Carderock Division
Naval Surface Warfare Center

Bethesda, MD 20084–5000

AD–A256 072

The Effect of a Seawater Environment on the Galvanic Corrosion Behavior of Graphite/Epoxy Composites Coupled to Metals

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Denise M. Aylor
John N. Murray

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ABSTRACT

Galvanic compatibility between graphite/epoxy (Gr/epoxy) composites and metals (HY80 steel and nickel aluminum bronze (NAB)) was evaluated in 180-day seawater galvanic couple tests and laboratory electrochemical tests. Results indicate that significant galvanic corrosion of NAB and HY80 can occur when each material is coupled to a Gr/epoxy composite containing exposed graphite fibers, with the rate of the metallic corrosion increasing as the exposed graphite fiber area in the composite is increased. Galvanic corrosion can also occur between Gr/epoxy composites with no graphite fibers initially exposed to the environment and a metal as a result of moisture absorption through the epoxy outerlayer to the graphite fibers. The electrochemical impedance spectroscopy evaluation demonstrated that Gr/epoxy composites with no graphite fibers initially exposed to the environment can act as an effective cathode for oxygen reduction in seawater. It was estimated that after 200 days' seawater exposure, 15% of the planar area of this Gr/epoxy composite contained seawater-exposed graphite fibers. The potentiodynamic polarization results suggest that short-term electrochemical testing is not a reliable method for assessing long-term galvanic corrosion behavior of Gr/epoxy-metal couples but does indicate a sensitivity to graphite fiber area effects.

ACKNOWLEDGMENTS

INTRODUCTION

Interest in utilizing advanced composites such as graphite fiber-reinforced epoxy in seawater environments has increased in recent years due to their enhanced properties over more conventional materials. Graphite/epoxy (Gr/epoxy) composites offer the advantage of high strength-to-weight and stiffness-to-weight ratios (1,2), resulting in substantial weight savings for seawater components. However, many marine applications require that the Gr/epoxy composites be used in direct contact with metals. Gr/epoxy composites electrically coupled to a metal structure in seawater may result in accelerated galvanic corrosion of the metal due to the cathodic influence of the graphite fibers in the composite.

Limited seawater corrosion data has been generated addressing the

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galvanic compatibility of Gr/epoxy composite-metal couples. The majority of the research to date has been conducted for aerospace applications and has been focused predominantly on the use of titanium, aluminum, and stainless steel with the Gr/epoxy composites (1-5). Research by Hack and Macander (6) evaluated the current demand on a zinc sacrificial cathodic protection system when coupled to Gr/epoxy composites. The objective of this research is to assess the galvanic compatibility of Gr/epoxy composites with HY80 steel and with nickel aluminum bronze by conducting both 180-day marine corrosion exposures and laboratory electrochemical tests. In service, protective measures in undersea vehicles may be required and will be addressed as needed in future research programs.

MATERIALS

The Gr/epoxy composite material used in the galvanic corrosion exposures and the electrochemical testing contained AS4 graphite fibers (62% fiber volume fraction) in a 3501-6 epoxy matrix. The composites were prepared at the Naval Surface Warfare Center (NSWC), Annapolis using pre-preg tape that was hand-layed in a $[0]_8$ orientation (8-ply, 0.16 cm thick composite containing unidirectional graphite fibers) and then cured in an autoclave. A composite panel measuring 0.1 m^2 was produced, which was then diamond-saw cut into smaller sections as required for the galvanic corrosion and electrochemical specimens.

The metallic specimens utilized in the corrosion tests were conventional wrought HY80 and nickel aluminum bronze (NAB) material. The chemical compositions for both alloys are included in Table 1.

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EXPERIMENTAL PROCEDURE

GALVANIC CORROSION TESTING

Galvanic corrosion tests were conducted for 180 days in quiescent, filtered, natural seawater at ambient temperature. The testing was performed at the LaQue Center for Corrosion Technology (LCCT). The galvanic couples consisted of HY80 steel and NAB individually connected to Gr/epoxy composites in the following conditions: (a) as-fabricated composite, (b) one composite face hand-sanded to expose graphite fibers and one composite face as-fabricated, (c) two composite faces hand-sanded to expose graphite fibers, or (d) one composite face machine-sanded to expose graphite fibers.

The composites were prepared by both hand and machine sanding techniques to alter the percentage of graphite fibers exposed to the seawater environment. Both the hand and machine sanded composites were ground with wet silicon carbide paper and baked in a 50°C oven overnight (approximately 15 hours) to remove any water that was absorbed during the grinding process.

Computer-aided optical measurements were made on the Gr/epoxy composites after sanding to determine the percentage of graphite fibers initially exposed to the environment for each condition. These measurements provided only an approximation because the technique is two-dimensional and relies on the judgment of the operator in identifying graphite fiber areas that contain no epoxy. Thus, the measurements provided an estimate of the minimum percentage of graphite fibers initially exposed on the surface of the composite specimens. Based on these measurements, it was determined that the percentages of graphite fibers that were initially exposed for the Gr/epoxy composites are as shown in Table 2.

