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ZINC ANODES IN SEA WATER

Robert Alan Bornholdt

Naval Postgraduate School
Monterey, California

June 1974

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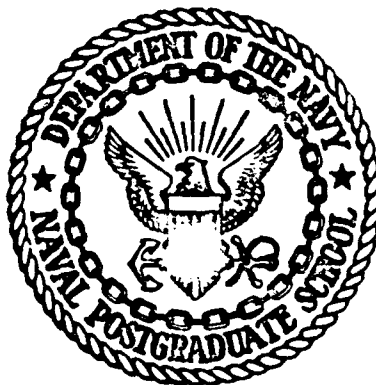
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THESIS

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ZINC ANODES IN SEA WATER

by

Robert Alan Bornholdt

June 1974

Thesis Advisor:

J. Perkins

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Corrosion Product Morphology on Zinc Anodes in Sea Water		5. TYPE OF REPORT & PERIOD COVERED Master's Thesis; June 1974
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Robert Alan Bornholdt		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Postgraduate School Monterey, California 93940		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Postgraduate School Monterey, California 93940		12. REPORT DATE June 1974
		13. NUMBER OF PAGES 63
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Naval Postgraduate School Monterey, California 93940		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Corrosion Zinc Anodes		
Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U.S. Department of Commerce Springfield, VA 22151		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The corrosion product morphology on a zinc alloy, exposed in a zinc/steel couple in sea water is investigated as a function of pressure. The results consist of corrosion data obtained from laboratory and ocean cells and data obtained from a scanning electron microscope. The corrosion products are observed to take two distinct microscopic forms. A porous "sheet" zinc oxide structure is observed on the samples exposed		

(20. ABSTRACT continued)

in stagnant sea water. A cloudy, somewhat less porous oxide is observed on the zinc samples exposed in the ocean.

Corrosion Product Morphology on
Zinc Anodes in Sea Water

by

Robert Alan Bornholdt
Lieutenant Commander, United States Navy
B.S.N.S., United States Merchant Marine Academy, 1961

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

from the

NAVAL POSTGRADUATE SCHOOL
June 1974

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LIST OF SYMBOLS

M	metal
M^{n+}	metal ion
n	number
e	electron
Fe	iron
I	current in amps
Ea	potential of the anode
Ec	potential of the cathode
Rm	resistance of the metal
Ra	resistance of the anode and electrolyte
Rc	resistance of the cathode
W	weight of the dissolved metal in grams
t	time in seconds
q	atomic weight divided by the valence
F	the faraday (96,500 coulombs)
ΔG	the free energy change
E	potential
b	number of electrons
ΔG°	standard molal free energy change
R	gas constant (8.314 Joules/degree·Mole)
T	absolute temperature
K	equilibrium constant
Cu-Mn	copper-manganese
Ti-Ni	titanium-nickel
SiC	silicon carbide

SEM	scanning electron microscope
XRD	x-ray diffraction
scuba	self-contained underwater breathing apparatus
C. and G.S.	coast and geodetic survey
Zn	zinc

ACKNOWLEDGEMENT

The work described herein was made possible through the sponsorship of the Department of Mechanical Engineering, USNPGS, Monterey, California. The author wishes to express his appreciation to Professor J. Perkins for his guidance and encouragement during the course of this investigation. A note of appreciation is also given to Professors Haderly, Tolles and Edwards for their constructive comments.

Appreciation is extended to K. Mothersell, Supervisor of the Mechanical Engineering Machine Shop for his effort in the construction of some of the experimental apparatus.

A special note of thanks goes to R. Edwards, Material Science Laboratory Technician, for his assistance throughout the course of the investigation.

I. INTRODUCTION

The corrosion of a piece of metal may be summarized as the change from the metal to the metal ion or the loss of one or more electrons from the metallic atom. This reaction can be written:



For example iron loses two electrons from each atom in forming ferrous ions.



If a piece of iron is placed in water, the metallic iron goes into solution as ferrous ions and the metal assumes a negative charge from the excess electrons that remain on it. Thus electric current flows from the metal into the solution.

Due to variations in potential over its surface, a metal immersed in an electrolyte will commonly form a number of microscopic corrosion cells (cathodic and anodic electrodes) over its surface.

By Ohm's Law the current flowing in the cell will be [1]

$$I = \frac{E_a - E_c}{R_m + R_a + R_c} \quad (3)$$

This current flow will cause "corrosion" (dissolution) of the anode, the rate of which will be proportional to the current according to Faraday's Law.

$$W = \frac{Itq}{F} \quad (4)$$

The tendency for any chemical reaction to occur, including the reaction of a metal with its environment is measured by the Gibbs free energy change for the reaction, ΔG . The more negative the value of ΔG , the greater the driving force for the reaction. The Gibbs equation is

$$\Delta G = - E_b F \quad (5)$$

Based on the thermodynamics, an equation can be derived to express the emf of a cell in terms of the concentrations of reactants and reaction products [2]

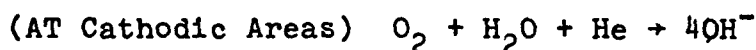
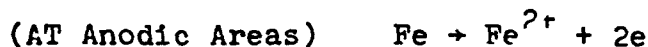
$$\Delta G - \Delta G^{\circ} = RT \ln K \quad (6)$$

And by substitution from equation (5), the Nernst equation is obtained.

$$E = E^{\circ} - \frac{RT}{bF} \ln K \quad (7)$$

The Nernst equation expresses the emf of a cell in terms of activities of products and reactants. The activity of a dissolved substance is equal to its concentration (molality) multiplied by a correction factor called the activity coefficient. The activity coefficient is a function of temperature and concentration and must be determined experimentally.

One method used to control corrosion is called cathodic protection. The principles of cathodic protection may be explained by considering the corrosion of iron in sea water. Electrochemical reactions occurring are the dissolution of the metal and the reduction of oxygen.



Cathodic protection is achieved by supplying electrons to the metal structure to be protected. The addition of electrons to the iron will suppress metal dissolution. There are two ways to cathodically protect a structure: (1) by an external power supply or, (2) by galvanic coupling.

Cathodic protection was employed before the science of electrochemistry had been developed. Humphrey Davy [3] used cathodic protection on British Naval ships in 1824. Today both types of cathodic protection systems are commonly used to protect U.S. Navy Fleet units. Zinc, which is electro-negative to steel, is the most common sacrificial anode used by the Navy.

It is a matter of common observation that as a metal corrodes it forms a surface film. This corrosion product can take many forms depending on the detailed features of the metal and the corrosive environment. Once a film has formed, either as a result of room air exposure or electrochemical corrosion, any one of the following may happen [4]:

- (a) general dissolution of the oxide film followed by corrosion;
- (b) dissolution of the oxide film at only a few discrete points with subsequent corrosion directed only at these points;
- (c) as (b) but with corrosion gradually extending over the whole surface;
- (d) as (b) but followed by plugging of the resultant pores by corrosion products;
- (e) no attack or, alternatively, further thickening of the film to the extent of stifling further attack.

The last statement can be taken to mean passivity, or as defined by Fontana and Greene [3], passivity is a loss of chemical reactivity under certain environmental conditions.

There is agreement [5] given certain conditions, that zinc will passivate due to the formation of a protective film. There is evidence [6,7] that this film consists of a metal-excess zinc oxide.

In the present investigation an effort was made to obtain further insight into the tendency of certain alloys, particularly sacrificial anode zincs, to form protective films. This investigation looked at environmental factors affecting film formation and morphology. Alloys studied also included Cu-Mn and Ti-Ni. The electrolyte in all tests was natural sea water obtained from Monterey Bay. Both laboratory

and ocean test exposures were conducted. The morphology of zinc corrosion products in zinc-steel couples was investigated as a function of ocean depth and in the laboratory as a function of pressure and anodic potential.

II. EXPERIMENTAL EQUIPMENT AND PROCEDURE

A. LABORATORY CORROSION CELL TESTS

Laboratory sea water corrosion tests were conducted using the zinc-steel couple shown in Figure 1. The test assembly, shown in Figure 2, included 2000-ml beakers filled with 1800 ml of sea water into which the couples were suspended for the desired length of time.

The zinc in the couple was 99.814 per cent pure (see Table I for the chemical analysis of the zinc); the steel was a low carbon steel. The area ratio of the couple was approximately 50-1 (cathode to anode). This closely simulates the area ratio used by the U.S. Navy [8] for cathodic protection on unpainted ship hulls.

The following laboratory corrosion cell tests were conducted:

<u>Number of zinc samples</u>	<u>Time (days)</u>
3	3
2	7
1	9
2	14
2	21
2	28

The zinc samples were ground on SiC grit paper, measured, and weighed prior to mating to the mild steel. Nylon nuts and bolts were used to join the couples. The mild steel was descaled and free of rust.

The laboratory corrosion cell couples were exposed for periods up to four weeks, with duplicate couples for each time frame. The zinc samples were subsequently rinsed in distilled water, dried, weighed, and mounted on SEM stubs for examination of corrosion film structure and morphology (XRD and SEM, respectively).

B. LABORATORY PRESSURE CELL TESTS

Zinc/steel cells were investigated in the laboratory as a function of equivalent ocean depth using a pressure chamber. The chamber, Figure 3, was constructed of stainless steel. The test procedure involved filling the chamber with sea water to within one-half inch from the top and suspending the cell from the cover plate. A glass liner was used to insulate the cell from the wall of the chamber. The desired equivalent depth was obtained by pressurizing with Argon gas. (Argon gas was chosen for its low sea water solubility.)

The zinc samples were ground (as previously described) and measured and weighed prior to testing. After the desired exposure they were rinsed in distilled water, dried, weighed, and mounted on SEM stubs; or alternately rinsed, dried, scrubbed, and weighed.

The following laboratory pressure cell tests were conducted:

<u>Number of Samples</u>	<u>Equivalent Depth (ft.)</u>	<u>Time (days)</u>
1	50	3
1	100	3
1	150	3
2	200	3
1	200	7
1	200	14

C. OCEAN EXPOSURE ARRAYS

The ocean exposure tests consisted of exposing zinc/steel couples at various depths and for various times with the primary aim of examining corrosion film morphologies and comparing with laboratory samples. Couple preparation was identical to that of laboratory test samples. Monterey Bay was chosen as the test site as it afforded proximity and provided desired water depths. In addition, oceanographic data was readily available from the Naval Postgraduate School Oceanography Department (see Table II for a summary of pertinent oceanographic data).

The initial ocean exposure couples were attached to 1/4 inch diameter nylon line weighted with ten pounds of lead. Two couples (one foot apart) were located at each station, with stations at 50, 100, 150, and 200 feet. The author, using scuba gear, tied an array such as described above, under each of buoys B, C, and D. (See C. and G.S. Chart No. 5402) Bad weather, inadequate rigging and a heavy concentration of commercial fishing boats in the area caused all three of the initial arrays to be lost. A second

attempt at obtaining ocean data using a home-made buoy located just north of buoy D, met with a similar fate.

