GALVANIC CORROSION OF STRUCTURAL ALUMINUM COUPLED WITH MILD STEEL IN A DILUTE SODIUM DICHROMATE ELECTROLYTE

Prepared by

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ABSTRACT

Galvanic Corrosion of Structural Aluminum Coupled with

Mild Steel in a Dilute Sodium Dichromate Electrolyte.

This study was concerned with the corrosion rate of aluminum coupled with, and insulated from, a large mild-steel cathode in five different solutions including seawater, tap water, distilled water, and two inhibitor solutions.

Aluminum cathodically protects steel when large cathode-to-anode area ratios exist. The corrosion rate of the aluminum anode may be reduced by more than two orders of magnitude by disconnecting the couple. The presence of an inhibitor increases the corrosion rate of the uncoupled aluminum by about 35 percent, but this disadvantage is more than offset by the reduced corrosion of the steel cathode, making the use of an inhibitor highly desirable.

It was found that the corrosion rate of the aluminum anode of the aluminum-steel couple had two components, a galvanic component which is a function of the galvanic current flow and a local component to which all other weight loss is attributed. For uncoupled specimens the galvanic component does not exist, and the local component is reduced by more than one order of magnitude.

This thesis contains photographs of the specimens, a graph of the galvanic corrosion rates of the five couples over a forty-day duration, and a table of corrosion rate data in various forms.

PREFACE

The report was primarily written by the senior author in partial fulfillment of the Master of Science degree requirement under the supervision of the junior author who was his major advisor.

The study was made as part of the Coastal and Ocean Engineering Program at Texas A&M University, and conducted at the Hydromechanics Laboratories.

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CHAPTER I

INTRODUCTION

The inspiration for this thesis was derived from this research-
er's amazement of how a nicely finished aluminum model could be
attacked so rapidly by an environment that was not supposed to be
hostile.

Research was being conducted by another person concerning
wave forces on a smooth pile; the model pile was a cylinder of
finished aluminum and had to be laboriously mounted and dismounted
each time a short test was made, rather than leave it mounted in
the wave tank for the duration of the study, to prevent total des-
truction of the finish. Despite this precaution and regular polish-
ing the pile was eventually pitted extensively, even though the so-
lution in which it was immersed contained a corrosion inhibitor.

This study is an outgrowth of an effort to describe this
phenomenon and suggest a method to control or eliminate the pro-
blem. The most obvious solution was to coat the pile or apply
impressed current cathodic protection. However, since neither of
these methods of protection were permissible for this situation the
idea for a personal study was born. The primary considerations
were to determine why the corrosion rate was so high and to find
a way to reduce the rate.

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The citations on the following pages follow the style of the
Journal of the Electrochemical Society.

Aluminum was chosen for the coupon material because it is a commonly used metal in the wave tank. Also, it is readily available and produces a good galvanic couple, being an active metal with respect to steel according to the galvanic series shown in Table I. It was determined that five solutions would be tested with four types of coupons with the hope of finding a suitable corrosion inhibitor and coating combination to protect the aluminum and steel subjected to the wave-tank environment.

Literature Review

What was once a trial-and-error art, or at best a pragmatic science, has become a highly sophisticated engineering discipline. Considerable effort has been expended to improve the stability of materials in situ. Of all possible combinations of materials and environments one of the most difficult to protect is the general class of bimetallic couples in an electrolyte.

The aluminum-steel couple was chosen for this study. Pryor[1] states that

In chloride containing solutions, aluminun completely protects steel cathodically within the pH range 0-14. The galvanic current and the corrosion rate of the aluminum are at a minimum in the nearly neutral pH range. At these neutral pH values, the rate of galvanic corrosion is controlled by the rate of diffusion of oxygen to the steel cathode. Consequently, the galvanic current and the corrosion rate of the aluminum are proportional to the area of the steel cathode and are independent of the area of the aluminum anode. Factors increasing the access of oxygen to the cathode surface, such as stirr-

Table I. Galvanic series in sea water

Cathodic (noble)	Platinum
	Gold
	Graphite
	Silver
	18-8-3 Stainless steel, Type 316 (passive)
	18-8 Stainless steel, Type 304 (passive)
	Titanium
	13% Chromium stainless steel, Type 410 (active)
	67Ni-33Cu alloy
	76Ni-16Cr-7Fe alloy (passive)
	Nickel (passive)
	Silver solder
	M-Bronze
	G-Bronze
	70-30 Cupro-nickel
	Silicon bronze
	Copper
	Red brass
	Aluminum brass
	Admiralty brass
	Yellow brass
	76Ni-16Cr-7Fe alloy (active)
	Nickel (active)
	Naval brass
	Manganese bronze
	Muntz metal
	Tin
	Lead
	18-8-3 Stainless steel, Type 316 (active)
	18-8 Stainless steel, Type 304 (active)
	13% Chromium stainless steel, Type 410 (active)
	Cast iron
	Wrought iron
	Mild steel
	Aluminum 2024
	Cadmium
Anodic (active)	Alclad
	Aluminum 6053
	Galvanized steel
	Zinc
	Magnesium alloys
	Magnesium

ing and aeration, increase the galvanic corrosion rate proportionately.

From a discussion with Horst[16] of the Aluminum Research Laboratory anodic protection is required to protect the aluminum anode, and for a couple with a large cathode-to-anode ratio absolute protection is impractical, if not impossible; however, several compounds are useful to reduce corrosion of both metals when the couple is submerged in natural waters. The concensus is that the chromate compounds are the most effective economical inhibitors for steel-aluminum couples[2, 3, 4, 5, 6]; however, the protection offered by a chromate alone is not absolute. Richman[7] suggests that sodium hexametaphosphate and sodium nitrite plus sodium silicate are possible compounds to replace sodium dichromate or sodium chromate but does not state that they offer better protection and further implies that the cost of the suggested compounds is higher. Hurst[8] suggests that a combination of sodium dichromate and boron nitrite is an effective inhibitor offering protection to steel-aluminum couples. Phosphates, silicates, and nitrites, acting alone, reduce the corrosion of aluminum but provide much better protection when used in combination with one another or with sodium dichromate[5].

Galvanic corrosion of an aluminum-steel couple is negligible in distilled water, even at elevated temperatures[9]. However, local cells are set up at the steel surface, causing unilateral attack of the cathode, the intensity of which is a function of

the available oxygen.

Data for the corrosion rate of an aluminum-steel couple with a large cathode-to-anode area ratio in seawater were not available; however, a sacrificial anode cathodic protection system approximates this test and may be used for comparison. The coulomb capacity of an Alcoa CB-75 anode[10] is 700 ampere-hours per lbm, coinciding with one of several anodes studied by Lennox, Peterson, and Groover[11], and it will be shown later that their value agrees very well with the results obtained in this study.

C H A P T E R   II

EXPERIMENTAL FACILITY AND PROCEDURE

The experimental facility consisted of the 120 ft. long by 2 ft. wide by 3 ft. deep wave tank and a control-solution tank (Fig. 1) with four compartments each containing a rack of four aluminum coupons (Fig. 2) in a control solution. The steel bottom of the wave tank served as the cathode for the rack in the wave tank while sheet-steel cathodes (Fig. 3) were inserted in each of the four control-solution compartments. A Hewlett-Packard Model 412A direct-current vacuum tube voltmeter served to make potential and current measurements during the test. Commercial oxygen was bubbled through the four control solutions for the duration of the experiment at an average rate of about 1.70 cubic feet per hour to insure that the solutions were saturated with oxygen.