The composite specimens were prepared for testing by depositing silver conducting paint along two transverse edges of each composite (to allow electrical connection of all graphite fibers) and then attaching an electrical lead. The edges were masked to expose two 6.5 cm^2 faces to the seawater for all Gr/epoxy composite specimens except the machine sanded composites, where only one 6.5 cm^2 face was exposed. A schematic of the test specimen is included in Figure 1.

Metal alloy specimens were prepared by sanding one 6.5 cm^2 surface to a 600-grit finish, attaching an electrical lead, and masking all edges and the remaining, unsanded face. Immediately prior to immersion in seawater, the metal alloy specimens were abraded with 800-grit SiC paper and rinsed in distilled water. This final sanding was done to obtain a minimal oxide layer on the surface of all of the metal specimens.

Individual galvanic couples were immersed in seawater, with the Gr/epoxy composite specimens oriented perpendicular to the metal alloy specimens. The two specimens in each galvanic couple were positioned approximately 3.8 cm apart. For the as-fabricated and hand sanded composite-metal galvanic couples, the cathode (composite) : anode (metal) area ratio was 2:1. A cathode:anode area ratio of 1:1 was utilized for the machine sanded composite-metal couples.

The area of the Gr/epoxy cathode used in the determination of the 2:1 and 1:1 cathode:anode area ratios was based on the total planar area of the Gr/epoxy composite specimen (including both Gr fibers and epoxy) rather than the actual planar area of only the cathodic Gr fibers exposed. Thus, the actual Gr fiber surface areas initially exposed in the composites are reduced to the estimated percentage (listed in Table 2) of the total surface

area. The objective in utilizing the hand and machine sanding techniques

was to vary the percentage of Gr fibers exposed to the seawater. This

objective was met by utilizing a 1:1 rather than a 2:1 cathode:anode area

ratio for the machine sanded composites and greatly reduced logistical

problems in preparing these composite specimens.

In addition to the galvanic couples, uncoupled control specimens were

immersed in seawater for 180 days. The controls included Gr/epoxy

composites in the four conditions listed above as well as HY80 and NAB

alloys.

For the galvanic couples, the specimen leads were electrically

connected through a zero resistance ammeter. Potential and current readings

were recorded ten times per week for the first two to three months of

testing, then reduced to one to three times per week for the remainder of

the 180-day test. Potential readings were taken on the uncoupled control

specimens with the same frequency as for the galvanic couple specimens.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY EVALUATION

After galvanic corrosion testing for 180 days at LCCT, the specimens

were returned to NSWC, Annapolis. Five Gr/epoxy composite specimens were

subsequently immersed at NSWC, Annapolis in unstirred, ASTM ocean water for

an additional re-exposure time of 500 hours. Electrochemical impedance

spectroscopy (EIS) spectra were measured on the specimens periodically

during the 500 hour re-exposure period. This testing was done to obtain

electrochemical information regarding the effectiveness of the composite as

a cathode when galvanically coupled to a metal. The five graphite/epoxy

specimens evaluated using EIS are described in Table 3. In addition, EIS
was conducted on COF6 (uncoupled specimen with one face hand sanded, one
face as-fabricated) at several controlled potentials to obtain further
polarization information on the Gr/epoxy composite material.

For the EIS evaluation, the composite specimens were placed in a
polycarbonate tank electrochemical cell with two graphite rod
counterelectrodes positioned approximately 2 cm from each of the specimen
surfaces. The composite potentials were taken utilizing a Luggin capillary
with a saturated calomel (SCE) reference electrode that was positioned at
the specimen surface. The PAR Model 388 EIS equipment was utilized and has
been described previously (7). EIS spectra were measured starting at 0.1
hours' exposure to ASTM ocean water and remeasured periodically for
approximately 500 re-exposure hours. The EIS frequency range for this
evaluation varied from 5×10^{-3} to 10^5 Hz. Between runs, the solution and
specimens were left undisturbed.

POTENTIODYNAMIC POLARIZATION TESTING

Potentiodynamic polarization curves were generated at NSWC, Annapolis
on Gr/epoxy composites, both as-fabricated and with one face machine sanded
to expose graphite fibers (68% graphite fibers initially exposed), pure
graphite, HY80, and NAB specimens. The pure graphite specimens were not of
the same composition as the graphite fibers used in the Gr/epoxy composites
but were included in these tests to evaluate general differences in
polarization behavior in graphite exposed with and without an epoxy matrix.

Specimens were individually exposed in aerated, natural, ambient

temperature seawater and allowed to stabilize for 30 minutes before beginning the potentiodynamic scan. A 0.1 volt/hour scan rate was used for all tests. Anodic potentiodynamic curves were generated on the HY80 and NAB materials, while cathodic potentiodynamic curves were generated for the Gr/epoxy composite and pure graphite materials. The anodic curves began approximately 10 mV electronegative to the material's corrosion potential (E_{corr}) and continued until reaching a potential of +100 mV versus a silver/silver chloride (Ag/AgCl) reference electrode. Likewise, the cathodic curves began approximately 10 mV electropositive to E_{corr} and continued until reaching a potential of -800 mV versus Ag/AgCl.