A new ocean exposure location was selected one and one-half miles west of Moss Landing stacks (C. and G.S. Chart No. 5402). This location was rigged with a home-made buoy consisting of a 25 pound scrap iron anchor, 170 feet of nylon line and a red wooden float. Two samples each were attached at the 50, 100, and 150 foot stations. The author's boat was used as transportation to and from the site. The following samples were obtained from this site:

<u>Number of Samples</u>	<u>Depth (feet)</u>	<u>Time (days)</u>
1	50	1
3	50	3
2	100	3
2	150	3
4	50	9
2	100	9
2	150	9

After recovery from the sea, the zincs were rinsed lightly in distilled water, dried, weighed and then put on SEM stubs for further examination.

D. SCANNING ELECTRON MICROSCOPE

The SEM, Figure 4, model S4-10, manufactured by Cambridge Scientific Instruments Limited, Cambridge, England, was used to study the corrosion product morphology of the various samples. Photographs of samples exposed under different

corrosive conditions were taken at various magnifications and compared.

E. POTENTIOSTATIC MEASUREMENTS

Anodic polarization studies, using a Model 200A TRW research potentiostat (Figure 5), were performed on Zn, Cu-Mn and Ti-Ni in sea water. See Appendix A for a discussion on the potentiostat.

Prior to testing, the samples were ground on SiC grit paper, and drilled and tapped to fit the sample holder. The test procedure followed was that of the ASTM [9], with the exceptions of the sea water electrolyte and the one minute time interval between readings.

The primary purpose of the potentiostatic investigations was to accelerate and control corrosion of the samples so that direct correlation could be made with the SEM and XRD studies. A secondary purpose was to examine the possible active-passive transition of Zn, Cu-Mn, and Ti-Ni in salt water.

F. X-RAY DIFFRACTION

A Norelco X-Ray diffraction machine (manufactured by the North American Philips Co. Inc.) and the complementary Dynamaster instrumentation were used to qualitatively identify the corrosion products formed on the zinc samples (See Figure 6). X-ray patterns were run on a clean zinc sample, several specimens corroded via the potentiostat and several specimens corroded in the sea.

G. DATA REDUCTION

Data reduction consisted of weight loss measurements using the balance scale shown in Figure 7.

III. DISCUSSION

A. LABORATORY CORROSION CELLS

As shown in Table III, a total of 12 steel/zinc couples were exposed to quiet sea water. The individual tests ranged from 3 to 28 days. Figure 8 shows the trend in weight loss of the more active metal (zinc). The plot of weight loss vs. time in days indicates an increase in corrosion with time and shows no evidence of passivity. Figure 9 shows a photograph of the original "clean" zinc surface, which has been subject only to slight room air oxidation. Figure 10 shows the resultant morphology of zinc corrosion product for a 7 day quiet sea water exposure in a steel/zinc couple. The morphology exhibited is a macroscopically porous oxide structure consisting of arrays of "sheets" or "plates", typically 1.2×10^{-3} inches in size. This general morphology is typical of all the laboratory quiet sea water exposures. Figures 11, 12 and 13 indicate that the oxide plates (sheets) get thicker and the population grows more dense as the time of exposure increases. The population increased from 4.04×10^6 to 5.04×10^6 to 6.48×10^6 (sheets per square inch) for Figures 11, 12 and 13, respectively. Figures 14, 15 and 16 show a sequence of a 2 and 3 week exposure, illustrating the apparent porous nature of the oxide film, thus indicating that passivity is not likely in these quiet sea water tests. In Figure 15

the exposed area between the larger plates seems to be a fine embryonic structure over the base metal.

B. LABORATORY PRESSURE TESTS

Table III lists the various laboratory pressure tests that were conducted. Figure 17 shows a plot for the couples exposed at a depth of 200 feet (89 psi). The trend, although based on limited data, does not indicate passivity. Figure 18 plots depth in feet against weight loss in grams for six samples exposed for 3 days. Although the data is sparse there is an indication that at 50 feet (22.25 psi) the zinc is less active than at the other stations.

Figures 19 through 23 show the oxide film on samples exposed for 3 and 7 days at 200 feet (89 psi). The oxide has the same form as observed in the previous laboratory tests. Comparison of the 3 and 7 day samples, Figures 19 and 22, indicates a greater diameter (2.7×10^{-3} in. for Figure 19, and 0.89×10^{-3} in. for Figure 22) of the individual sheets at the shorter exposure. As shown in Figure 21 the sheet structure has a greater concentration in certain areas than in others. Not at all surprising is the observation that the area with the least population of sheets is that area which was covered by the head of the nylon bolt.

Figure 24 shows the plot of the weight of the corrosion product vs. depth for samples at 0, 50, 100 and 150 feet. Again there is evidence that the anodic zinc is less active at 50 feet than at the other stations.

Figure 22, a 7 day exposure at 89 psi, shows a much finer oxide than observed in the laboratory cell tests, namely Figure 10. The weight loss comparison between these samples was inconclusive as shown in Table III.

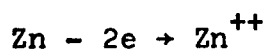
C. POTENTIOSTATIC MEASUREMENTS

Figure 25, an anodic polarization curve of zinc, indicates that this particular alloy has no tendency to passivate in a stagnant salt water solution. Figures 26 to 28 are photographs of oxides taken at three reference points on the curve. As shown the oxide initially takes on a form which is clearly similar to that known commonly as a "fourling" structure (tetrahedrally-arrayed spines). Consultation with Professor W. Tolles, Physics and Chemistry Department, USNPGS, indicated that the structures were not precisely of the fourling variety. As described by Powell and Donn [10], and as observed in photographs of ZnO combustion products obtained by Professor Tolles, the fourling structure has an exact well-defined geometry. After closer examination this geometry was not in evidence in the oxides studied. The spike-like oxide structure apparently elongated (0.5×10^{-4} inches for Figure 26 to 1.0×10^{-4} inches for Figure 27 and 2.08×10^{-4} inches for Figure 28) with increased anodic polarization. Figure 29, an oxide that has seen the complete anodic polarization exposure, indicates that the oxide eventually forms into a cloudy, apparently non-porous layer.

An interesting feature of these accelerated corrosion tests is illustrated in Figure 30. The photograph reveals that the oxide has received and held an electric charge. This charge appears to form in an alternating pattern over the sample's surface.

D. X-RAY DIFFRACTION

Diffraction powder x-ray diffraction patterns were obtained from representative corroded zinc samples using $\text{CuK}\alpha$ radiation. Analysis of these patterns using the standard Hannawalt-ASTM method has shown that the corrosion product consists in all cases of essentially zinc oxide (ZnO -ASTM Card No. 5-0664). This reinforces the assumption that the overall anodic reaction in the cells can be represented as



E. OCEAN EXPOSURE ARRAYS

As anticipated there was a sharp contrast between the laboratory and ocean testing results. As indicated by Monney [11], seawater is perhaps the most complex heterogeneous mixture on earth. It is composed of water, dissolved gases and salts, suspended organic and inorganic matter and live organisms. When these parameters are combined with wide variations in temperature, pressure and velocity, it is apparent that there are inherent difficulties involved in laboratory simulation.

Table III summarizes the sea exposures. Figures 31 and 32 show plots of weight loss vs. depth for 3 and 9 day ocean exposures. The test site was 1.5 miles west of Moss Landing stacks as shown on C. and G.S. chart number 5402. Figures 31 and 32 indicate a greater increase in weight loss with time and depth than seen in the laboratory tests. The plots themselves do not indicate anything unusual about the 50 foot station. The investigator, however, upon removing the 9 day samples from the ocean noted that the four 50-foot cells were quite different from any of the other samples. All four of these cells had apparently stopped performing as designed as the steel in the zinc/steel couple was completely covered with rust. The zinc was intact, in good electrical contact with the steel, and appeared macroscopically to have a normal surface oxide. No unusual marine fouling was noted. For comparison a 1 day, 50 foot ocean exposure was looked at. Figures 33 and 34 show the morphology of the corrosion product for this sample. Figure 33 shows a heavy surface oxide with numerous cracks. Figure 34 looks into one of these cracks and shows the familiar sheet-like structure observed in the stagnant sea water tests. The steel in this particular couple was rust free. Observations were made on a 3 day-50 foot couple and the results were similar to those observed in the 1 day exposure.

Figures 35 to 37 show the oxide most typical of the 9 day, 50 foot exposures. The oxide is cloua-like and apparently less porous than the sheet type oxide previously

described. An explanation as to why these particular zinc samples apparently went passive was first thought to lie in the chemical makeup of the sea water. Specifically, it was suspected that a concentrated layer of marine organisms at and around the 50 foot layer would have provided a partial explanation. However, after a consultation with Professor E. Haderly, USNPGS Oceanography Department, this speculation was discarded. Professor Haderly offered that a more probable explanation would involve a detailed study of the corrosion behavior of the particular zinc alloy. The conclusion drawn is that somewhere between 3 and 9 days this particular zinc alloy when coupled to mild steel and subjected to an ocean depth of 50 feet will passivate.

An oxide sequence for the 100 foot, 9 day ocean exposures is shown in Figures 38 to 40. Macroscopic observation of the couple showed the steel to be clean and the zinc to have slight to moderate deterioration on its edges. See Figures 44 and 45. Unlike the 50 foot exposures, Figures 39 and 40 show large surface cracks giving evidence of a porous film.

Visual observation of the 150 foot, 9 day exposures revealed the steel to be clean and showed the zinc to be approximately 50 per cent deteriorated. See Figure 46. This illustrated a marked increase in weight loss with depth for the same length of exposure. Figures 41 to 43 show a sequence of these oxides. Again as observed in the 100 foot exposures the oxides appear relatively porous.

Detailed results were not obtained from either the Cu-Mn or Ti-Ni samples.

F. GENERAL CONCLUSIONS

In conclusion it was observed that the zinc oxide had two distinct forms. In the laboratory, in a quiet sea water solution, the oxides obtained from the cell exposures were sheet like, with a varied growth pattern. The oxides obtained from the potentiostatic tests were cloudy and apparently less porous. In the ocean tests, most of the samples contained both types of oxides. The surface of the ocean exposed samples revealed the cloudy oxide, and in most cases, cracks and crevices. The internal structure of the ocean samples, as observed through the cracks and crevices, showed the sheet type oxide typical of the stagnant sea water tests. Although the mechanism is not clear, the adverse behavior of the zinc alloy, namely the apparent passivation at 50 feet of ocean depth, and the progressive deterioration with depth in the ocean, is believed related to the alloy content or the zinc and specifically to the amount of iron present [1].

TABLE I

Chemical Analysis of Zinc Samples
(Provided by Mare Island Naval Shipyard)

<u>Metal</u>	<u>Per Cent Composition</u>
lead	0.07
iron	0.016
cadmium	0.08
copper	0.005
aluminum	0.005
silicon	0.01
zinc	99.814

TABLE II

Oceanographic Data - Monterey Bay

[Data obtained from a survey conducted
in 1970 at a depth of approximately
200 feet.]