The assumptions made for this study are as follow:

1) Structural aluminum was used for the test. Alcoa 2024-T86 aluminum was chosen as a representative material with the following physical properties[12]:

Specific gravity - 2.77

Nominal composition; copper - 4.5 percent, manganese - 0.6 percent, magnesium - 1.5 percent, and 93.4 percent aluminum and normal impurities.

Modulus of elasticity - 10.6 x 10^6 psi
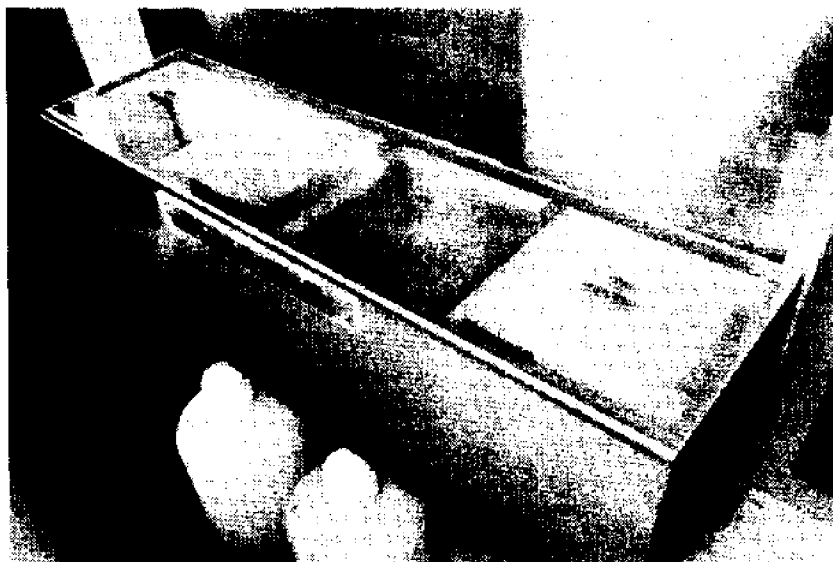
Shear stress - 45,000 psi
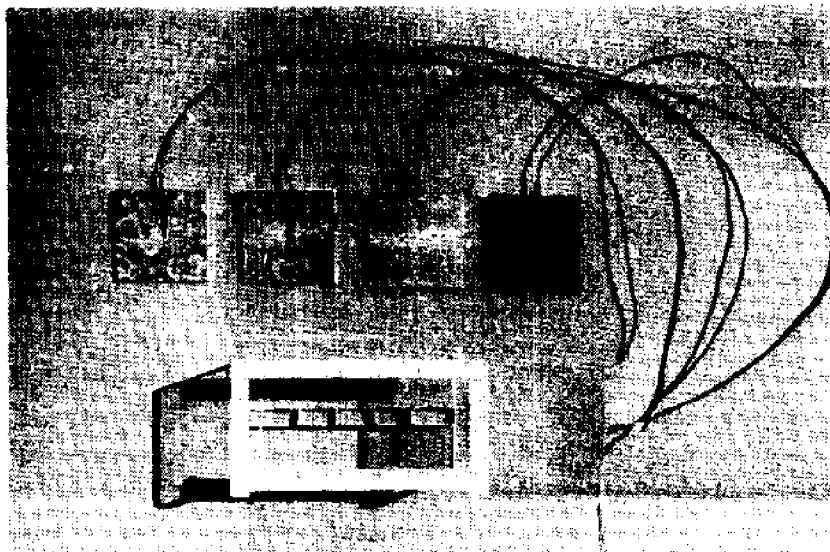
Fig. 1. Control-solution tank.
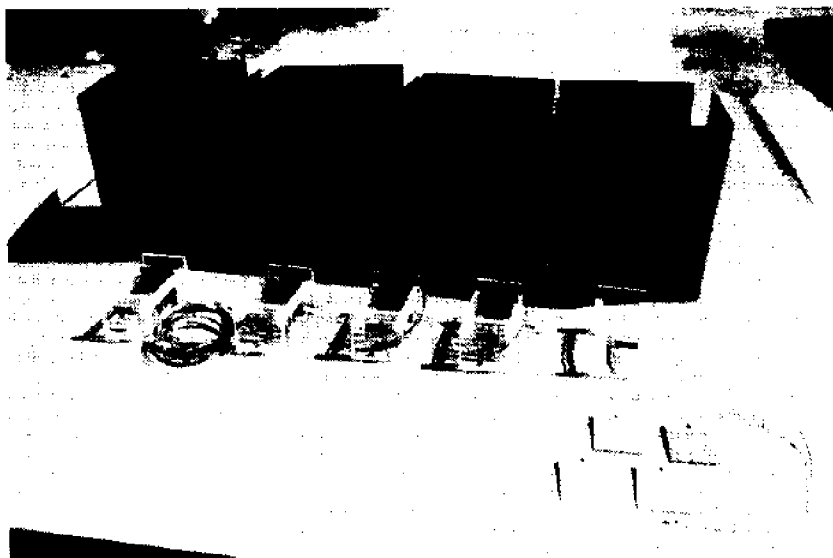

Fig. 2. Typical rack and coupons.

Fig. 3. Steel cathodes, racks, and coupons.

Tensile stress - 75,000 psi ultimate

Hardness - Brinell number 135 for 500 kg load on a 10 mm ball.

Melting range - 935 to 1180°F

Electrical conductivity at 20°C - 38 percent of the international annealed copper standard.

Thermal conductivity at 25°C - 0.36 cal/cm^2/°C/sec.

The wrought alloy designation has followed a four-digit index system since October, 1954. The first digit indentifies the alloy type, where 1 signifies aluminum, 2 - copper, 3 - manganese, 4 - silicon, 5 - magnesium, 6 - magnesium and silicon, and 7 - zinc; the second digit indicates the specific alloy modification. The last two digits identify the specific aluminum alloy or indicates the aluminum purity. "T86" designates a particular heat treatment.

2) The control solutions were saturated with oxygen. About 12 liters of oxygen per hour were bubbled through each of the control solutions for the duration of the test to satisfy this requirement and should have been sufficient to provide the maximum concentrations of 29.38 ml of oxygen per liter of distilled water or tap water and 23.6 ml/L of seawater at about 24°C[13], the average temperature of the solutions during the test. The sodium dichromate and Du Pont solutions should have had similar concentrations.

3) Contamination of the solutions was negligible. A plexi-

glas cover sealed the control-solution compartments during the test. Oxygen was piped through the plexiglas to the bottom of the tank causing a small positive internal gage pressure which continually bled to the atmosphere through a one-inch standpipe preventing dust particles or other contaminating particles from entering the compartments.