RESULTS AND DISCUSSION

GALVANIC CORROSION TEST RESULTS

HY80-Composite Couples

Potential values measured for the HY80-composite couples remained stable during the 180-day galvanic test. The galvanic couple potentials ranged from -0.600 to -0.700 V versus a Ag/AgCl reference electrode, which were similar in magnitude to the potentials reported for the uncoupled HY80 control specimens.

Current versus time data for the HY80-composite galvanic couples is included in Figures 2-5. The current data for all of the HY80-composite couples indicated an initial rise in current immediately after exposure to seawater The amount of the initial current increase varied among the different composite specimen types coupled to HY80, and it was found to be related to the percentage of graphite fibers initially exposed in the

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Gr/epoxy composites. The HY80-CAR (as-fabricated Gr/epoxy with no graphite fibers initially exposed) couples exhibited initial maximum current levels of 0.08-0.15 mA, while the HY80-COF (Gr/epoxy with one face hand sanded to expose a minimum of 4% graphite fibers) couples showed maximum initial levels of 0.29-0.36 mA. As the percentage of graphite fibers initially exposed increased even more with the HY80-CTF (Gr/epoxy with two faces hand sanded to expose a minimum of 8% graphite fibers) couples, the initial current level also increased to an average of approximately 0.4 mA, with current spikes as high as 0.7 mA. The initial maximum current levels for the HY80-COFM (Gr/epoxy with on. face machine sanded to expose a minimum of 68% graphite fibers) couples varied from 0.3-0.4 mA, which was within the same initial current range as was reported for the HY80-COF and HY80-CTF couples.

The initially high current levels exhibited by the HY80-COF, HY80-CTF, and HY80-COFM couples within the first 50 days of seawater exposure decreased and leveled off to values less than 0.1 mA by 70-80 days of seawater exposure. The HY80-COF and HY80-CTF couples remained in the 0.04-0.1 mA current range between days 70 and 130, then displayed another decrease in current to a level of 0.0001-0.03 mA for the remainder of the 180-day exposure period. The HY80-COFM couples leveled off to 0.01-0.04 mA by 70-80 days' exposure and remained at that level for the rest of the 180-day exposure period.

The HY80-CAR couples exhibited slightly different current behavior from the other HY80-composite galvanic couples. The HY80-CAR couples reached a maximum current level of 0.15 mA within the first 10 days of exposure, leveled off to approximately 0.05 mA for approximately 35 days, then

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displayed a second increase in current which was at a maximum level of 0.35 mA by day 70. The current then continually decreased from day 70 through 125 until leveling off at 0.001-0.003 mA for the rest of the 180-day exposure.

Figure 6 shows a representative photograph of the HY80-composite galvanic couple specimens after the 180-day testing. The specimen surfaces had been brush cleaned prior to photographing. At the conclusion of the galvanic couple testing, the HY80 specimens contained voluminous, rust-colored corrosion products on their surfaces, while the Gr/epoxy composites exhibited tenacious calcareous deposits over the majority of their surfaces. After removing the corrosion products from the HY80 specimens, it was found that the HY80 specimens coupled to the CAR, COF, and CTF composites contained corrosion that was predominantly concentrated along the specimen edges. In contrast, the uncoupled HY80 control specimens and the HY80 specimens coupled to the COFM composites exhibited general corrosion across their surfaces. The maximum depth of corrosion attack measured on the HY80 specimens from the HY80-CAR and HY80-COFM couples was 0.20 mm, similar to the 0.18 mm maximum depth of corrosion attack measured on the uncoupled HY80 controls. The HY80 specimens from the HY80-COF couples reported a maximum depth of corrosion attack of 0.38 mm, and the HY80 specimens from the HY80-CTF couples exhibited a maximum corrosion attack depth of 0.79 mm.

NAB-Composite Couples

Potential versus time data measured for the NAB-composite couples showed stable potential values ranging from approximately -0.100 to -0.170 V versus Ag/AgCl over the 180 days of seawater exposure. This range of

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potential values was somewhat electropositive to the uncoupled NAB control specimens, which varied from -0.210 to -0.270 V versus Ag/AgCl during the 180-day period. The electropositive shift in E_{corr} for the NAB-composite couples as compared to the NAB control specimens suggests that the graphite fibers in the Gr/epoxy composite had a slight effect in polarizing the galvanic couple in the electropositive direction.

Current versus time data for the NAB-composite galvanic couples is included in Figures 7 and 8. As seen in these figures, all of the NAB-composite couples exhibited a rise in current immediately after seawater exposure. The amount of the initial current increase was found to be related to the percentage of graphite fibers initially exposed in the Gr/epoxy composites. A similar trend in the initial current data was exhibited by the HY80-composite couples.