<u>Variable</u>	<u>Value</u>
salinity	32.8 to 33.8 parts per thousand
oxygen	1.33 ml/liter
temperature	8°C

TABLE III
Data Compilation Sheet

<u>Zinc Sample No.</u>	<u>I.D.</u>	<u>Exposure Time</u>	<u>Exposure Depth</u>	<u>SEM</u>	<u>X-RAY</u>	<u>grams wgt. loss</u>	<u>corr. prod. wgt.</u>
1	Lab	7	-	X		.1544	
2	Lab	7	-	X		.1004	
3	Lab	14	-	X		.2231	
4	Lab	14	-			.2301	
5	Lab	21	-	X		.4267	
6	Lab	21	-			.4130	
7	Lab	28	-	X		.4955	
8	Lab	28	-			.5580	
9	Lab	3	-			.1167	.0007
10	Lab	9	-			.2021	.0308
11	Lab	3	-			.1003	
12	Lab	3	-			.1292	
13	(Clean zinc)			X	X		
14	Lab-P	3	50 ft			.0588	.0004
15	Lab-P	3	100 ft			.1121	.0011
16	Lab-P	3	150 ft			.0639	.0025
17	Lab-P	3	200 ft	X		.1003	
18	Lab-P	3	200 ft			.1245	
19	Lab-P	7	200 ft	X		.1288	
20	Lab-P	14	200 ft			.2444	
21	Sea	1	50 ft	X		.3572	
22	Sea	3	50 ft	X		.4056	
23	Sea	3	50 ft	X		.3898	
24	Sea	3	50 ft			.4065	
25	Sea	3	100 ft	X		.4419	
26	Sea	3	100 ft			.4950	
27	Sea	3	150 ft	X		.5616	
28	Sea	3	150 ft			.4237	
29	Sea	9	50 ft	X		.7077	
30	Sea	9	50 ft	X		.1978	

TABLE III (continued)

<u>Sample No.</u>	<u>I.D.</u>	<u>Exposure Time</u>	<u>Exposure Depth</u>	<u>SEM</u>	<u>X-RAY</u>	<u>grams wt. loss</u>	<u>corr. prod. wt.</u>
31	Sea	9	50 ft		X	.7446	
32	Sea	9	50 ft			.6936	
33	Sea	9	100 ft	X		1.0235	
34	Sea	9	100 ft		X	1.0243	
35	Sea	9	150 ft	X		2.1431	
36	Sea	9	150 ft		X	2.1542	
37	Dockside	7	5 ft	X			
38	Dockside	14	5 ft	X			
39	Dockside	60	5 ft	X			
40	Pot.	-	-	X	X		
41	Pot.	-	-	X	X		
42	Pot.	-	-				
43	Pot.	5 min.	-	X		-	-
44	Pot.	5 min.	-	X		-	-
45	Pot.	5 min.	-	X		-	-
46	Pot.	-		X		-	-
47	Pot.	-		X		-	-

Other samples

Ti-Ni	Pot.	-		X			
Cu-Mn	Pot.	-					

X indicates that the particular sample was examined on the instrument indicated.

IV. RECOMMENDATIONS FOR FURTHER WORK

Prior to an undertaking of further work in this area a review of N.T. Monney's comments [11] would be helpful.

The investigation described herein could be extended to:

1. the study of other zinc alloys, particularly those containing less amounts of iron and lead.
2. the study of the zinc oxide (and the oxides of other metals) as a function of a greater depth range than was covered in the investigation. With proper pre-planning and assistance from the USNPGS Oceanographic Vessel ACANIA, a buoy system could readily be assembled and planted to obtain data to a depth of several hundred to a thousand feet.
3. the study of polarization as a function of pressure. The pressure vessel used in this experiment was designed so that it may be connected to the potentiostat.

APPENDIX A

THE POTENTIOSTAT

A potentiostat is an electronic device which maintains a metal at a constant potential with respect to a reference electrode. The basic unit is essentially a three-terminal device, being used with an ancillary electrochemical cell and electrodes. The cell contains three electrodes and an electrolyte of reasonably high conductivity.

The three electrodes are called the working, reference and auxiliary electrodes. The electrical characteristics of the unit are complex and are dealt with by Von Fraunhofer and Banks [12].

In operation the potentiostat is used both as a research tool and for accelerated corrosion testing of materials. Corrosion is primarily concerned with anodic processes and therefore anodic polarization studies are of interest to corrosion workers. Anodic polarization consists of imposing an electrode potential upon a metal and observing the current transients that occur. If the potential is continuously varied and the current measured, a polarization or $E/\log i$ curve may be obtained. These polarization curves may be used both to interpret corrosion phenomena and predict corrosion behavior of a metal in a given environment.

For additional comments on the potentiostat consult Von Fraunhofer and Pickup [13].

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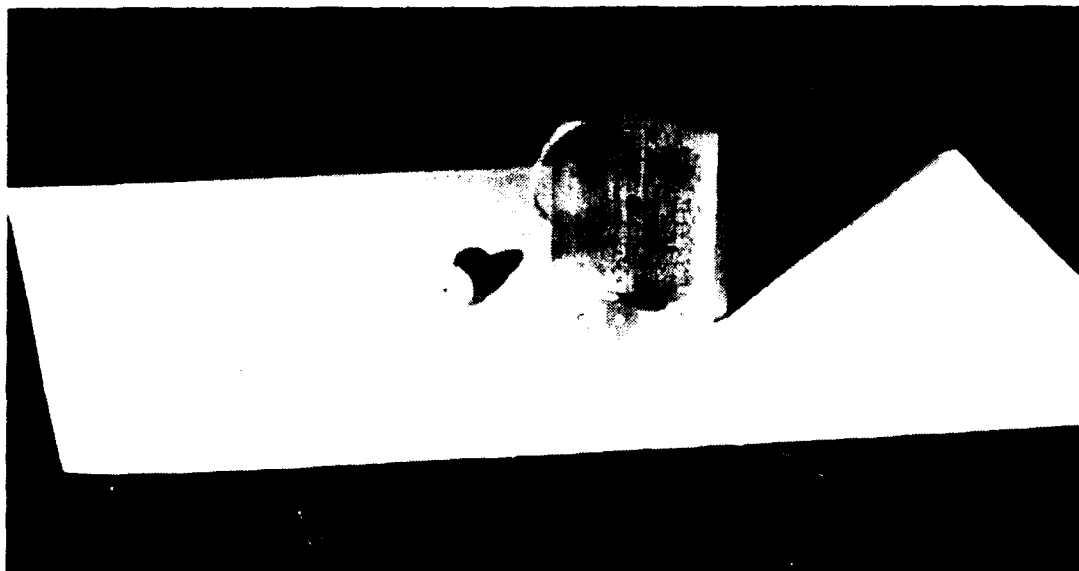