4) All solutions were constantly at room temperature. The room temperature varied slightly (on the order of a few degrees centigrade); however, the effect of temperature change is to change the oxygen concentration of the solution. Since the solutions were always saturated with oxygen with the rising bubbles causing slight motion of the liquid,it is unlikely that even at the highest temperature the oxygen concentration decreased to a value that was less than an excessive amount to sustain the reaction between anode and cathode.

5) Algae in the solutions was negligible. The inhibitor solutions are bactericidal, and it is not likely that bacteria entered the distilled water solution. The seawater was allowed to stagnate for several days before the test began, sufficient time for most, or all, algae to die.

6) Velocity of the fluid was low. Rising bubbles produced very small currents which were considered to have negligible effect upon corrosion rate. The corrosion rate was observed to be velocity-dependent when, during a potential/current measurement, the flow rate of oxygen was momentarily increased to a high

value producing higher velocities. The anode-to-cathode current flow increased sharply with increased velocity and decreased to the normal value a short time after the normal oxygen flow rate was resumed.

7) The aluminum coupons were not stressed. The coupons were sawed, not sheared, to the proper dimensions. Had the coupons been sheared,residual stresses at the edges would have produced stress corrosion cells, accelerating local galvanic corrosion.

8) The gage pressure on the coupons was low and constant over the surface. The coupons were positioned about one foot below the surface of the solutions causing an average hydrostatic pressure of about one-half psi on each coupon. Pressure affects corrosion rate by increasing the solubility of oxygen with increasing pressure. Since the solution was saturated and moving, oxygen was available uniformly over the surface of each coupon.

9) There could be no active protective measures provided for the coupons. Cathodic protection (either impressed current or sacrificial anodes) would produce stray fields that would affect the corrosion rate of adjacent coupons.

10) Each electrical measurement was made with respect to ground potential. The bottom of the wave tank (cathode) was grounded, and all control-solution cathodes were electrically connected to ground to simulate the conditions in the wave tank. All potential/current measurements were made with respect to the respective cathodes.

11) The edge area of the coupon was small compared with the plane area to prevent a misleadingly high corrosion rate caused by the fact that machined edges, and especially sheared edges, are often less resistant to corrosion attack than the plane surfaces[1]. One-eighth inch aluminum plate was chosen for the coupons. A three-inch square coupon was calculated to have a much larger plane area than edge area and was the dimension used for the test coupons.

12) The solution volume was large compared with the surface area of the coupons to prevent exhaustion of elements of the solutions as the reactions progressed. The recommended ratio is 4 liters of solution per square decimeter of coupon area[2]. About sixty percent more solution than this estimate was used to insure reliability, each control-solution compartment containing 8.5 gallons of solution.

13) The cathode-to-anode area ratio was large to simulate the conditions in the wave tank. The control-solution cathodes had approximately 640 square inches of exposed area (one side) producing a 32:1 area ratio.

Five solutions were chosen to be tested. Solution A, in the wave tank, was tap water with 4.9 ppm Cl^- and a pH of 8.3. Solution B was a 1000 ppm dilute solution of sodium dichromate ($Na_2 Cr_2O_7$) and tap water with sufficient sodium hydroxide (NaOH) added to raise the pH to 8.8. Solution C was tap water and the recommended concentration, 18 liquid ounces, of a patented auto-

motive cooling system inhibitor, Du Pont "Anti-Rust". Solution D was seawater, 0.6N NaCl, pH of 8.2. Solution E was distilled water.

As mentioned previously, the coupon dimensions were 3 inches x 3 inches x 0.13 inches. The coupons were sawed to the approximate size and machined to the dimensions above. They were stamped for identification, and electrical connections were made to the coupons which were to be coated. These coupons were coated and weighed. The coatings tested were polyester resin and submarine enamel. The coupons to be tested bare were drilled and tapped for the electrical connection, cleaned with dilute nitric acid (HNO_3) and weighed. Electrical connections were then made to these coupons.

Four coupons, mounted in a plexiglas holder, were submerged in each of the five solutions. Coupon 1 was bare and grounded to the cathode. Coupon 2 was bare and insulated from the cathode, or ground potential. Coupon 3 was coated with polyester resin and insulated. Coupon 4 was coated with submarine enamel and insulated from the cathode. Table III may be used as a handy reference, henceforth. The electrical connections from each coupon and cathode were connected to a terminal board for convenient potential/current measurements. According to Uhlig[2], the potential measurements have limited usage, being only an indication of which metal would be severely corroded if electrical contact were made. These potential measurements were made between

the insulated coupons and the cathode, or ground potential. The current measurements, a meaningful indication of the corrosion rate, were made by connecting the ammeter momentarily between the anode and cathode and recording the average steady-state current for that period of time.

The potential/current measurements were made hourly from the beginning of the test until the rate of change of the corrosion rate decreased to a more predictable value and the cathodes became passivated. As the test progressed, measurements could be made less frequently until daily measurements were sufficient.

The coupons were removed from the solution after forty days immersion, dried, and weighed. The corrosion products were chemically removed with dilute nitric acid (HNO_3), and the coupons were weighed again, defining the weight loss of each coupon, and the weight of the corrosion products adhering to each coupon at the end of the test.

C H A P T E R   III

OBSERVATIONS

The experiment began when the test racks of aluminum coupons were submerged with the cathodes in the solutions. Within an hour the formerly clear seawater clouded red with an iron compound from the cathode until the test rack could barely be seen. The distilled water solution was only very slightly clouded for the same period. Within two hours considerable oxidation of the seawater cathode had occurred. Within four hours a white corrosion product had covered coupon D1 while gas bubbles evolved from the plate. Within eight hours small adsorbed bubbles surrounding a corrosion product were sparsely distributed over coupon B1. Within twelve hours a massive formation of white corrosion product had formed on coupon D1 and evolved gas was bubbling from both coupons D1 and D2 with the smaller, less frequent bubbles being emitted from coupon D2.

After a few days a dark brown corrosion product became suspended in the distilled water solution, precipitating considerable amounts of the compound to the bottom of the compartment. At the same time it was noted that the corrosion products on coupon B1 had enlarged and multiplied. As the size of an individual bubble increased it would eventually break away from the surface of the coupon, bringing a part of the loose corrosion product with it.

After several days a froth of air bubbles and corrosion products covered part of the surface of the solution from the perimeter growing towards the center of tank B. At the same time the cathode in the seawater solution had become completely covered with a thin white layer of corrosion products over a relatively thick layer of red corrosion products. The corrosion products on coupon D1 had grown to about five times the original thickness of the coupon with bubbles continuing to rise from it. Coupon B1 was about 30 percent covered with bubbles and corrosion products. The white corrosion product in the seawater solution had precipitated from solution and piled to a depth of about 2 inches in the bottom of the tank. The slightest turbulence would cause it to become suspended.

After about ten days, the racks were removed from the solutions and photographed. The effects of galvanic corrosion were dramatic even at that early date. It was obvious that the seawater was the most damaging electrolyte with the Du Pont inhibitor, the sodium dichromate inhibitor, tap water, and distilled water being less corrosive in that order. The corrosion process in distilled water did not seem to be galvanic but more generally local corrosion of the cathode. It was noted that the corrosion product on the cathode of the seawater solution would periodically fall away and repair, which may account in part for the alternating component of the galvanic current flow between the electrodes of the aluminum-steel couple, shown in Fig. 13.