The NAB-CAR (as-fabricated Gr/epoxy with no graphite fibers initially exposed) couples displayed initial maximum current levels of approximately 0.08 mA. As the percentage of graphite fibers initially exposed increased to a minimum of 4% in the NAB-COF couples, the initial maximum current level increased to approximately 0.17 mA while the NAB-CTF (Gr/epoxy with two faces hand sanded to expose a minimum of 8% graphite fibers) couples showed a maximum current level as high as 0.54 mA. The initial maximum current level for the NAB-COFM couples was 0.3 mA, which was within the range of initial maximum current reported for the NAB-COF and NAB-CTF couples.

The initial maximum current level for the NAB-CAR couples was reached within the first ten days of testing, after which the current level decreased to 0.01 mA or less and remained there until the end of the 180-day test period. The NAB-COF and NAB-CTF couples reached their peak current

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levels within the first 25 days of seawater exposure and then steadily decreased to a current level of 0.1 mA or less by day 60. The couple current then remained constant until approximately 125-135 days of exposure. At that time, the current level for the NAB-COF couples and one of the two NAB-CTF couples decreased to 0.01 mA or less. The remaining NAB-CTF couple stayed at the 0.1 mA current level until the end of the 180-day exposure period.

The NAB-COFM couples attained their maximum initial current level within the first 20 days, after which the couple current decreased slightly but never stabilized through the 180-day seawater exposure period. The couple current fluctuated between 0.05 and 0.3 mA during days 20 through 180.

At the conclusion of the 180-day galvanic corrosion tests, the NAB specimens from the NAB-composite galvanic couples contained greenish-brown and brown corrosion products in localized areas on their surfaces. As in the HY80 tests, the Gr/epoxy composites from these NAB-composite galvanic couples had tenacious calcareous deposits on their surfaces. Figure 9 shows a photograph of one NAB-CTF galvanic couple at the conclusion of the seawater testing. The specimen surfaces had been brush cleaned to remove the bulk of the corrosion products prior to photographing. The photograph in Figure 9 represents the localized corrosion typically present on the NAB surfaces after the NAB-composite galvanic couple testing was completed, but the depth and quantity of pitting present varied among the various galvanic couples.

All of the NAB specimens from the NAB-composite galvanic couples exhibited localized corrosion that was predominantly oriented along the

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specimen edges. The NAB specimens from the NAB-CAR couples contained minimal pitting (0.03-0.05 mm deep) on their surfaces. The quantity and depth of pitting was very similar to the pitting present on the uncoupled, control NAB specimens. The NAB specimens from the NAB-COF and NAB-CTF couples all displayed a maximum depth of pitting of 0.76 mm, although the quantity of pitting was significantly greater on the NAB specimens from the NAB-CTF couples. The maximum depth of pitting measured for the NAB specimens from the NAB-COFM couples was 1.45 mm, significantly higher than on any of the other NAB-composite couples.

DISCUSSION OF GALVANIC CORROSION TEST RESULTS

The individual galvanic current versus time curves for all of the metal-composite couples (Figures 2-5, 7, and 8) were oscillatory in nature. The oscillations were presumably due to localized differences in the active anodic and cathodic areas contributing to the galvanic corrosion reaction, with the actual contributing areas being related to the stability of the films present on the composite and metal surfaces. A similar oscillatory nature was also seen in the galvanic current data reported by Hack and Macander (6) on Gr/epoxy-zinc and NAB-zinc couples in seawater.

The current trends determined from the galvanic couple testing are incorporated into the plot shown in Figure 10. This plot divides the current versus time curve into four distinct regions. Region I shows the initial current increase upon exposure in seawater, which was attributed to the activation of both the metal and graphite fiber surfaces by immersion in seawater. As corrosion product films were formed on the active surfaces,

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the currents decreased (Region II) and leveled off (Region III) due to a reduction in the active surface areas. After a period of time, calcareous deposits accumulated on the graphite fiber surfaces and controlled the ongoing cathodic processes, which resulted in a second decrease in the measured current to negligible values (Region IV).

The formation of calcareous deposits on the Gr/epoxy composites occurred due to the oxygen reduction reaction, $O_2 + 2H_2O + 4e^- = 4OH^-$, taking place at the cathode (composite). The generation of hydroxyl ions from this reduction reaction raises the pH of the seawater at the graphite surface and typically results in the precipitation of $CaCO_3$ and $Mg(OH)_2$ (8).

The corrosion product films formed on the anodic and cathodic surfaces of the galvanic couple specimens reduced the measured galvanic couple currents for a significant portion of the seawater test period. Thus, the extent of galvanic corrosion exhibited by the anodic metal specimens was highly dependent on the formation and maintenance of these protective films. Under seawater flow conditions, the growth and maintenance of the corrosion product films can be severely limited and the supply of dissolved oxygen to the cathode increased (9), thus resulting in significantly higher galvanic corrosion rates. Research by Hack and Macander (6) showed as much as an order of magnitude increase in the galvanic currents measured for Gr/epoxy-zinc and NAB-zinc couples in 10 m/s flowing seawater as compared to 0 m/s seawater.