FIGURE 1. ZINC/STEEL COUPLE W/NYLON NUT AND BOLT

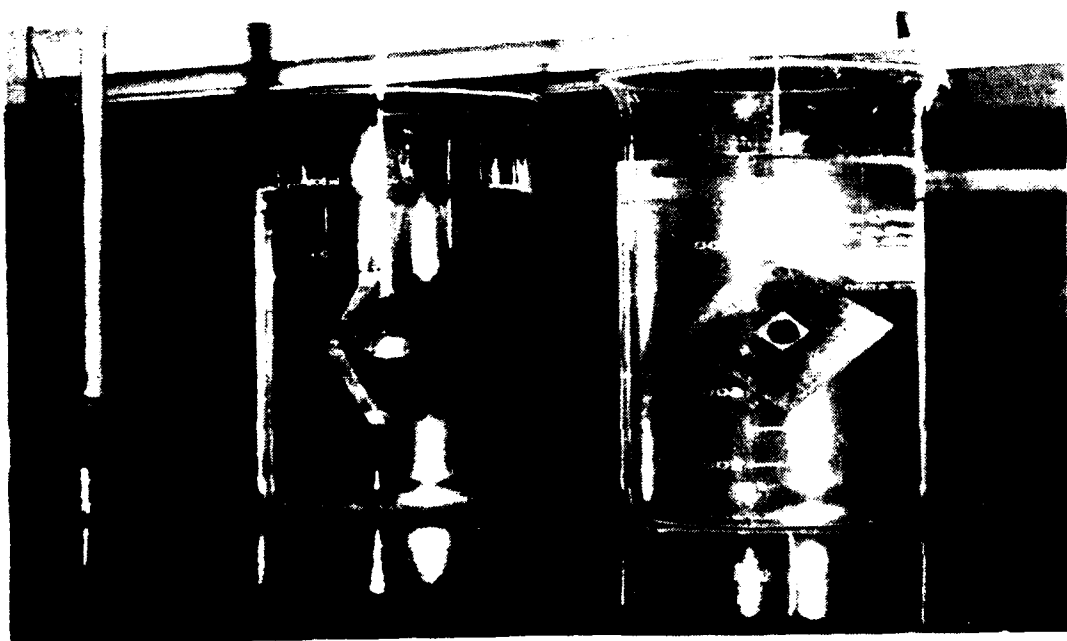


FIGURE 2. LABORATORY QUIET SEA WATER CORROSION TEST

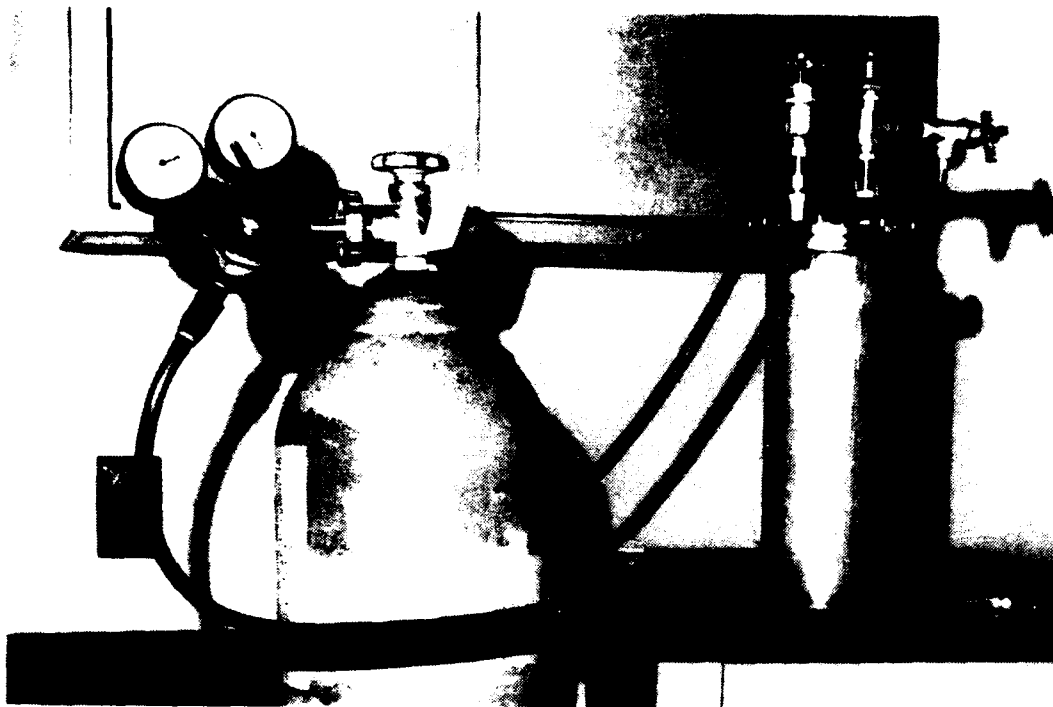


FIGURE 3. STAINLESS STEEL PRESSURE VESSEL

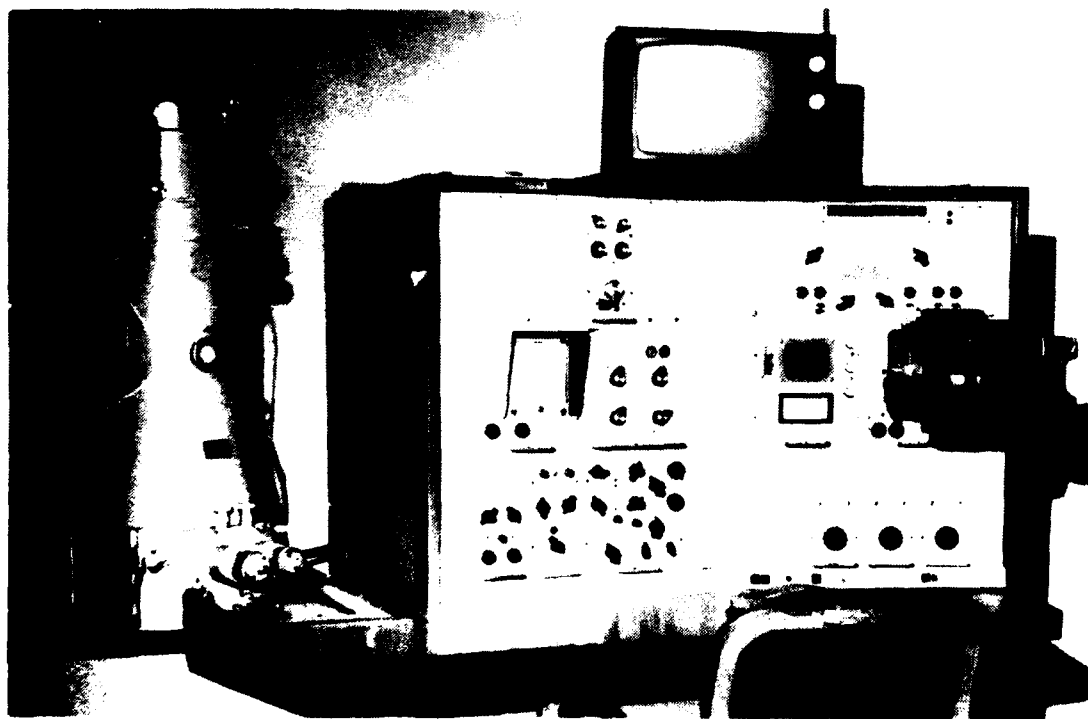


FIGURE 4. SCANNING ELECTRON MICROSCOPE

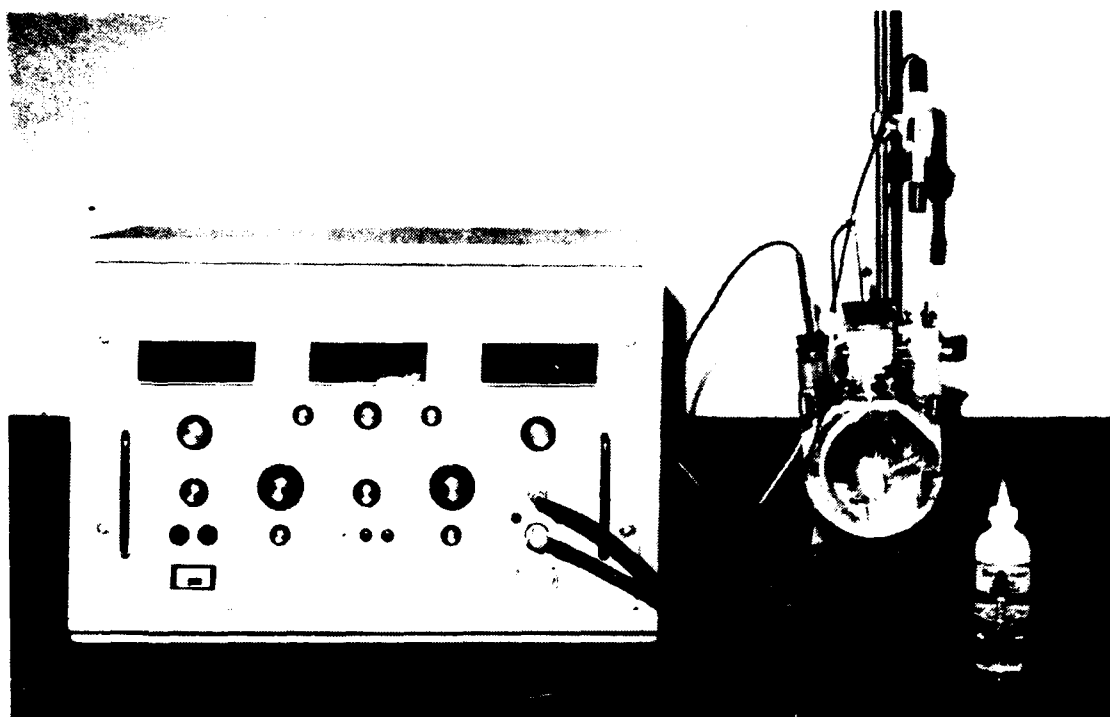


FIGURE 5. RESEARCH POTENTIOSTAT

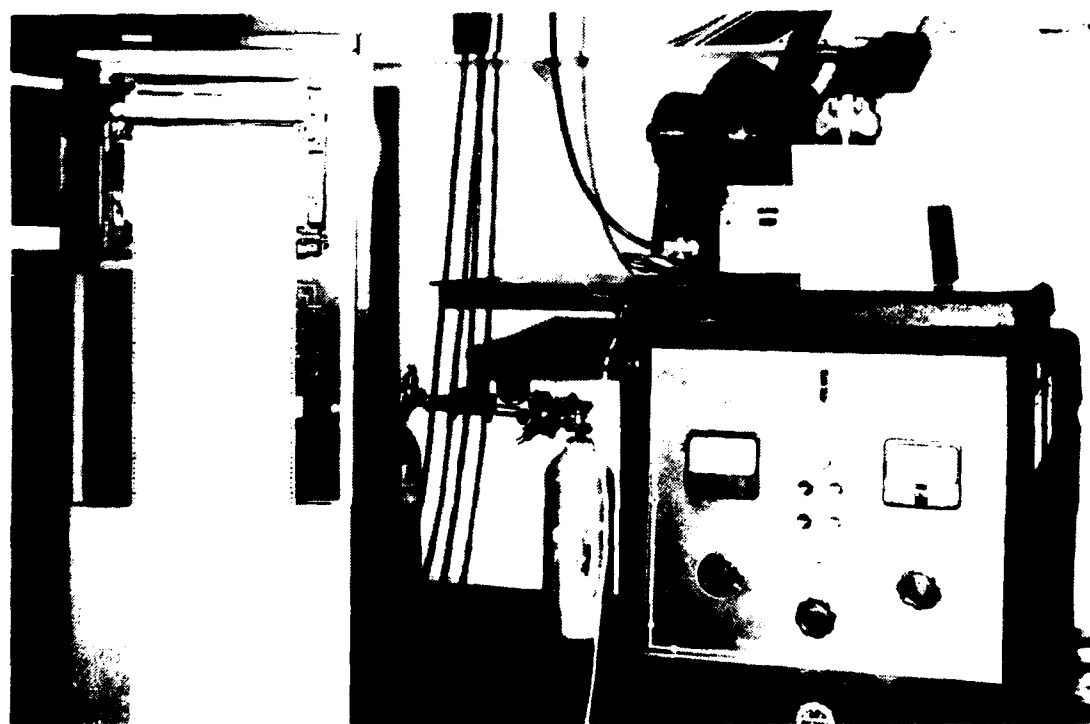


FIGURE 6. X-RAY DIFFRACTOR AND RECORDER

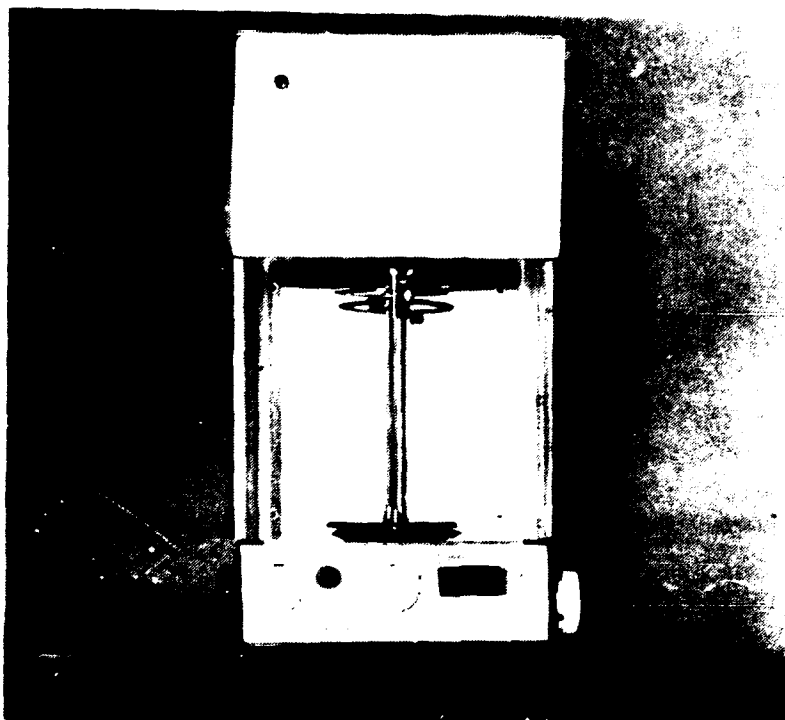


FIGURE 7. SARTORIUS BALANCE SCALE

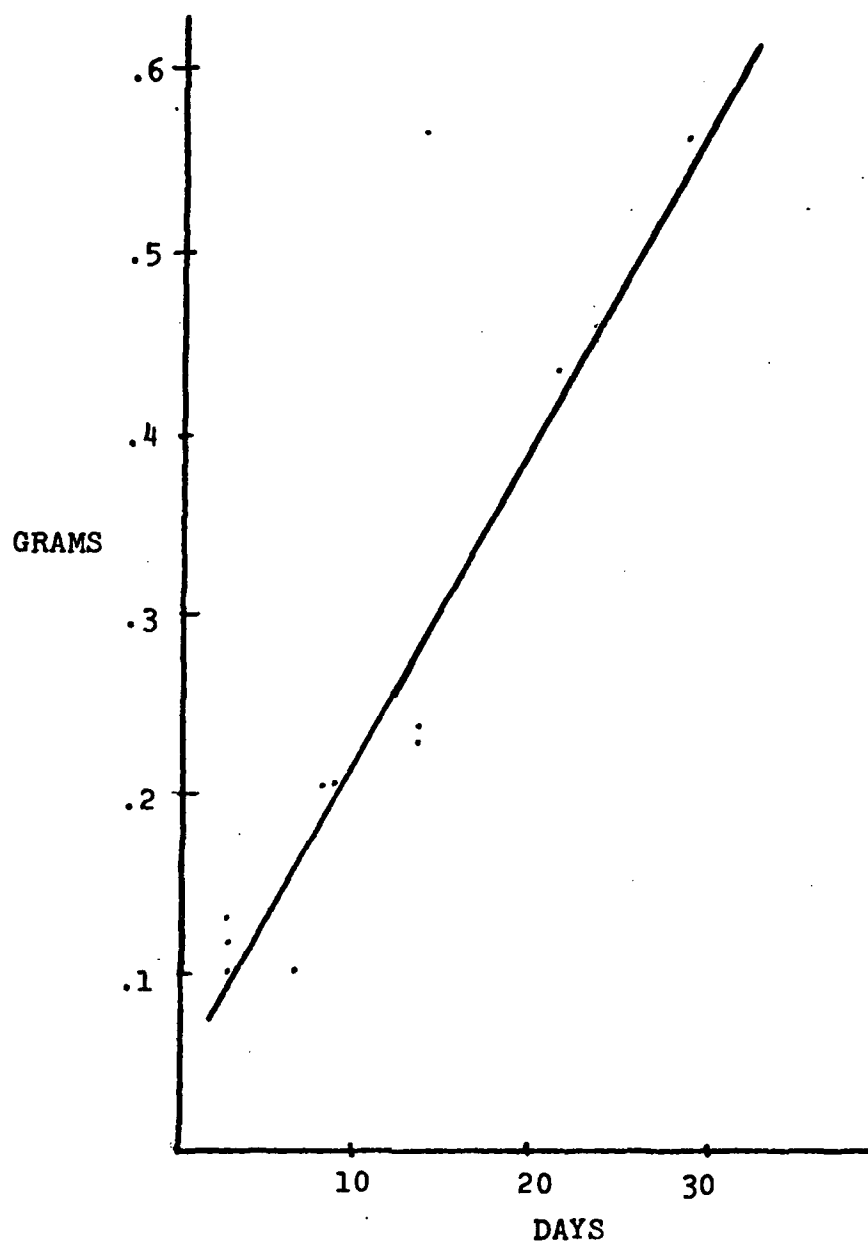


FIGURE 8. ZINC WEIGHT LOSS. LABORATORY, QUIET SEA WATER CORROSION TESTS