After about three weeks rather steady-state conditions had been reached. No apparent corrosion of the coupons in the distilled water had occurred, but dark brown local corrosion products covered the steel cathode while that which had fallen away from the cathode covered the bottom of the tank. A hard narrow crust had formed around the perimeter of the seawater surface on the steel cathode while the cathodes in solutions B and C were clean and bright. It was at this point that it was noticed that the rate of corrosion was definitely fluid-velocity dependent. The oxygen flow rate was momentarily increased during a current measurement between coupon D1 and cathode D. The galvanic current increased quickly from the rather steady-state value and slowly decreased to its normal value after the normal oxygen flow rate was resumed.

When the test was terminated after forty days the following observations were made:

Cathode B was clean with a dull haze over the surface. There was some local corrosion on the outside of the cathode and minor local corrosion and pitting at the surface of the solution on the inside. The corrosion products were brown with those on the outside being lighter than the products on the inside, soft, and fine-grained. The products on the inside were darker, hard, and coarse.

Cathode C was clean, bright, and rust-free on the inside. There was minor general corrosion on the outside, but the electrode

had the general appearance of being very well protected.

Cathode D was extensively corroded both inside and out. The inside was completely covered with a bicolored corrosion product in layers, a thin off-white compound over a relatively thick rust-colored compound adjacent to the steel. This product was soft and easily removed by light scrubbing and fell away in sheets. The product at the water line was similar to this product except that it had a hard crust formation and was much more difficult to remove. The outside of the cathode had relatively light corrosion products covering the entire surface and was light colored deepening to rust and finally black adjacent to the surface. There was no apparent pitting.

Cathode E was covered over most of the inside area with a rust-colored corrosion product over a black general corrosion product. The black product was thin, hard, and magnetic while the rust-colored product was soft and fine-grained with a peculiar paisley pattern of a vertical orientation. The outside of the cathode was covered with the black product except at the seam where water saturated with oxygen was able to diffuse into the stagnant region behind the cathode. At this area there was a pattern of rust-colored product over the black product indicating the oxygen concentration gradient that existed in that region. The rust-colored product was rather concentrated at the seam and diminished with the distance from the seam.

As a general rule the grounded coupons were attacked severely

with the ungrounded coupons suffering negligible damage.

Rack A is shown in Fig. 4. Coupon A1 was covered over about 50 percent of its surface with fragile white patches of corrosion products that had a general tubular formation growing upward from pitting corrosion origins. The pits had a rather small hole at the surface, expanding in cross-sectional area once into the body of the aluminum. The weight loss for this coupon was about 2.5%.

Coupon A2 had slight corrosion at the points where the holder touched the coupon. The product was white with an area similar to the shape of the notch in the plexiglas. The coupon was dark colored but was in excellent condition with negligible weight loss and few pits.

Coupon A3 appeared to be unaffected. The seal of the coating had been broken allowing water to reach the metal; however, there was no corrosion. This coupon was in the wave tank, and the coating probably fatigued and cracked due to the wave action jostling the coupon in the holder.

Coupon A4 had one very small point beginning to corrode where the coating was thin, but was otherwise unaffected.

Rack B is shown in Fig. 5. Coupon B1 was completely covered with very fragile lichen-like corrosion products. The surface was mottled with pale yellow, yellow-green, burnt umber, moss grey, and rust being the principle colors. After cleaning it was noted that the coupon was dark grey with uniform corrosion
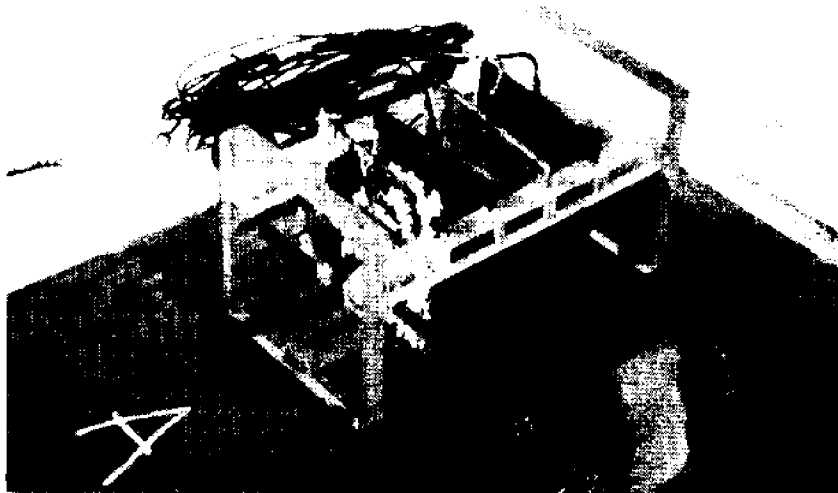
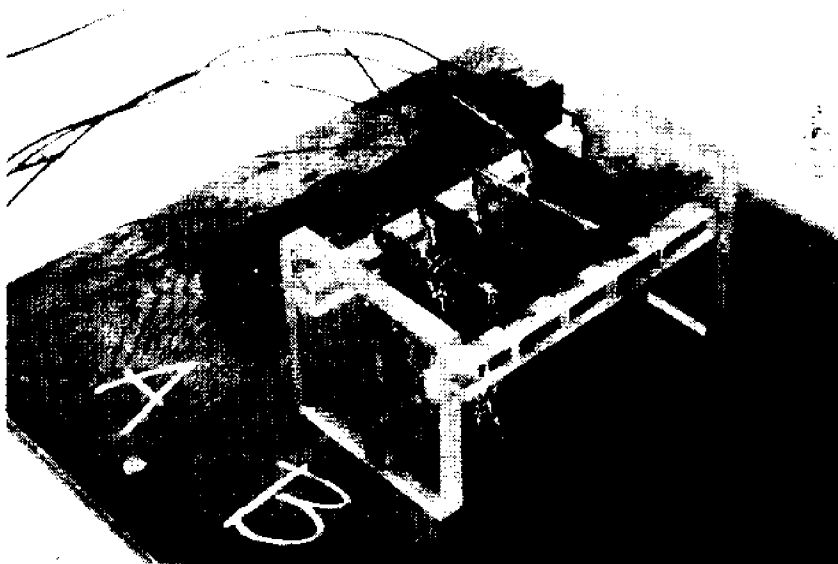Fig. 4. Rack A, after 40 days in tap water.

Fig. 5. Rack B, after 40 days in sodium dichromate inhibitor
         solution.

and extensive pitting over most of the surface area. The portion of the coupon that rested in the holder notch was protected in this case. The weight loss was only about 6 percent, but the damage appeared to be extensive.

Coupon B2 had a dull grey finish with bright spots where the coupon rested in the holder notches. It appeared to be in excellent condition with no apparent corrosion.

Coupon B3 had small white spots at the edges where the coating was thin or not well bonded; otherwise, the coupon was in good condition with no pitting.

Coupon B4 had small spots of white corrosion where the paint coating failed at the edges. It was generally in good condition with no pitting.