All of the HY80-composite and NAB-composite couples displayed the initial current increase and subsequent reduction in current as described for Regions I and II, but after that variations from Figure 10 were evident for individual galvanic couples. In general, it was found that the

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magnitude of the initial current level increased as the graphite fiber

surface area increased. The HY80-CAR couples showed a second increase in

corrosion current after the initial current increase and reduction (Regions

I and II). This second corrosion current increase was presumably due to

increased moisture penetration within the composite which increased the

active cathodic graphite fiber surface area. The eventual buildup of

calcareous deposits on the CAR surface then resulted in the current decrease

to a negligible level. The NAB-CAR couples did not show a second increase

in current, but only an initial current increase followed by a reduction in

current to a very low level. The second increase in current that was seen

on the HY80-CAR couples and not found on the NAB-CAR couples was presumably

related to differences in the permeability of the films formed on the

Gr/epoxy composite surfaces.

It should be noted that the HY80-CAR and NAB-CAR couples did display an

increase in the current level almost immediately upon seawater exposure

(Figures 2 and 7) even though these composites contained an approximately

0.01 mm thick epoxy layer on their surfaces, which initially prevented any

graphite fibers from being exposed to the environment. A computer program

(10) based on Fickian diffusion was used in this study to estimate the time

required for moisture to penetrate through the epoxy layer to the graphite

fibers within the composite. Input for this program included a resin

diffusivity of 1.48×10^{-6} in^2/hour and a maximum moisture content of the

resin equal to 6%. The basis for the selection of these input values is

explained in reference (11). The program calculations showed that moisture

could penetrate through the epoxy layer to the graphite fibers within ten

minutes after exposure, which is consistent with the increase in the

measured galvanic currents almost immediately upon immersion for both the HY80-CAR and NAB-CAR couples.

After the 180-day seawater test period, inspection of the HY80 and NAB specimens that were coupled to the CAR composites showed that the extent of the corrosion attack was similar to the respective, uncoupled control specimens, suggesting no increased corrosion from the galvanic coupling. However, the galvanic current measurements for these couples indicated galvanic activity during part of the exposure period as evidenced by rises in the measured current level. The minimal corrosion on the metal alloy specimens that were coupled to the CAR composites was attributed to the small area of graphite fibers available to promote the galvanic corrosion reaction with the anodic metal and to the corrosion product films formed on both the anode and cathode which also reduced the effective surface areas for the reaction.

The HY80-COF, HY80-CTF, NAB-COF, and one of two NAB-CTF couples exhibited the four regions of corrosion current behavior as depicted in Figure 10. The HY80-COFM couple and the remaining NAB-CTF couple displayed corrosion currents as defined by Regions I through III, but never showed the Region IV reduction in current to very low levels. In addition, the NAB-COFM couples showed the initial current rise and subsequent reduction in current but did not exhibit a stable current level by the end of the 180-day test. The active currents evident in the HY80-COFM, NAB-COFM, and one NAB-CTF couple are presumably related to active surface areas of graphite fibers available to promote the galvanic corrosion reaction with the metal surface, thus preventing a reduction in the current level to negligible values.

Although the shape of the current versus time curve varied for the

metal-composite couples, the corrosion test results indicate that galvanic corrosion will occur when NAB or HY80 is coupled to a Gr/epoxy composite with exposed graphite fibers. In general, it was found that the magnitude of the galvanic current increased as the graphite fiber area was increased. Also, the depth of corrosion attack was greater on the NAB specimens coupled to Gr/epoxy composites than on the HY80 specimens coupled to the Gr/epoxy.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY TEST RESULTS

The EIS spectra obtained for the five graphite/epoxy composite specimens after 500 re-exposure hours were analyzed assuming that the conventional nested RC equivalent circuit model approximates the specimen and electrolyte interface parameters. The nested model is shown as Figure 11. The physical test system is considered to be the composite surface with pores in the polymer which can allow the test solution to contact the reinforcing graphite. When the composite is electrically coupled to a metal surface in an aqueous solution, the graphite surfaces become O_2 reduction areas for the galvanic couple. The resulting alkalinity from the O_2 reduction reaction can allow precipitation of magnesium and calcium compounds from the seawater onto the composite which then forms a calcareous coating on the surface which should act as an electrical capacitor (C_{calc}). The calcareous deposit is anticipated to have some open porosity which would then limit the solution exposure to the exposed graphite and in effect act as an electrical (ionic) resistor ($R_{calc. pore}$). The organic phase of the composite may also act as a capacitor (C_{poly}) in parallel with the calcareous coating. An initial solution resistance (R_0) exists between the test surface and the Luggin capillary leading to the reference electrode. Finally, the

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graphite surface itself responds electrochemically as a resistive element (R_P) (for the electrochemical reduction of O_2) in parallel with the capacitive nature (C_{dl}) of the graphite and electrolyte interface.