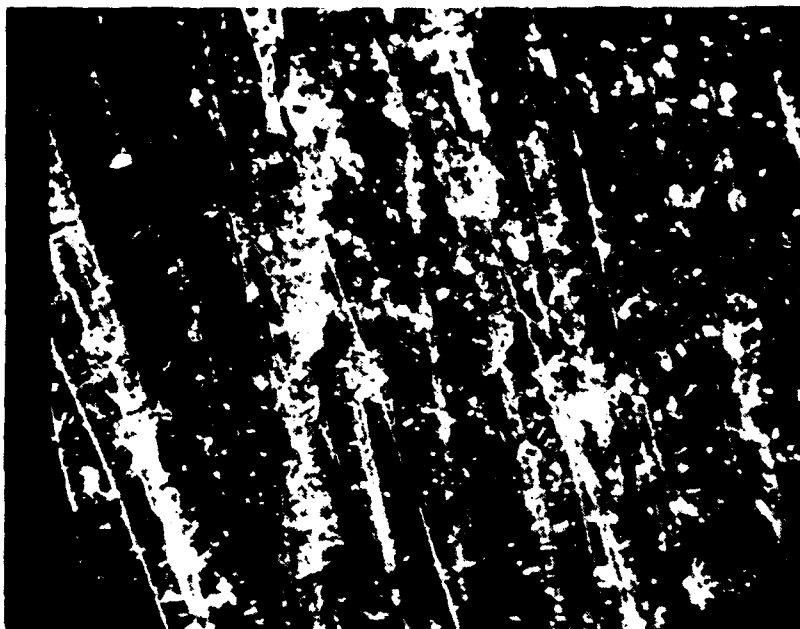


FIGURE 9. "CLEAN" ZINC (ROOM AIR OXIDATION) 610X



FIGURE 10. ZINC, 7 DAY QUIET SEA WATER EXPOSURE, 620X

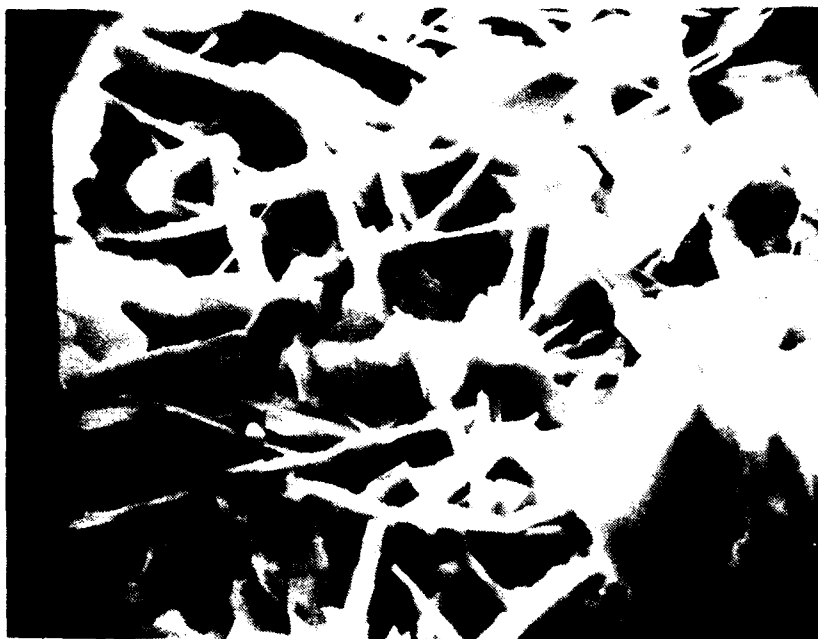


FIGURE 11. ZINC, 14 DAY QUIET SEA WATER EXPOSURE, 670X



FIGURE 12. ZINC, 21 DAY QUIET SEA WATER EXPOSURE, 600X



FIGURE 13. ZINC, 28 DAY QUIET SEA WATER EXPOSURE, 600X

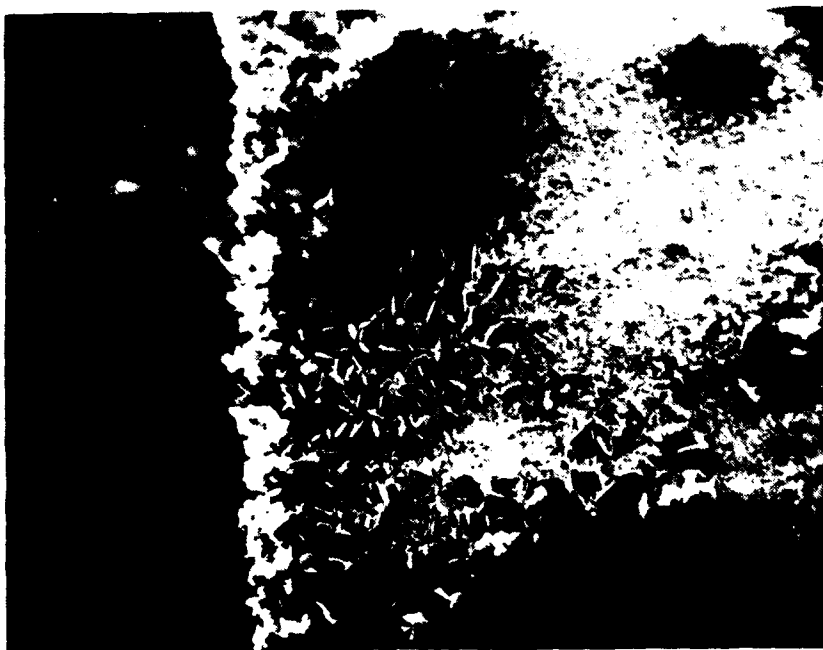


FIGURE 14. ZINC, 21 DAY QUIET SEA WATER EXPOSURE, 24X



FIGURE 15. ZINC, 14 DAY QUIET SEA WATER EXPOSURE, 620X



FIGURE 16. ZINC, 21 DAY QUIET SEA WATER EXPOSURE, 2400X

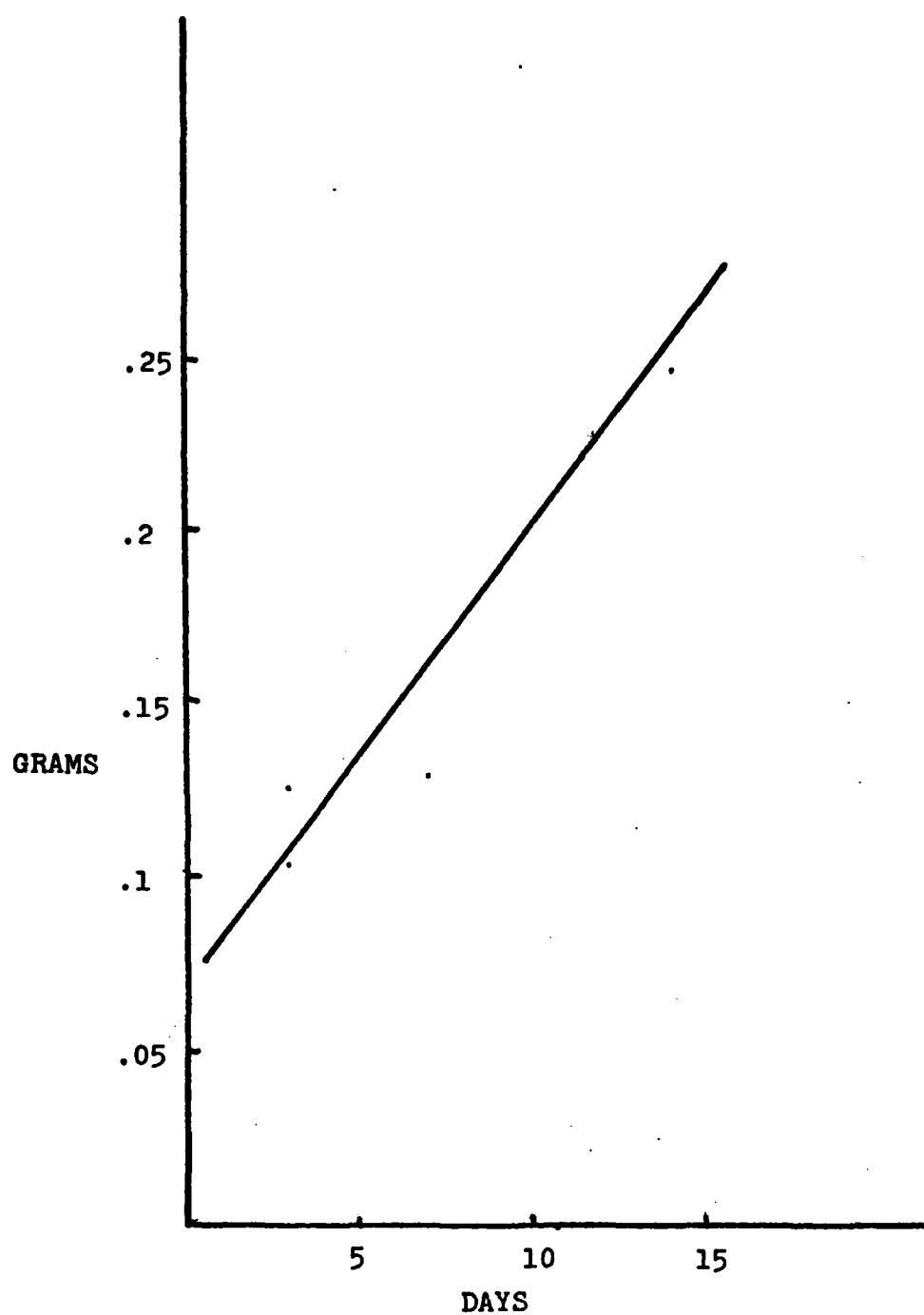