Rack C is shown in Fig. 6. Coupon C1 was mottled with greyish-green fragile corrosion products with lichen-like formation over the entire surface. The attack was severe, being rather deep uniform corrosion, except those small areas where access to the electrolyte was inhibited. The edge attack was minor by comparison with plane surfaces. The weight loss was about 14.6 percent.

Coupon C2 had a generally bright, clean surface except for one small area with a fragile off-white corrosion product and had a negligible weight loss.

Coupon C3 appeared to be unaffected but did have many small white spots on the metal where the solution got under the

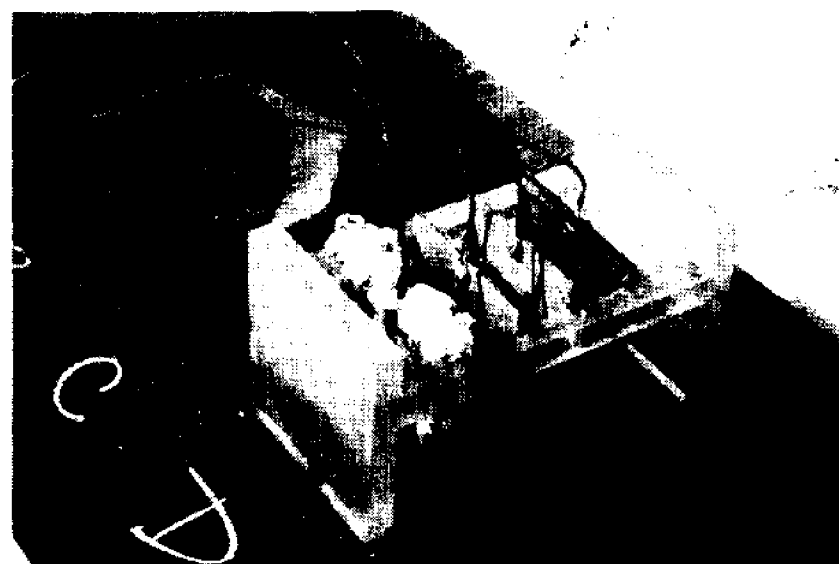Fig. 6. Rack C, after 40 days in Du pont "Anti-Rust" inhibitor solution.

Fig. 7. Rack D, after 40 days in seawater.

coating.

Coupon C4 had two small spots of yellow-green corrosion products at the edges where the coupon rested in the holder. One of the spots had started a pit, but the general condition of the coupon was good.

Rack D is shown in Fig. 7. Coupon D1 was covered with a massive formation of rather fragile off-white corrosion products. Craters had formed at the uppermost edge where gas bubbles evolved during the test. The coupon was almost totally destroyed. Areas with limited access to the electrolyte were relatively protected. The weight loss was about 63 percent.

Coupon D2 had a thin, tough uniform film of ochre corrosion products over the entire surface. The coupon would have been in good condition except for several large pits that enlarged in cross-sectional area once the surface had been penetrated.

Coupon D3 had several small areas of corrosion products around the edges where the coating was poor, but was generally in good condition.

Coupon D4 had a blister of about 1 square centimeter area, at an edge where the coating failed, that was filled with a gelatinous material. There was minor corrosion with one small pit at this location. The coupon was generally in good condition.

Rack E is shown in Fig. 8. Coupon E1 had many extremely small spots of ochre corrosion products that covered a very small portion of the total area. There were several extremely small

pits, but there was negligible damage.

Coupon E2 had a light brown film over the surface but was otherwise in excellent condition.

Coupon E3 had many small white spots under the coating but was in excellent condition.

Coupon E4 was not attacked.

Hurst[8] suggested that a combination of sodium dichromate and boron nitrite was effective in preventing corrosion of aluminum-steel couples. A separate test was conducted by this student during this study to determine the value of the inhibitor solution suggested by Hurst. Approximately equal portions of sodium dichromate and sodium nitrite were mixed with tap water to obtain a total concentration of 2000 ppm, more than adequate solute for the test. A coupon was coupled with a steel cathode and immersed in five gallons of solution. The corrosion rate and products were similar to the coupled coupon in the Du Pont solution; it was obviously not absolutely protected.
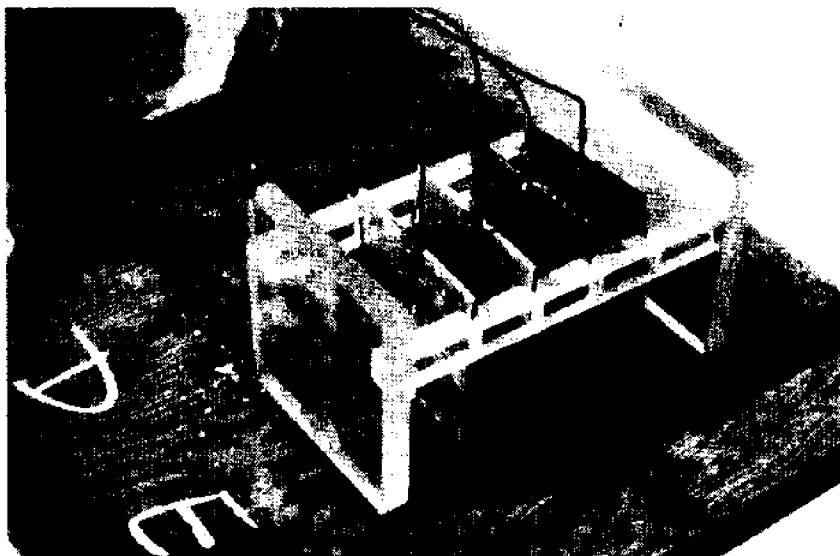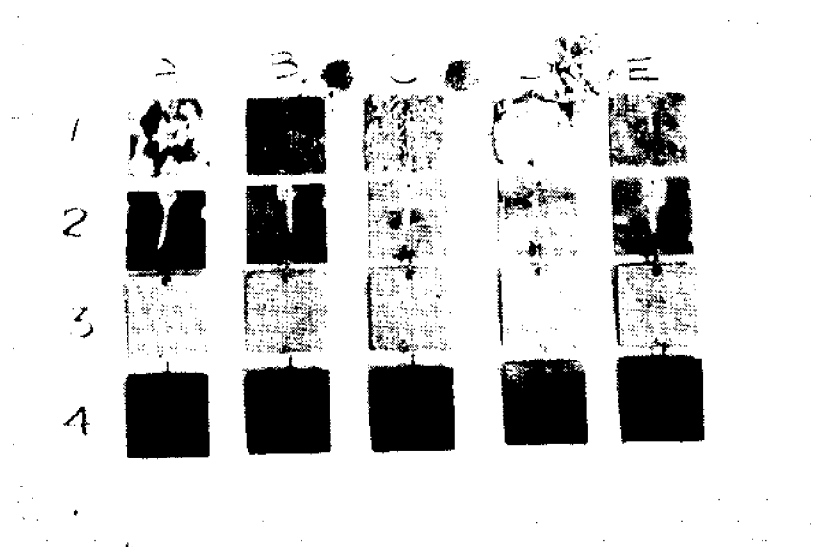
Fig. 8. Rack E, after 40 days in distilled water.

Fig. 9. Display of all coupons after test.