For the composite specimens that were galvanically coupled, the equivalent circuit simplifies somewhat as the C_{poly} and C_{calc} elements add and the two pore resistances add. The resulting equivalent circuit is shown as Figure 12.

For the uncoupled composite specimens, the graphite surface corrosion rate is very low and requires quite low O_2 reduction current, therefore yielding little local alkalinity. Under these conditions, very little (if any) calcareous deposit forms on the composite. The polymer capacitance, which would be expected to be observed in the high frequency range, appears to be too small to be detected in the presence of the large polymer pores (and therefore small pore impedances). The equivalent circuit then simplifies even further to one of two possible cases. In the one case, the O_2 reduction process at the specimen potential is moderate, therefore the polarization resistance is measurable and the equivalent circuit reduces to that shown as Figure 13. This equivalent circuit results in the general response seen for the uncoupled composite specimens with one or two hand-sanded faces. For the as-fabricated, uncoupled composite specimen with no faces sanded, the equivalent circuit reduces even further in that the polarization resistance is so large as to be unmeasurable at the lowest frequency (0.005 Hz and in one case 0.0001 Hz) normally utilized.

The graphite fiber area exposed to the ASTM ocean water solution was calculated from the EIS C_{dl} data as a function of re-exposure time for each of the five graphite/epoxy composites. For these calculations, a specific

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double layer capacitance of 25 $\mu F/cm^2$ was assumed. This value was selected from the 15 to 40 $\mu F/cm^2$ range established for a smooth metallic mercury surface in a variety of aqueous solutions (12) and appears to be reasonable for graphite as well as several very slowly corroding metals.

Figure 14 presents the calculated graphite fiber areas for the five composites as a function of re-exposure time. The data shows that all three types of composites (as-fabricated, one face hand sanded, or two faces hand sanded) contain an active, cathodic graphite fiber surface area which can act in the oxygen reduction process. This data also indicates that the area of the active graphite fiber surface increases as the initial, exposed graphite fiber surface area is increased. Even the as-fabricated composite specimen, CAR5, has graphite fiber area which can act in the O_2 reduction process and, after the initial penetration period, the composite appears to be stable to at least 500 hours' re-exposure.

The O_2 reduction currents and current densities for the five composite specimens in the unstirred, ASTM ocean water solution were also calculated using the low frequency impedance values and the areas calculated from the C_{dl} values. These R_p values were then converted to corrosion current densities using the Stern-Geary equation (13). In general the uncoupled, hand-sanded composite specimens (COF6 and CTF6) would allow 0.03 $\mu A/cm^2$ cathodic current at the uncoupled potential of approximately 0 V vs. SCE. The coupled, hand-sanded composite specimens (COF3 and CTF3) allowed approximately 90% of that value or 0.027 $\mu A/cm^2$, with this lower current density presumably due to diffusional constraints as a result of the presence of the calcareous films. The uncoupled, as-fabricated composite specimen CAR5 would then allow approximately 0.0045 $\mu A/cm^2$ at the uncoupled

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potential based on the total exposed composite area.

The total O_2 reduction current possible from the graphite reinforced composite is also a function of the cathode potential. The potential can range from +0.2 V vs. SCE, as seen for these composite specimens retested in the uncoupled mode to a low potential in the coupled mode which would depend on the metal to which the composite was coupled and the relative anode to cathode areas. EIS runs were made at several controlled potentials using the composite specimen COF6 with one face hand-sanded. The O_2 reduction polarization data from the EIS runs are shown as Figure 15, with the general schematic dashed line added to identify the Tafel and the limiting current density ranges. As can be inferred, a large area steel anode (uncoupled corrosion potential of -0.6 V vs. SCE (14)) could "drive" a small area graphite cathode at 0.8 $\mu A/cm^2$ in an unstirred solution. For the as-fabricated composite material, the calculated cathodic current density is 0.12 $\mu A/cm^2$, which is considerably lower than the current density determined for the Gr/epoxy composite with one face sanded. The cathodic currents for the composites could be increased with increasing electrolyte flow.

In summary, the EIS investigation showed that after approximately 200 days of seawater exposure, all of the Gr/epoxy composites (COF, CTF, and CAR composites) contained active cathodic graphite fiber surface areas which can act in the oxygen reduction process. Even the Gr/epoxy composites in the as-fabricated condition, which contained a 0.01 mm thick epoxy layer on their surfaces, had exposed graphite after the seawater exposure (probably through the surface porosity in the polymer matrix). It was estimated that 15% of the planar area of the as-fabricated composite contained seawater-exposed graphite fibers. When this as-fabricated Gr/epoxy composite is

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galvanically coupled to a metal, the composite can allow between 0.0045 and 0.12 $\mu A/cm^2$ current density, with the specific value depending on cathode to anode area ratios and seawater flow rate conditions.