FIGURE 17. ZINC WEIGHT LOSS. LABORATORY, QUIET
SEA WATER CORROSION TESTS, 89 PSI

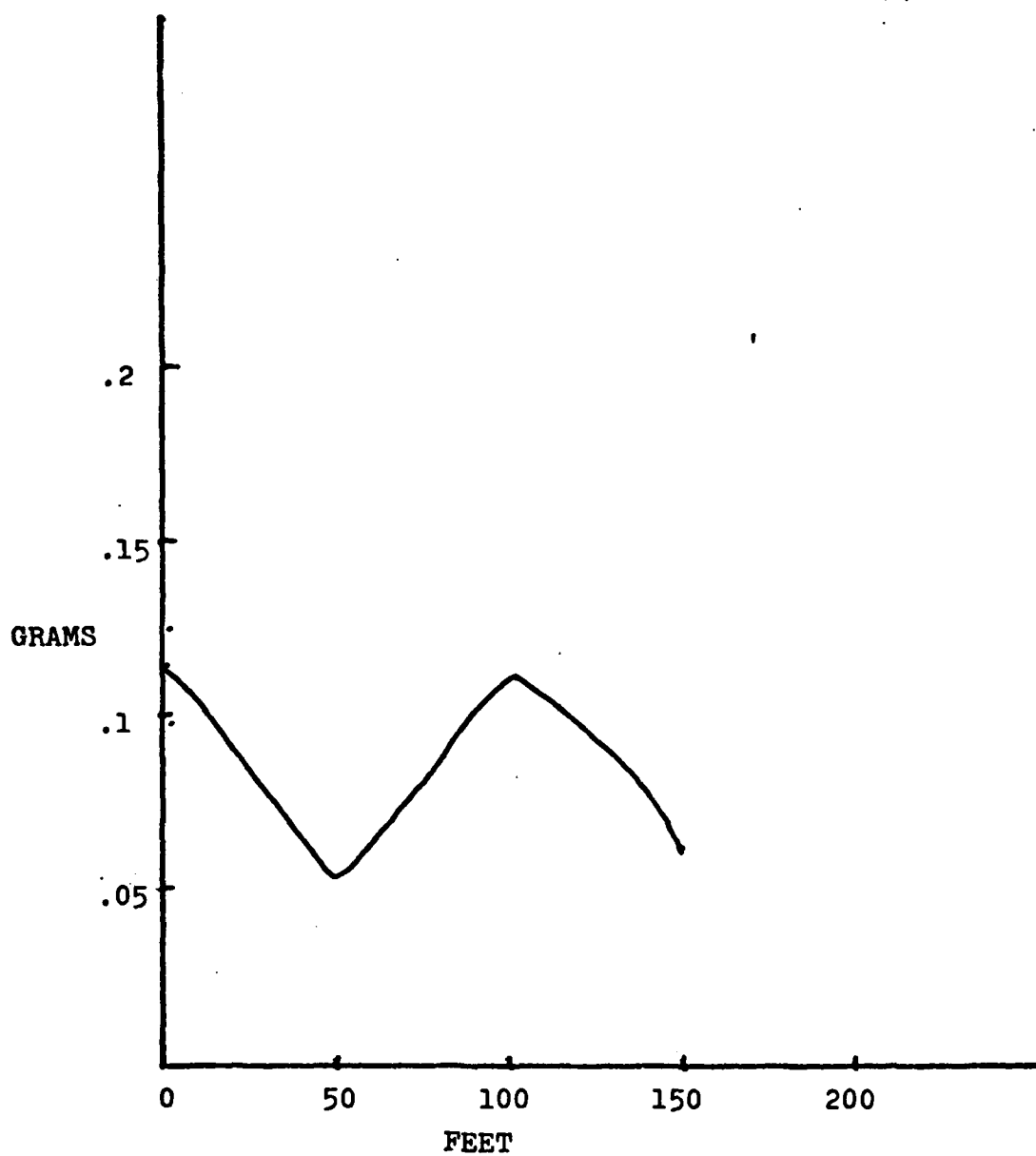


FIGURE 18. ZINC WEIGHT LOSS. LABORATORY QUIET SEA WATER, 3 DAY EXPOSURES AT VARIOUS PRESSURES



FIGURE 19. ZINC, 3 DAY QUIET SEA WATER EXPOSURE
89 PSI, 650X



FIGURE 20. ZINC, 3 DAY QUIET SEA WATER EXPOSURE
89 PSI, 1300X



FIGURE 21. DRY, 1/2 DAY AFTER THE WATER EXPOSURE
AT 100 PSI, 10X



FIGURE 22. DRY, 1/2 DAY AFTER THE WATER EXPOSURE
AT 100 PSI, 10X



FIGURE 23. ZINC, 7 DAY QUIET SEA WATER EXPOSURE
89 PSI, 2300X

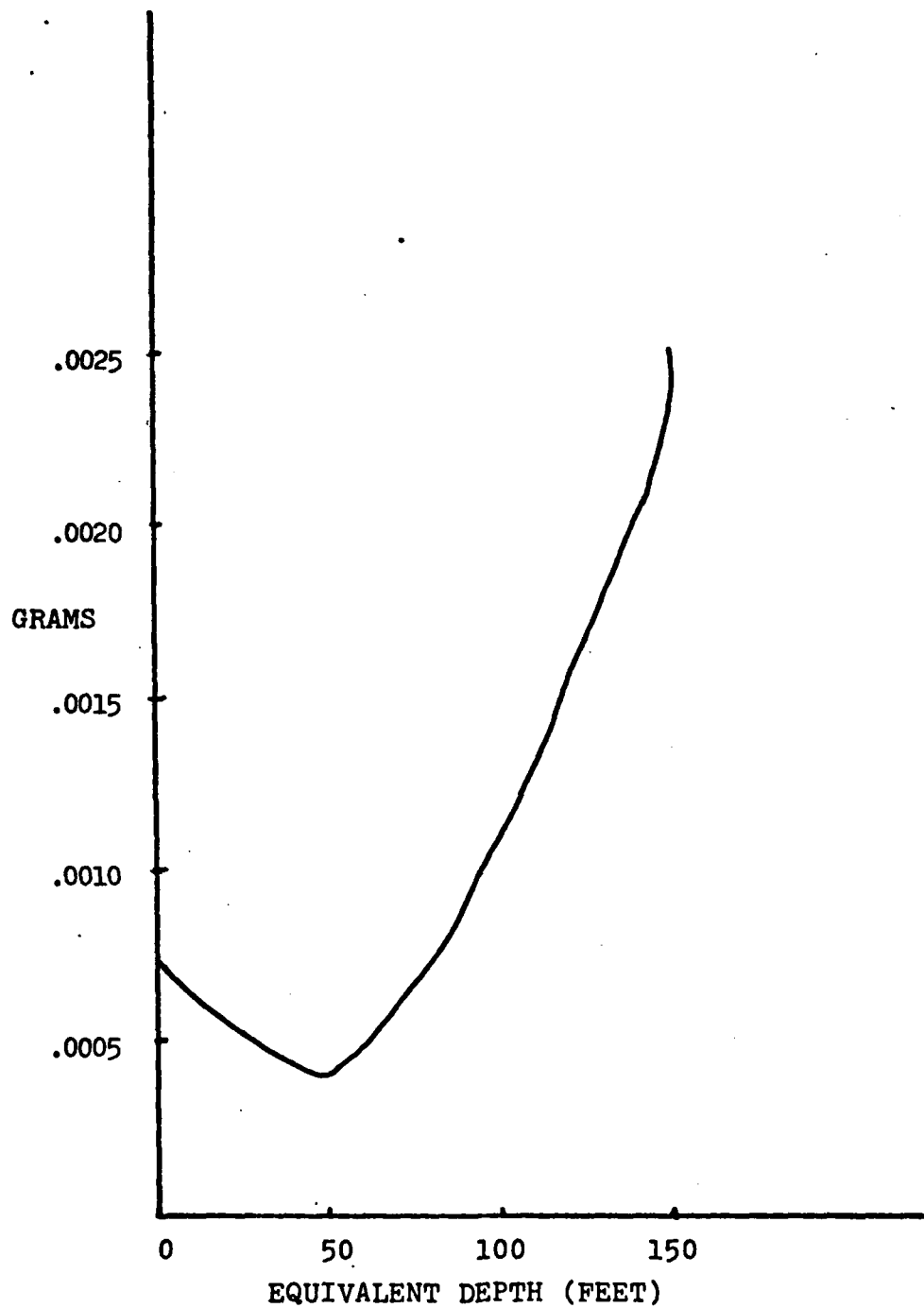


FIGURE 24. WEIGHT OF ZINC OXIDE AT VARIOUS EQUIVALENT DEPTHS (3 DAY EXPOSURE)