C H A P T E R   IV

RESULTS AND ANALYSIS

One should note, by comparison of Fig. 10 and Fig. 11 with Fig. 12, the relative corrosivity of the fluids and the dramatic difference between the grounded and insulated coupons. The most important single factor to be considered when designing a poly-metallic system exposed to an electrolyte is that bimetallic couples be prevented from occurring during the expected life of the system. Even for the highly corrosive seawater the precaution of insulating the aluminum coupon from the cathode provided a return on the investment of slightly more than two orders of magnitude; the grounded coupon had about 130 times the percent weight loss of the ungrounded coupon. Except for distilled water where the weight loss in either case was negligible, the savings due to insulating the coupons were substantial.

Coating insulated coupons is especially effective for pre-vention of pitting in seawater and tap water. The coatings had less noticeable effect in the inhibitor solutions but were of some value. It must be understood that had the coated coupons been grounded during the test pitting would have been extremely severe since the rate of corrosion does not change, being generally a cathodically controlled reaction, and the attack would have been much more intense. Pores or imperfections in the coatings would have offered a highly unfavorable cathode-to-anode area ratio
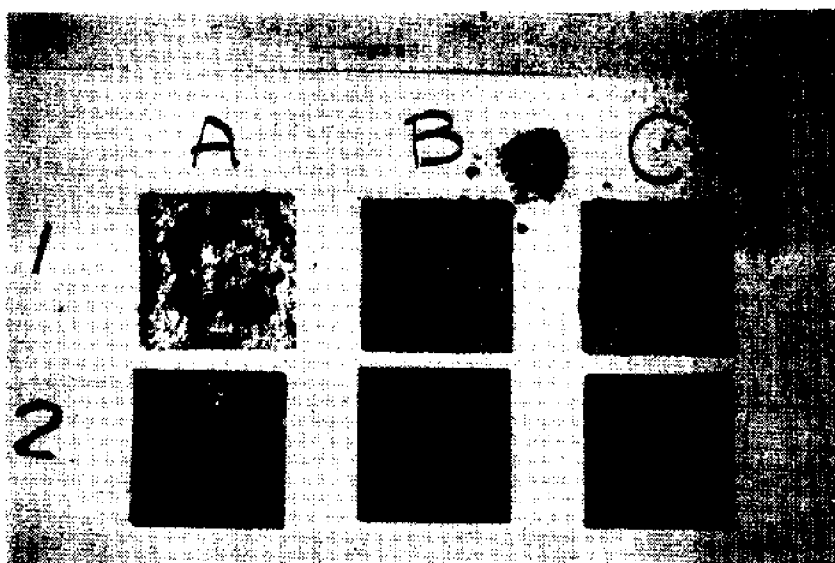
Fig. 10. Comparison of the coupled and uncoupled coupons of racks A, B, and C.
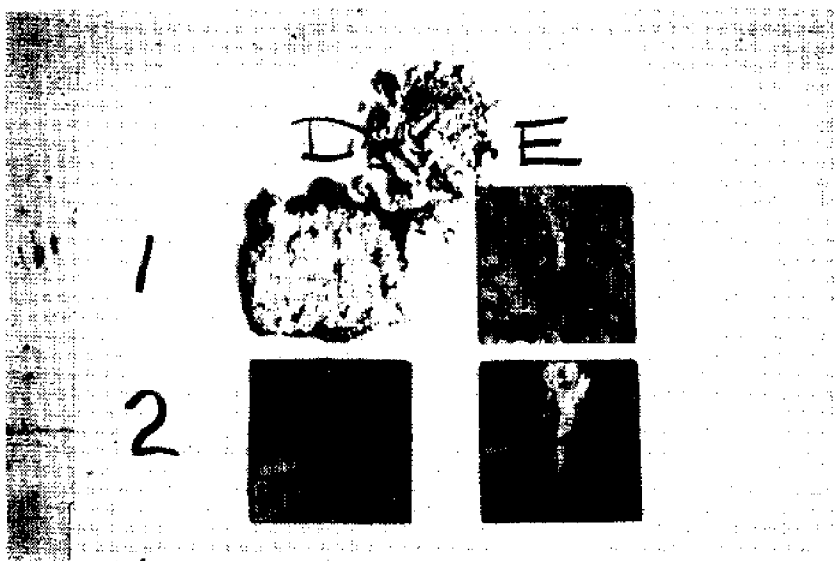

Fig. 11. Comparison of the coupled and uncoupled coupons of racks D and E.
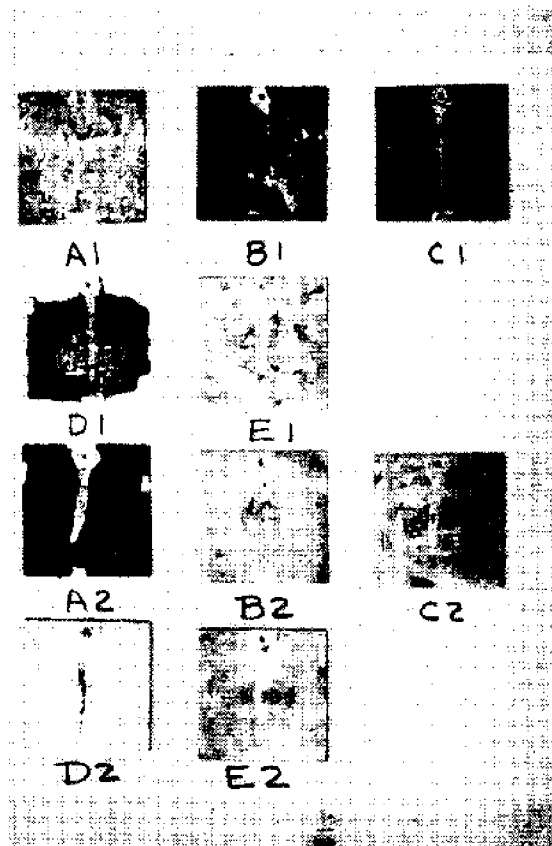
Fig. 12. Comparison of the coupled and uncoupled coupons
after cleaning.

with the resulting severe pitting.

The average weight loss per unit area per unit time was
calculated as

$$Mdd = \frac{cW}{AT} ;$$

where c = 371 $in^2 \cdot hr/dm^2 \cdot day$

W = total weight loss, mg;

A = area of coupon, in^2; and

T = exposure time, hrs.

The average penetration per unit time was calculated[14] for uniform-
ly corroded coupons as

$$MPY = \frac{KW}{\rho AT} ,$$

where K = 534 $gm \cdot in^3 \cdot mil \cdot hr/mg \cdot cm^3 \cdot in \cdot yr$, and

ρ = density, gm/cm^3.

These data are tabulated in Table II.

