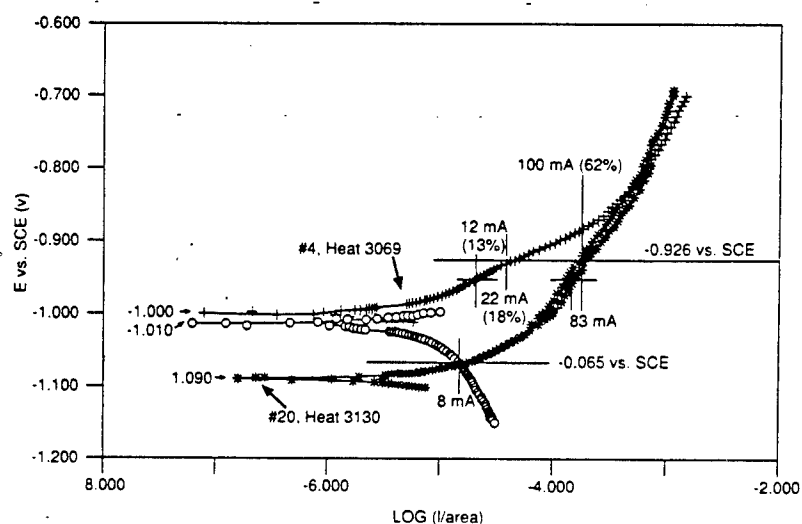


Figure 5. Polarization curves from Anode 20 (Heat 3130) and Anode 4 (Heat 3069) after overnight galvanic coupling.

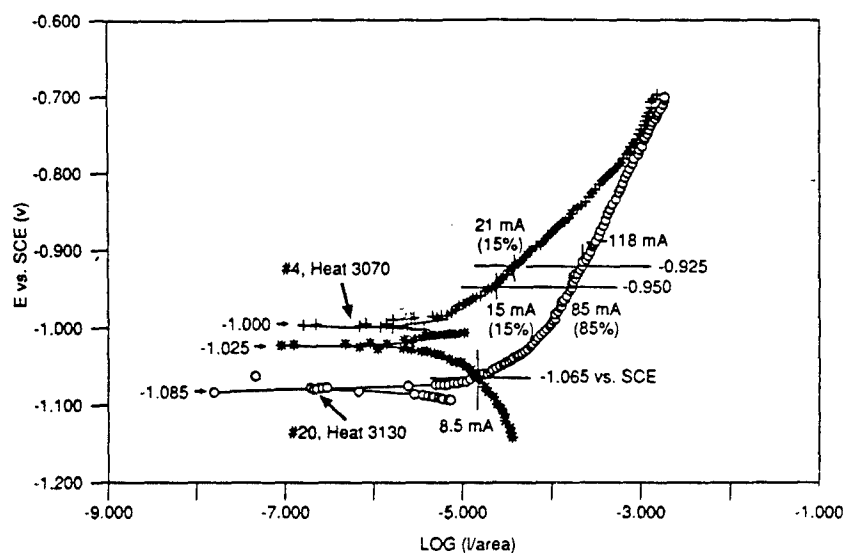


Figure 6. Polarization curves from Anode 20 (Heat 3130) and Anode 14 (Heat 3070) after overnight galvanic coupling.

Table 3
Chemistry Values for Relevant Heats

Element	Specification		Heat	Heat	Heat	Lot
	Min.	Max.	3069	3070	3130	Avg.
Zinc	2.5	6.0	4.5	4.0	4.0	4.2
Silicon	-	0.210	0.10	0.113	0.11	0.098
Indium	0.012	0.020	0.003	0.013	0.0125	0.0127
Iron	-	0.090	0.046	0.049	0.020	0.046
Copper	-	0.004	0.006	0.005	0.003	0.004
Mercury	-	0.020	0.027	0.0006	0.0001	<0.0001
Tin	-	0.020	<0.004	<0.004	<0.004	<0.004
Bismuth	-	0.020	0.0046	0.0032	0.0035	<0.0020
Cadmium	-	0.020	<0.001	<0.001	<0.001	<0.001
Titanium	-	0.020	<0.002	<0.002	0.004	<0.002
Magnesium	-	0.020	<0.001	<0.001	<0.001	<0.001
Lead	-	0.020	<0.002	<0.002	<0.002	<0.002
Boron	-	0.020	<0.001	<0.001	<0.001	<0.001