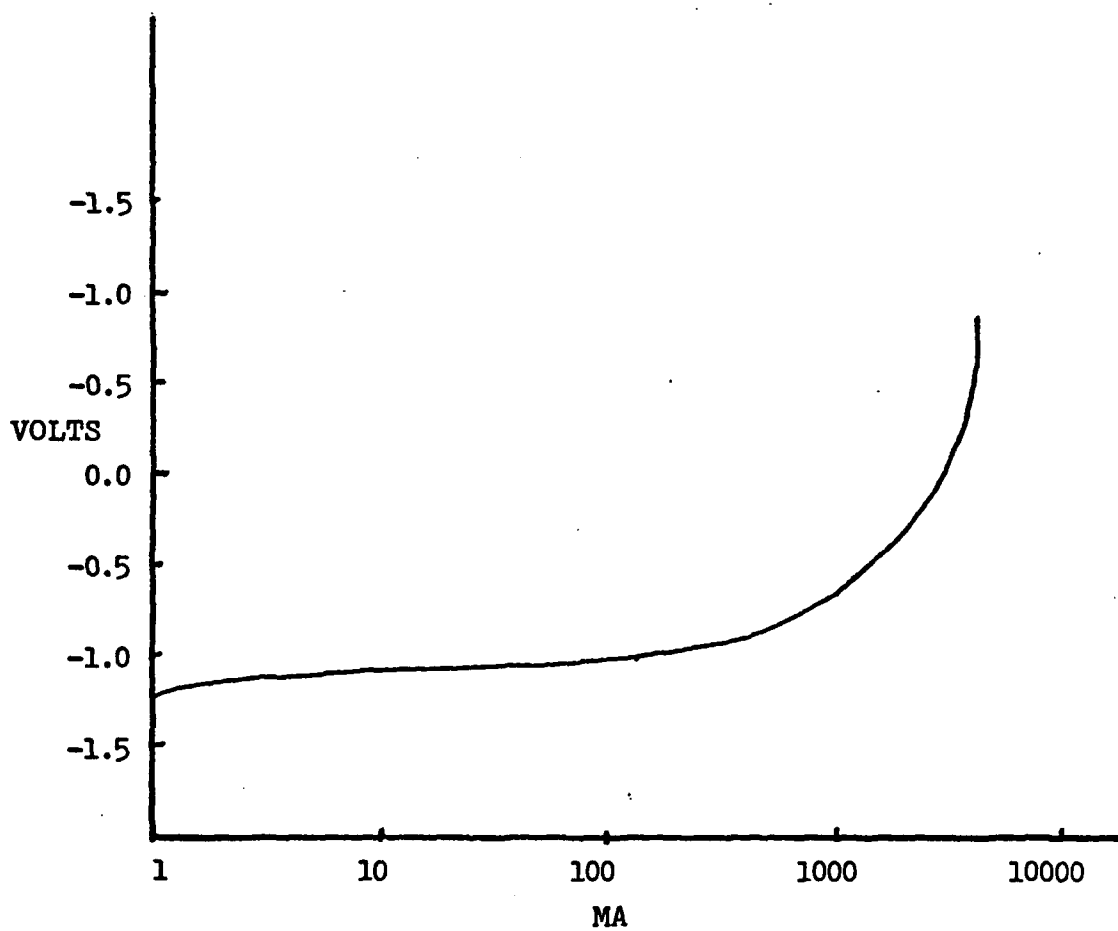


FIGURE 25. ANODIC POLARIZATION CURVE OF ZINC
IN QUIET SEA WATER

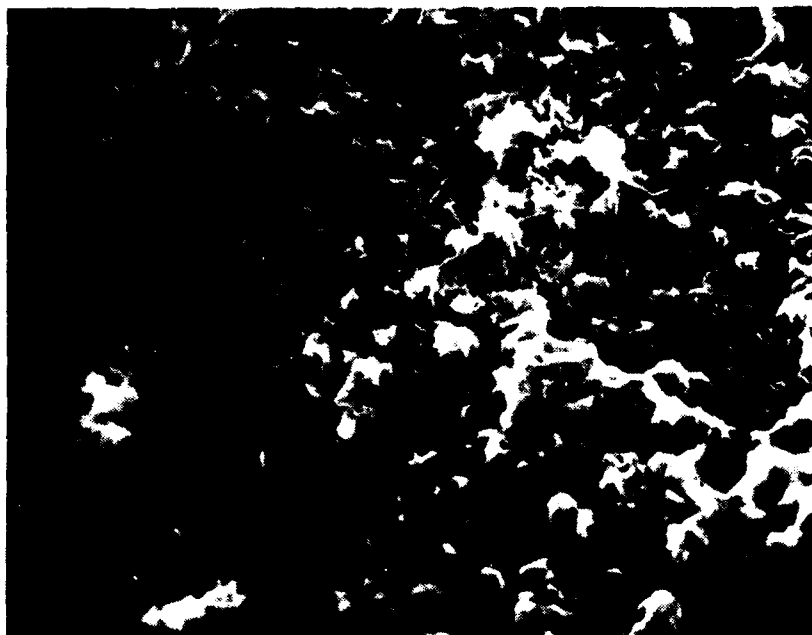


FIGURE 26. ZINC, ANODIC POLARIZATION, 5 MIN. AT
10MA, -1.0V, 2500X

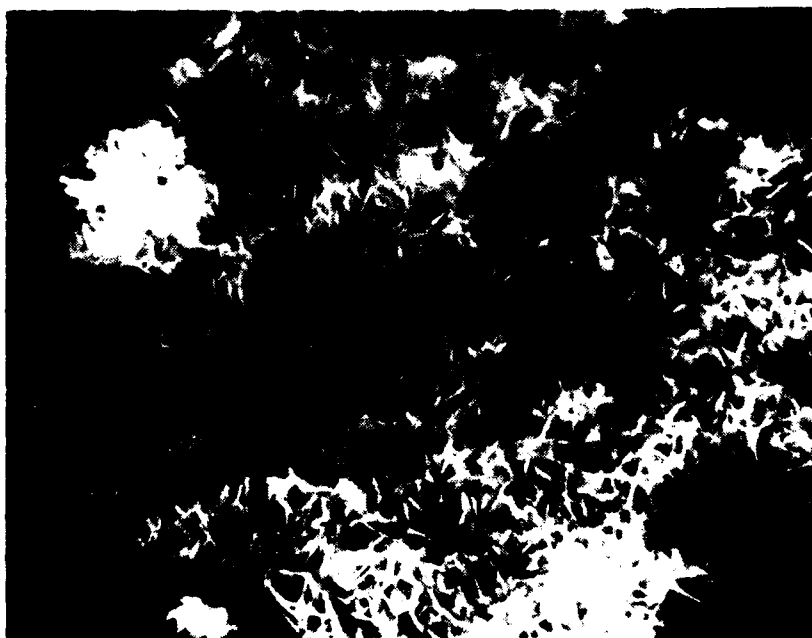


FIGURE 27. ZINC, ANODIC POLARIZATION, 5 MIN. AT
100MA, -0.9V, 2300X



FIGURE 28. ZINC, ANODIC POLARIZATION, 5 MIN. AT 1000MA, -0.5V, 2400X

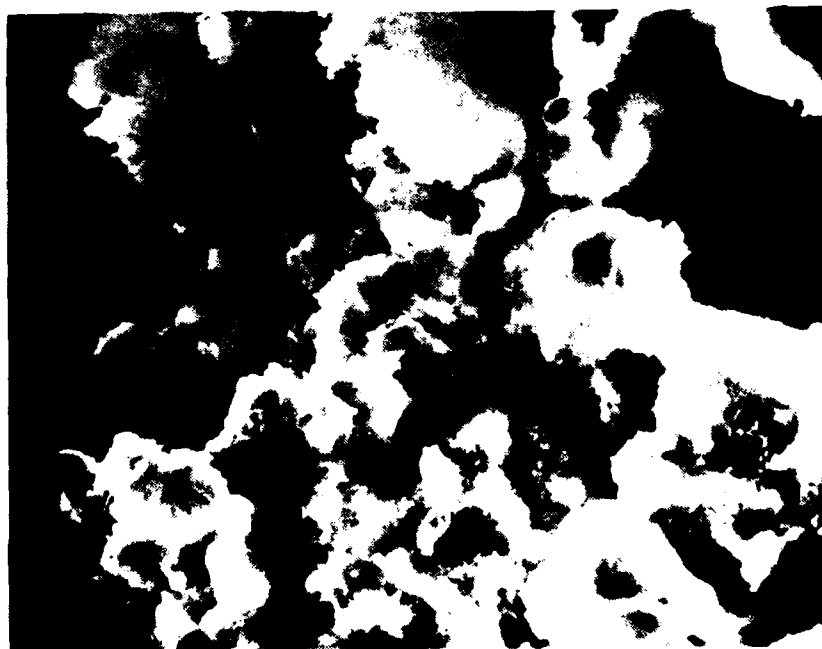


FIGURE 29. ZINC, ANODIC AND CATHODIC POLARIZATION CYCLE, 2400X

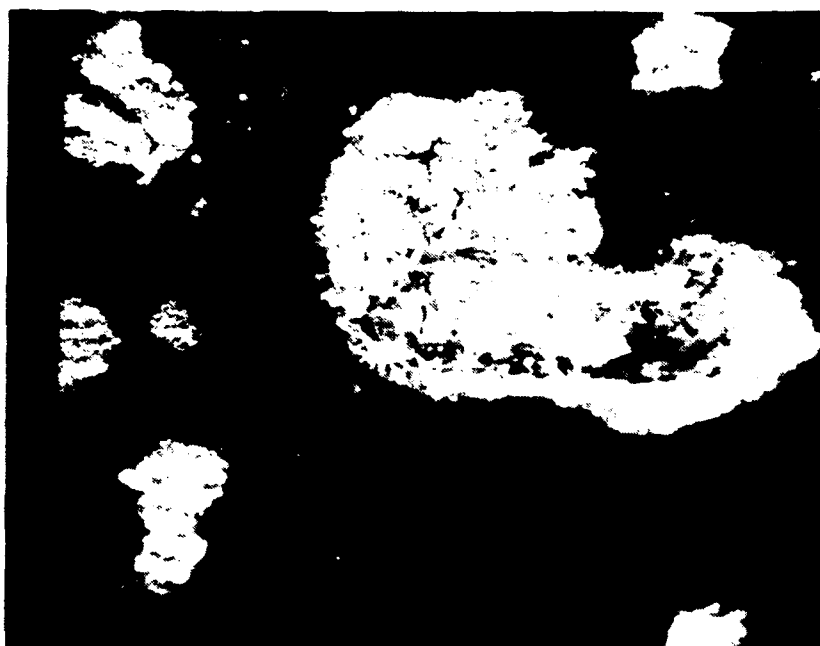


FIGURE 30. ZINC, ANODIC POLARIZATION, 5 MIN. AT 100MA, -0.9V, 575X, "CHARGING EFFECT OBSERVED DURING SEM STUDIES"