By graphically integrating the areas under the corrosion
rate curves (Fig. 13), it was found that the aluminum-steel couples
dissipated the following approximate charges during the forty-day
test period:

tap water solution - 2.37 ampere-hours

sodium dichromate solution - 3.88 ampere hours

Du Pont solution - 6.47 ampere-hours

seawater - 38 ampere-hours

distilled water - .05 ampere-hours

The coulomb capacity was calculated by dividing the total dissi-
pated charge in ampere-hours by the total weight loss in lbm with

the following results:

tap water solution - 990 amp-hr/lbm

sodium dichromate solution - 736 amp-hr/lbm

Du Pont solution - 620 amp-hr/lbm

seawater solution - 693 amp-hr/lbm

distilled water solution - 780 amp-hr/lbm

One of these data, the capacity of the couple in the seawater solution, agrees well with work done by Horst and Ponchel[10] and by Lennox, Peterson, and Groover[11].

It is interesting to note that the weight loss calculated from current flow (total charge dissipation) is not equal to the actual weight loss. The mass of the atoms leaving the coupon as indicated by the total current flow for forty days does not coincide with the measured weight loss of the coupon for the same period. The weight loss calculated from current flow is about 12.9 gms for the couple in seawater. The galvanic process causes chemical reactions that are evident only as local action, with the associated weight loss. For this case the galvanic weight loss comprises about 52 percent of the total weight loss; however, depending upon the pH of the solution[15] this value might range from 35 percent to 90 percent of the total weight loss. This trend was maintained as shown in Table II with galvanic weight losses ranging from 46.5 percent to 74 percent of the respective total weight losses of the couples in the various solutions.

The very low corrosion rate of the coupon in distilled water may be attributed to the high resistivity of the electrolyte causing resistance-controlled polarization rather than cathodically controlled polarization normally encountered when electrolytes of lower resistivity are present.

According to Tieh[17] of Texas A&M University the corrosion products on the seawater and distilled water cathodes may be identified as the following:

The white product from the surface of the seawater cathode was an amorphous compound, probably a hydrous aluminum oxide $(Al_2O_3 \cdot 3H_2O)$ called "Bayerite" that originated from the aluminum coupon. The orange compound had a crypto-crystalline structure and is called "lamenite", a mixture of ferric oxide and ferric hydroxide $(Fe_2O_3$ and $Fe(OH)_3$, respectively).

The black compound on the distilled water cathode had a cubic structure and is called "magnetite" $(FeO \cdot Fe_2O_3$ or $Fe_3O_4)$. The orange compound had a crypto-crystalline structure and was probably "hematite" (Fe_2O_3), similar to lamenite but less hydrous.

According to Reinhart[12] the usual product that forms on aluminum in waters below 70°C is "Bayerite" $(Al_2O_3 \cdot 3H_2O)$.

Electrolytic potential data were taken for coupon series 2, 3, and 4 but were not presented because this type of data is not a quantitative measurement of galvanic corrosion[2] and is primarily used to determine which of the dissimilar metals will be more severely corroded. Since aluminum is known to cathodically

protect steel in chloride-containing solutions[1] these data are superfluous.

CHAPTER V

SUMMARY AND CONCLUSIONS

Each of five solutions saturated with oxygen, including sea-water, distilled water, tap water, and two inhibitor solutions were tested for corrosivity with four aluminum coupons. One of the bare coupons was coupled to a large steel cathode; the remaining three coupons were uncoupled. Two of these coupons were coated, and one was bare. The coupons were carefully prepared, weighed, and immersed in their respective solutions for forty days. During this time current measurements were made between the coupled electrodes, and potential measurements were made between the uncoupled electrodes. The potential measurements were not presented, not being useful data for this study. Upon completion of the test the coupons were dried, weighed, cleaned, and weighed again. Corrosion rate was calculated as percent weight loss, weight loss in milligrams per square decimeter per day (Mdd), mils per year (MPY), pit depth, dissipated charge, and coulomb capacity, and the components of the corrosion rates of the couples due to galvanic and local action were calculated. The current flow data were presented graphically in Fig. 13 while the calculated data were presented in Table II.

The high rate of corrosion of the aluminum pile in the wave tank was due to a situation approximately duplicated in the test, a small anodic aluminum area coupled to a relatively large mild-

steel cathode in a tap water or dilute sodium dichromate electro-
lyte. The model pile was supported by a truss that was grounded,
and, therefore, directly coupled the small aluminum pile to the
large mild-steel tank bottom. The electrolyte varied, either
being tap water or dilute sodium dichromate solution. A contribut-
ing factor could have been an insufficient concentration of sodium
dichromate in the solution. Colegate[5] states that

> If an anodic inhibitor is not present in a sufficiently
> high concentration, even in absence of interfering ions
> such as chlorides, there may be parts of the surface which
> are not protected and these areas, surrounded by areas
> covered with a protective film, will be anodic to the
> latter and if the area ratio is favorable, as is often
> the case, considerable intensification of attack may
> take place.

Previously, the concentration of sodium dichromate in the sump
water that is used in the wave tank has not been known accurately.
An approximate measure of sodium dichromate has been added to
provide what is hoped to be a concentration of 500 ppm. Since
sodium dichromate is consumed in forming the passivating film
on the steel and is absorbed by the surface of the concrete in
the system, it is reasonable to assume that if the initial con-
centration were not sufficiently high to compensate for these
losses the concentration might drop to a value where not only
would the inhibitive value be decreased, but the corrosion rate
might actually be accelerated. The corrosion that generally
occurs when the concentration of this type of inhibitor falls
below a minimum value is pitting corrosion. The bottom of the
wave tank has been subjected to this type of attack and causes

one to suspect that the proper concentration of sodium dichromate inhibitor has not been maintained.

Provided that bimetallic couples are avoided, sodium dichromate appears to be an effective, convenient, and relatively inexpensive inhibitor for the wave-tank system. The Du Pont inhibitor provided slightly better protection of the steel and uncoupled aluminum, but it is almost opaque, contains a messy soluble oil, and is expensive and, therefore, is impractical for this system.

A coating over the steel tank bottom is desirable. An enamel of the same or similar type used in this test is adequate provided that it is sufficiently tough to resist the abrasive action within the tank. Since a good bond is more important than resistance to abrasion the polyester resin coating is undesirable.

A coating over the aluminum surface will not be necessary but, if convenient, will provide slightly more protection. A resistance test should be made for all light-metal models placed in the tank to insure that they are not coupled to the bottom of the tank. This test may be easily accomplished by draining the tank, mounting the model as it will be used, and testing for the desirable high-resistance electrical separation between the model and steel tank bottom.

Additional corrosion of the wave paddle and the wave absorbers may be prevented by insulating them from ground, the steel tank bottom. The spacers between the plates of the absorbers should

be aluminum, preferably of the same composition as the plates, with connecting bolts of a similar material, or cadmium-plated steel, to prevent an undesirable galvanic couple.

The sump should be cleaned and filled with a 1000 ppm sodium dichromate solution with sufficient sodium hydroxide added to raise the pH of the solution to between 8.0 and 8.5. A filter should be installed, and the system should be completely closed from that time. Very little maintenance will be required from the time these precautions are taken.