	<u>Zn</u>	<u>Si</u>	<u>In</u>	<u>Fe</u>	<u>Cu</u>
MIL-A-24779	4.0-6.5	0.08-0.2	0.014-0.020	≤0.19	≤0.004

Remainder ≤0.020 each, ≤0.10 Total.

(Added in 1992) Hg and Sn .0010 each.

As might be expected, the galvanic coupling of a Heat 3130 anode with an anode from Heat 3069 or 3070 showed the Heat 3130 material to protect the inferior material cathodically at a low level of between 5 and 10 mA. Polarization curves obtained following the overnight galvanic couple runs are presented as Figure 5 (Heat 3130 sacrificial anode, Heat 3069 protected "cathode") and Figure 6 (Heat 3130 anode, Heat 3070 cathode).

Evans-type diagram is included in the figure and the anodic/cathodic intercept currents agree with the measured galvanic couple currents. Although these data show the different levels of mercury contamination can result in an anode which could be cathodically protected, in the real application, coupled with a moderate current source, the anodes would probably all be involved in the discharge process but at significantly different rates.

The anodic curves from each heat can be used to quantify the nonuniform consumption rates. Each anode maintains the same potential as determined by the overall protection system current demand. In Figure 5 as an example, if the overall requirements are such that Heat 3130 anode is at -0.925 V (vs SCE) consuming 100 mA current, the Heat 3069 anode also held to or polarized at -0.925 V would consume 22 mA current or 18% of the total. If the demand were slightly lower so that the potentials were -0.95 V, then the anode from Heat 3130 would consume 83 mA whereas the Heat 3069 anode would decrease to 12 mA (12% of total). As can be seen in the figures, if the current consumption were sufficiently high so as to polarize the anodes to approximately -0.82 V, the anodes would consume equal currents.

Previously, a question was raised as to the resulting performance from a mixed aluminum alloy anodes and zinc anodes in a given installation. Several experimental runs were made using either a previously used or a new zinc anode in combination with several of the used Galvalum III aluminum alloy anodes. The effort was intended to demonstrate the mixed potentials and the probable cathodic protection of the zinc by the aluminum alloy. One, frustrating and perhaps interesting, result reoccurred when the two anodes were kept in the same 28 tank for longer than 3 hours during the non-coupled, pre-run electrolyte soak period; the zinc anode potential would decrease to that of the aluminum alloy anode. The polarization curves taken at that point would indicate approximately the same anodic activity. Possibly indium ion (introduced from the native corrosion of the aluminum alloy) into the electrolyte may have electrodeposited onto the zinc anode resulting in a surface alloy with lower (more negative) potentials than is usually observed and reported. This would suggest that for a mixed anode system in a closed tank application, the potential of the zinc would change and the current would essentially match that of the Galvalum III alloy.

However, on open sea stern arrays, where the ionic reaction products should be more completely removed, no indium addition to the zinc surfaces would be expected and the aluminum alloy should consume the majority of the cathodic protection current. Successful polarization runs were made by pre-soaking the two anodes in separate tanks for the 24 hour pre-run period and then limiting the co-exposure to approximately two hours. A comparison of the polarization curves for a new aluminum alloy anode (Heat 3253) and a used zinc anode tested using the modified test protocol is presented as Figure 7. As can be seen, the aluminum alloy anode with the more negative discharge curve would consume the majority of the current. The zinc discharge curve tends to show one smooth transition from the corrosion potential to the current limit. The discharge potential range is also in the same general range as the potential inflection in the aluminum alloy discharge curve. Natishan et al,⁶ studying surface implanted binary aluminum alloys had considered the inflection to be the pitting potential of aluminum, shifted to these low potentials by the presence of zinc in the alloy. However, the inflection as seen in Figure 7 would also appear to be associated with the onset of the anodic oxidation of zinc itself and not necessarily a pitting process in aluminum. Additional work would be required to determine the relative role of each process.