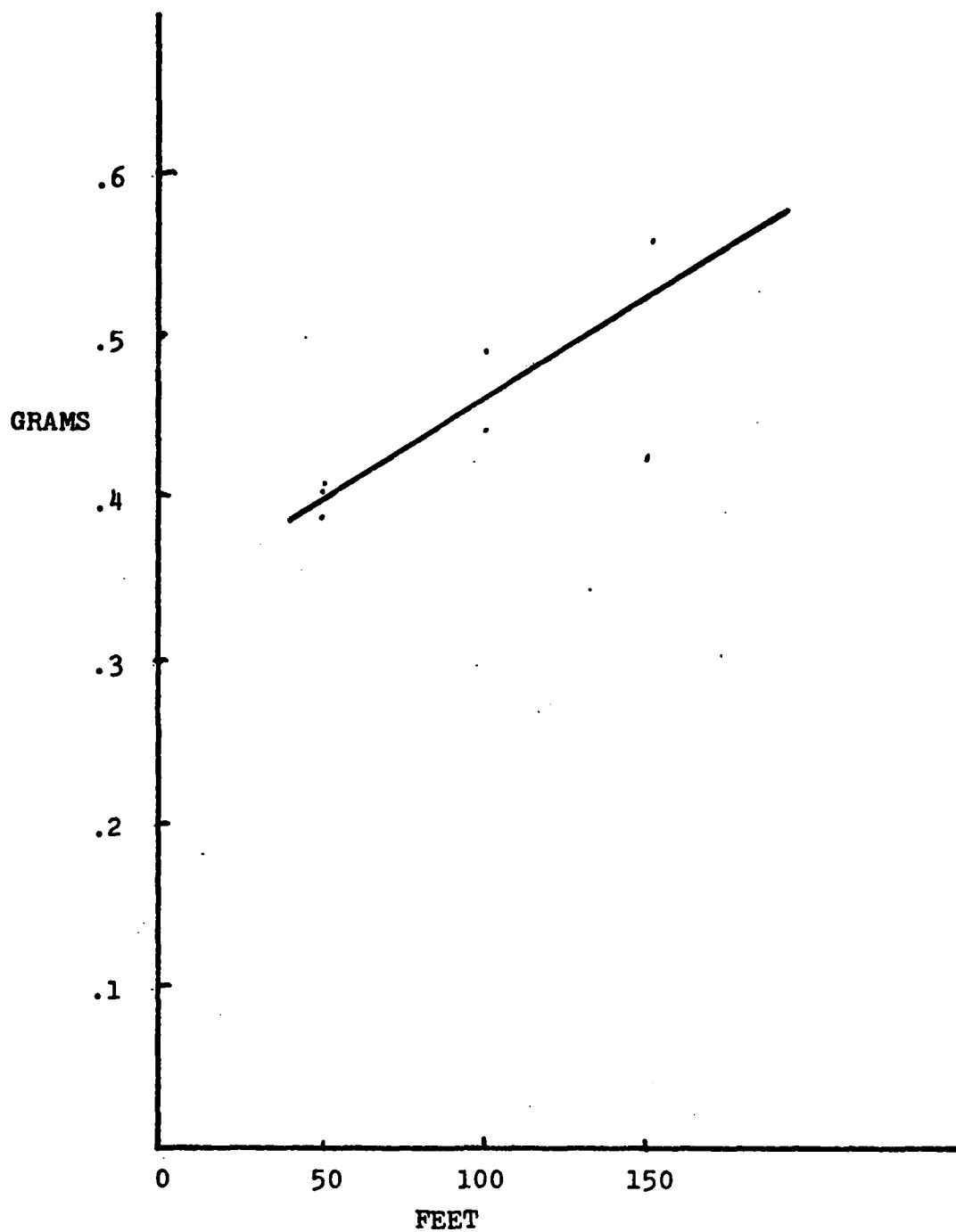


FIGURE 31. ZINC WEIGHT LOSS. OCEAN
3 DAY CORROSION TESTS

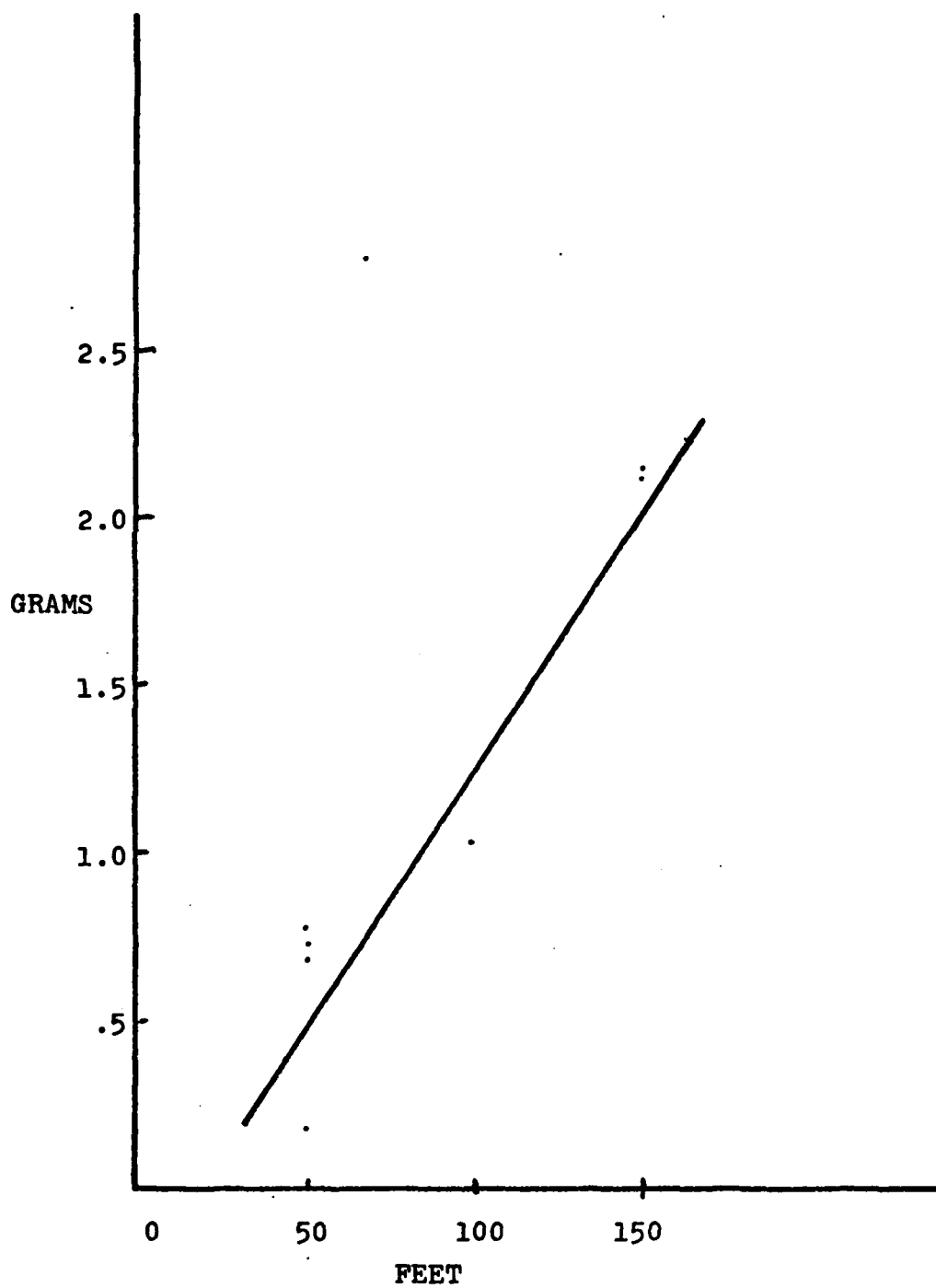


FIGURE 32. ZINC WEIGHT LOSS. OCEAN
9 DAY CORROSION TESTS



FIGURE 33. ZINC, 1 DAY, 50 FOOT, OCEAN EXPOSURE 25X



FIGURE 34. ZINC, 1 DAY, 50 FOOT OCEAN EXPOSURE 630X



FIGURE 35. ZINC, 9 DAY, 50 FOOT OCEAN EXPOSURE 24X

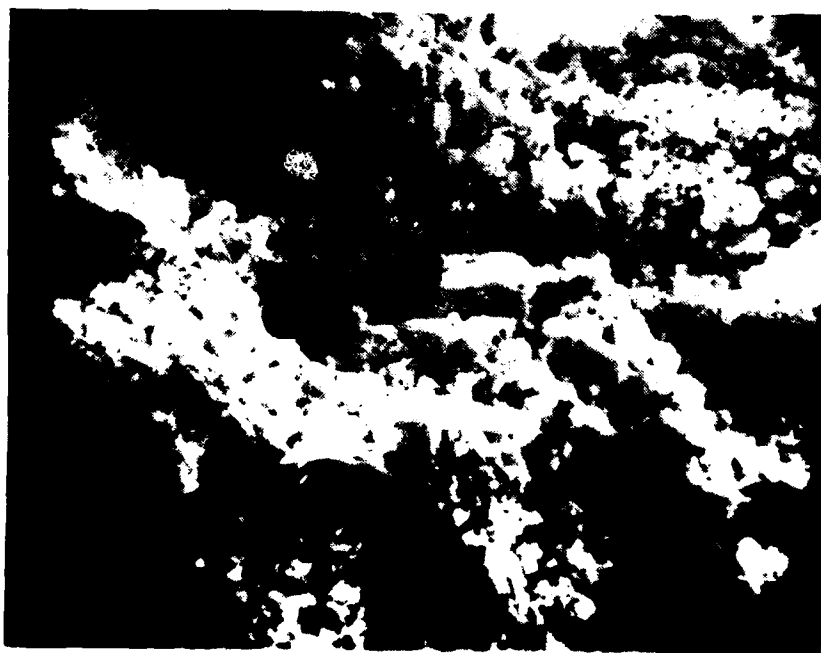


FIGURE 36. ZINC, 9 DAY, 50 FOOT OCEAN EXPOSURE 600X
"ZINC OXIDE STRUCTURE"



FIGURE 37. ZINC, 9 DAY, 50 FOOT OCEAN EXPOSURE 2400X
"CLOUDY, APPARENTLY CONTINUOUS COHERENT
COATING"



FIGURE 38. ZINC, 9 DAY, 100 FOOT OCEAN EXPOSURE 24X

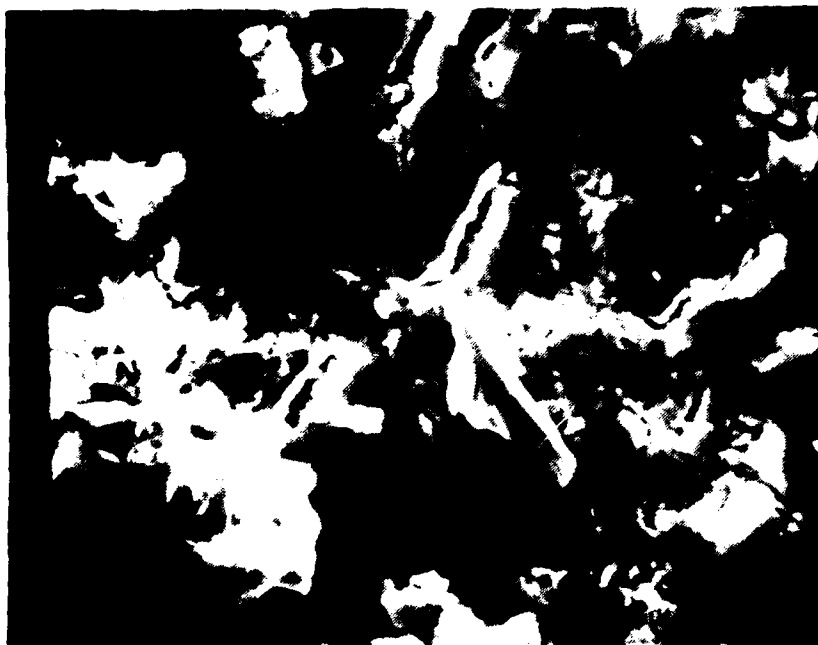


FIGURE 39. ZINC, 9 DAY, 100 FOOT OCEAN EXPOSURE 600X
"CRACKED COHERENT COATING"



FIGURE 40. ZINC, 9 DAY, 100 FOOT OCEAN EXPOSURE 2400X



FIGURE 41. ZINC, 9 DAY, 150 FOOT OCEAN EXPOSURE 2GX



FIGURE 42. ZINC, 9 DAY, 150 FOOT OCEAN EXPOSURE 600X



FIGURE 43. ZINC, 9 DAY, 150 FOOT OCEAN EXPOSURE 2400X



FIGURE 44. ZINC, 9 DAY, 100 FOOT OCEAN EXPOSURE
"MACROSCOPIC DETERIORATION"



FIGURE 45. ZINC, 9 DAY, 100 FOOT OCEAN EXPOSURE
"MACROSCOPIC DETERIORATION"



FIGURE 46. ZINC, 9 DAY, 150 FOOT OCEAN EXPOSURE
"50 PER CENT DETERIORATION"