POTENTIODYNAMIC POLARIZATION TESTING

The potentiodynamic curves produced for the pure graphite, Gr/epoxy composite, and metallic materials are included in Figure 16. The anodic curve for NAB indicates a reduction in current density at a potential of -200 mV. This behavior was also reported by Scully (15) in potentiostatic testing of 70/30 and 90/10 copper-nickel, which he attributed to either passivity of the alloy or the buildup of a resistive film. The anodic curve generated for HY80 showed no indication of passive behavior.

The cathodic curves produced for pure graphite, Gr/epoxy with one face machine sanded (COFM - estimated 68% graphite fibers initially exposed), and as-fabricated Gr/epoxy (CAR - no graphite fibers initially exposed) all showed an orientation in the vertical direction at negative potentials, indicating that the system had become diffusion limited. This vertical orientation occurred at approximately -100 mV for the CAR specimens and at approximately -400 mV for the COFM and pure graphite specimens.

Similar cathodic polarization curves were generated by Belucci, et al. (16) on Gr/epoxy and pure graphite specimens in 3.5% NaCl. Their results correlated well with the cathodic curves determined for the COFM and pure graphite specimens in this research, with similar materials displaying limiting current densities within the same order of magnitude.

By coupling an individual anodic and cathodic curve, it is possible to predict the potential and corrosion current density for that galvanic

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couple. Coupling NAB to the three cathodic curves (CAR, COFM, and pure graphite) yielded a couple E_{corr} of approximately -300 mV in all three cases due to the flatness of the anodic NAB curve. The couple corrosion current densities, however, varied from 0.04 $\mu A/cm^2$ for the NAB-CAR couple to 2 and 7 $\mu A/cm^2$ for the NAB-COFM and NAB-graphite couples, respectively. This approach showed a two-fold order of magnitude increase in the couple corrosion current density between the NAB-CAR couple with no graphite fibers initially exposed and the NAB-COFM (68% graphite fibers initially exposed) and NAB-pure graphite couples.

The HY80 material coupled to the three cathodic curves (CAR, COFM, and pure graphite) all showed a predicted couple E_{corr} of -550 mV due to the flatness of the anodic HY80 curve. The predicted couple corrosion current densities were significantly higher for the HY80 couples than for the NAB couples, but the data still indicated an increase in corrosion current density with increasing graphite area (as was found for the NAB-composite couples). The HY80-CAR couple showed a corrosion current density of 0.1 $\mu A/cm^2$, and the HY80-COFM and HY80-graphite couples exhibited corrosion current densities of 20 and 80 $\mu A/cm^2$, respectively.

The polarization results for both the NAB-composite and HY80-composite couples showed differences in predicted corrosion rates for the couples as the amount of exposed graphite area was varied. Thus, this potentiodynamic test method does indicate a sensitivity to graphite fiber area effects in Gr/epoxy-metal couples.

A comparison of the couple potential and current density values predicted from the polarization curves with the actual values measured during the galvanic couple testing is reported in Table 4 This table

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provides data for the NAB and HY80 alloys coupled to both CAR and COFM Gr/epoxy composites. The poor correlation in data between the predicted values from the polarization curves and the actual, measured values from the galvanic couple tests indicates that the short-term polarization testing is not an accurate method for predicting long-term galvanic couple corrosion rates. These results agree with the conclusion stated by Belucci (17) after evaluating Gr/epoxy composites and metals in 3.5% NaCl using potentiostatic polarization and with research by Scully (15) on metals in seawater. The poor correlation between the potentiodynamic and galvanic couple tests is not unexpected, since film formation on the composite and metal specimens can markedly affect the material's polarization behavior. Film formation is severely limited in the potentiodynamic testing due to the short-term nature of these tests.

As seen in Table 4, the couple current density values predicted from the polarization testing were generally closest to the actual couple current density values reported within the first 30 days of seawater testing. Also, the predicted current density values were generally lower than the actual couple current densities averaged over the entire 180-day exposure period. The one exception to this statement was for the HY80-COFM couples, where the actual couple current densities were measured at approximately 20 $\mu A/cm^2$ for the first 30 days and then significantly decreased to an average 2 $\mu A/cm^2$ over the last 90 days. The predicted couple current density of 20 $\mu A/cm^2$ was more similar to the initial actual current densities than the average actual current densities over the last half of the exposure period.

For the couple potentials, it was found that the predicted couple potentials correlated with the actual couple potentials measured after one

day of exposure for the NAB-CAR and NAB-COFM couples. The HY80-CAR and HY80-COFM couples did not show any correlation between the predicted and actual couple potentials. The predicted potentials were more electropositive than the actual couple potentials.