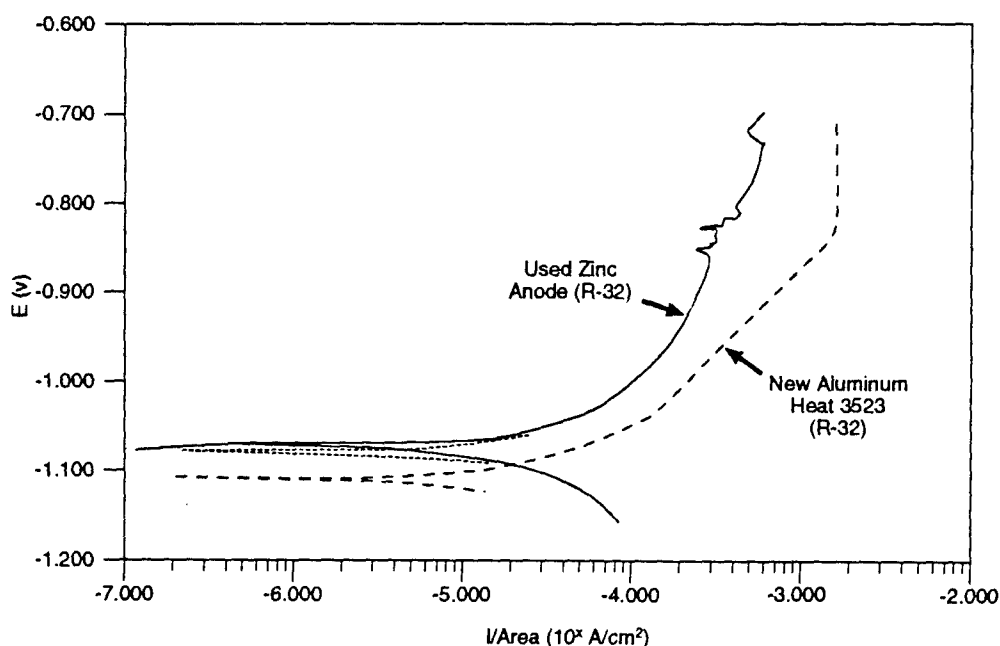


Figure 7. Polarization curves from new aluminum alloy anode (Heat 3253) and used zinc anode after overnight soaking.

SUMMARY

The objective for this study was to attempt to determine if the cause of non-uniform anode consumption on the stern hull array could be identified.

- A test protocol was constructed demonstrating that the electrochemical characteristics of used, air dried aluminum alloy anodes can be evaluated after removal from an installation.
- The evidence clearly points to the cause of non-uniform anode consumption as being the initial material composition used in fabricating the anodes.
- Anodes shown to be associated with a heavily mercury contaminated aluminum alloy (Heat 3069) were shown to have more positive (less negative) anodic potentials than properly fabricated material. Anodes with what might be considered as a minor mercury contamination (Heat 3070) were also shown to be affected. The anodes with the more negative potentials would subsequently consume more of the cathodic protection current and exhibit greater weight and dimension losses.
- Properly fabricated aluminum alloy anodes could be substituted into existing zinc anode arrays and would tend to be selectively consumed.

CONCLUSIONS

- The significant non-uniform consumption of Galvalum III, AHC-10 aluminum alloy anodes in a linear array on the stern of the submarine was the result of differences in anode alloy composition and not the result of passivated anode surfaces.
- Reasonable care must be maintained by vendors to adhere to the required chemical composition for the aluminum alloy in fabricating anodes. The presence of even low levels of mercury contamination in the Galvalum III composition is sufficient as to affect anode discharge rates.
- For the case of ballast or CHT tanks, installed but unused zinc anodes (eg., located high in tanks) could be left in place, replacing only the lower anodes with the aluminum alloy pieces as consumption allowances dictate.

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