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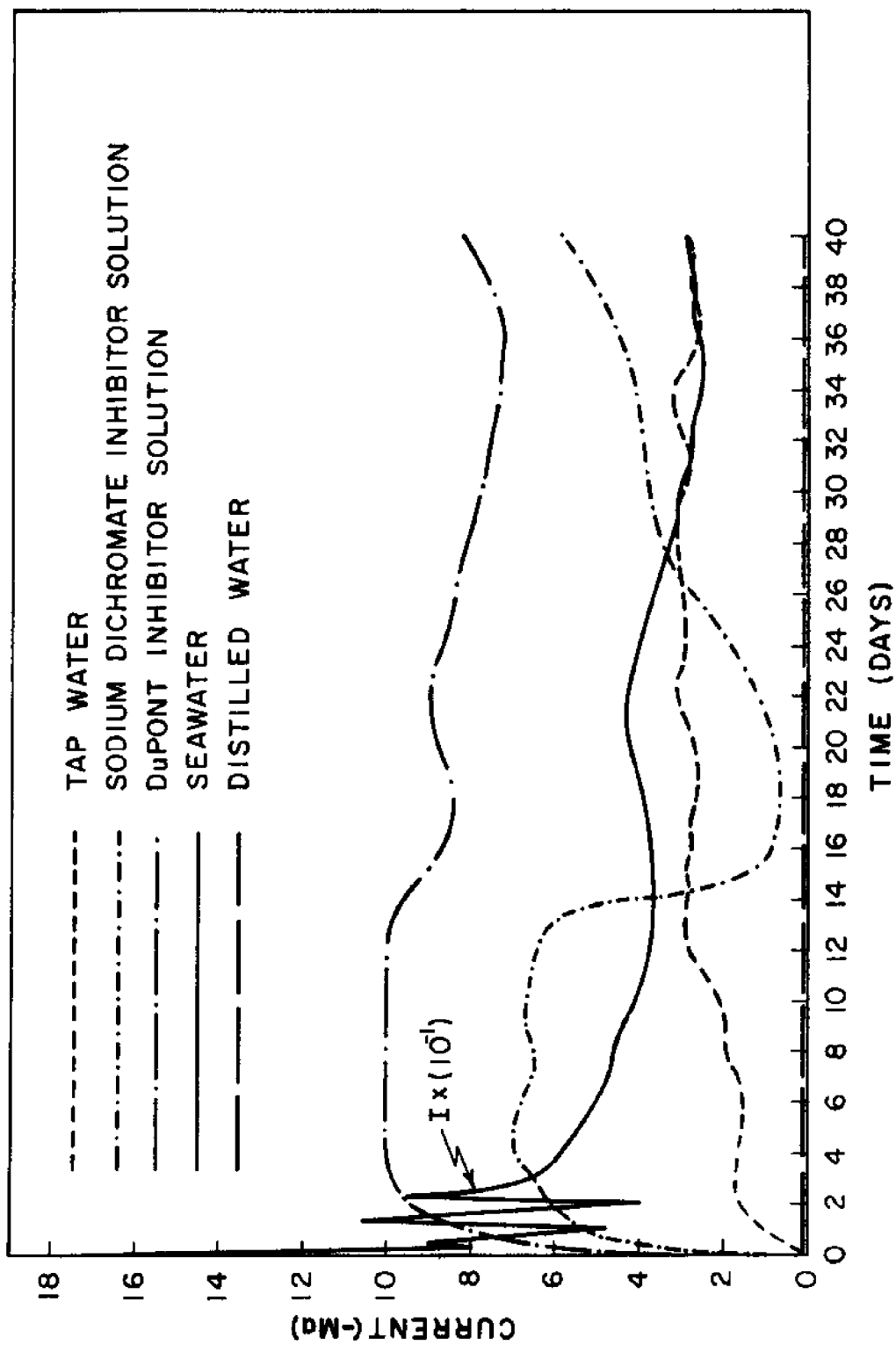
APPENDICES

Appendix I

Data

Fig. 13. Comparison of the galvanic corrosion rates.

Table II. Weight losses of Al coupons due to galvanic and local action corrosion.

Coupon	Original weight (gms)	Weight loss (gms)	Weight loss (%)	Weight loss (Mdd)	Weight loss (MPY)	Pit depth (Mil)	Weight of corrosion products (gms)	Dissipated charge (amp-hr)	Coulomb capacity (amp-hr/lbm)	Galvanic weight loss (gms)	Galvanic weight loss (%)
A1	39.7856	1.085	2.73	21.6		15	2.663	2.37	990	0.807	74
A2	39.7156	0.028	NEG	0.56	0.291		0.015				
A3	77.2691	0.123	0.159	2.44	1.27						
A4	75.3242	0.152	0.216	3.02	1.57						
B1	39.7157	2.392	6.02	47.4		15	2.763	3.88	736	1.32	55
B2	39.6317	0.038	NEG	0.755	0.393		0.032				
B3	51.5425	-0.01	NEG	-0.2	-0.104						
B4	50.3245	0.014	NEG	0.268	0.139						
C1	39.8087	4.722	11.85	93.8		12	6.698	6.47	620	2.19	46.5
C2	39.6995	0.041	0.104	0.818	0.425		0.034				
C3	53.8606	0.004	NEG	0.079	0.041						
C4	50.4856	0.034	NEG	0.68	0.354						
D1	39.5969	24.753	62.7	491.0	255.0		20.561	38.0	693	12.9	52
D2	39.8934	0.193	0.48	3.83		30	0.77				
D3	51.9778	-0.167	-0.322	-3.31	-1.72						
D4	50.4518	-0.09	-0.178	-1.78	-0.925						
E1	39.942	0.029	NEG	0.582	0.303		0.037	0.05	780	0.017	58.7
E2	39.8968	0.03	NEG	0.591	0.308		0.072				
E3	52.7030	-0.01	NEG	-0.198	-0.103						
E4	50.4326	-0.009	NEG	-0.177	-0.092						

Appendix II

Abbreviations

Abbreviations

Symbol	Description
A	area of coupon, in^2
amp-hr	dissipated charge, ampere-hours
amp·hr/lbm	coulomb capacity
c	371 $in^2 \cdot hr/dm^2 \cdot day$
cal	calorie
Cl^-	chloride ion
cm	centimeter
°C	degrees centigrade
dm	decimeter
°F	degrees Fahrenheit
gm	grams
hr	hour
in	inches
K	534 $gm \cdot in^3 \cdot mil \cdot hr/mg \cdot cm^3 \cdot in \cdot yr$
kg	kilogram
l	liters
lbf	pounds force
lbm	pounds mass
ma	milliamperes
Mdd	corrosion rate, $mg/dm^2 \cdot day$
mg	milligrams
mil	milli-inch

Symbol	Description
ml	milliliter
mm	millimeter
MPY	corrosion rate, mil/yr
N	normal solution
NEG	negligible
pH	measure of hydrogen ion activity
psi	pressure, lbf/in^2
ρ	density of coupon, gms/cm^3
sec	seconds
T	exposure time, hours
W	total weight loss, mg
yr	year

Appendix III

Coupon Identification

Table III. Coupon identification

	Tap water	Sodium dichromate	DuPont "Anti-Rust"	Seawater	Distilled water
Bare, grounded	A1	B1	C1	D1	E1
Bare, insulated	A2	B2	C2	D2	E2
Coated(polyester resin), insulated	A3	B3	C3	D3	E3
Coated(submarine enamel), insulated	A4	B4	C4	D4	E4