SUMMARY AND CONCLUSIONS

The galvanic compatibility of Gr/epoxy composites with HY80 steel and with nickel aluminum bronze was assessed by conducting 180-day seawater galvanic couple tests and laboratory electrochemical tests. The galvanic couple tests were conducted in quiescent seawater on Gr/epoxy-metal (HY80 or NAB) couples and uncoupled control specimens. Results of these tests indicated that galvanic corrosion of HY80 and NAB will occur when these metals are individually coupled to Gr/epoxy composites with exposed graphite fibers and immersed in quiescent seawater. As the exposed graphite fiber area in the composite increases, galvanic corrosion of the NAB or HY80 will also increase. The depth of corrosion attack due to galvanic coupling with the Gr/epoxy composite is greater for NAB than for HY80. Galvanic corrosion can also occur between Gr/epoxy composites with no graphite fibers initially exposed to the environment and a metal. This corrosion is believed to be due to moisture absorption through the epoxy outerlayer to the graphite fibers. The extent of galvanic corrosion occurring on the metal will be related to 1) the graphite fiber area contributing to the reaction due to moisture absorption and 2) the presence of corrosion product films on the anode and cathode which further limit the effective anodic and cathodic areas.

The galvanic couple test results also showed that corrosion product

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films present on both the Gr/epoxy and metal components of the galvanic couple in quiescent seawater can significantly reduce the magnitude of the galvanic corrosion occurring. Substantially higher galvanic corrosion rates could, however, occur in flowing seawater conditions, where 1) the growth and maintenance of the corrosion product films may be severely limited and 2) the supply of dissolved oxygen to the cathode would be increased.

The laboratory electrochemical evaluations consisted of both electrochemical impedance spectroscopy and potentiodynamic polarization testing. The EIS evaluations were conducted on Gr/epoxy composites that were exposed for 180 days in the seawater galvanic couple testing. These composites were re-immersed in ASTM ocean water for an additional re-exposure of 500 hours, with EIS spectra measured periodically on the specimens during this period. The EIS results showed that the graphite/epoxy composite in the as-fabricated condition with no graphite fibers initially exposed can act as an effective cathode for oxygen reduction in seawater. After a total 200 days of seawater exposure, it was estimated that 15% of the planar area of the composite contained seawater-exposed graphite fibers. Under galvanic corrosion conditions, this composite can allow between 0.0045 and 0.12 $\mu A/cm^2$ current density, with the specific value dependent on the cathode:anode area ratio and the seawater flow conditions.

The potentiodynamic polarization testing was conducted on Gr/epoxy composites, pure graphite, HY80 steel, and nickel aluminum bronze specimens in ASTM ocean water. The results of this evaluation confirmed that, as with metals, this accelerated electrochemical test method is not accurate for predicting long-term galvanic corrosion rates for Gr/epoxy-metal couples but

does indicate a sensitivity to graphite fiber area effects in these composite-metal couples.

Table 1. Chemical compositions of HY80 steel and nickel aluminum bronze.

HY80 Steel

	Fe	Ni	Cr	Mo	Si	Mn	C	Cu	S	P	V
	BAL	2.83	1.61	0.47	0.27	0.23	0.15	0.046	0.020	0.012	<0.001
MIL-S-16216K	BAL	2.50-3.50	1.40-1.80	0.35-0.60	0.15-0.38	0.10-0.40	0.13-0.18	0.25 max	0.008 max	0.015 max	--

Nickel Aluminum Bronze

	Cu	Al	Ni	Fe	Mn	Sn	Si	Zn
	79.61	10.90	5.35	2.77	1.16	0.031	0.020	0.012
UNS C63000	78.0-85.0	9.0-11.0	4.0-5.5	2.0-4.0	1.5 max	0.20 max	0.25 max	0.30 max

Table 2. Planar area estimate of graphite fibers in Gr/epoxy composites
initially exposed to the seawater environment.

Surface Condition	Designation	Planar Area % of Graphite Fibers Initially Exposed (Optically Measured)
(a) Composite As-Fabricated (As-Received)	CAR	0
(b) Composite One Face Hand-Sanded, One Face As-Fabricated	COF	4
(c) Composite Two Faces Hand-Sanded	CTF	8
(d) Composite One Face Machine Sanded	COFM	68

Table 3. Electrochemical impedance spectroscopy specimen test conditions.

Specimen Code	Condition	Exposed at LCCT for 180 Days	Specimen Area (cm2)
CAR5	As-Fabricated	Uncoupled	12.9
COF6	One Face Hand-Sanded, One Face As-Fabricated	Uncoupled	6.45
CTF6	Two Faces Hand-Sanded	Uncoupled	12.9
COF3	One Face Hand-Sanded, One Face As-Fabricated	Coupled to HY80 Steel	6.45
CTF3	Two Faces Hand-Sanded	Coupled to HY80 Steel	12.9

Table 4. A comparison of the composite-metal galvanic couple results from the potentiodynamic polarization tests and the 180-day seawater exposures.

Material		Exposure Time (days)	Couple Current Density (uA/cm2)		Couple Potential (mV vs Ag/AgCl)	
Anode	Cathode		Actual (Measured)	Predicted	Actual (Measured)	Predicted
NAB	Gr/Epoxy – As-Fabricated (CAR)*	1	0	0.04	-272	-290
		30	0.6		-123	
		60	0.5		-133	
		90	0.2		-159	
		120	0.2		-158	
		150	0.2		-155	
		180	0.1		-154	
NAB	Gr/Epoxy – One Face Machine Sanded (COFM)*	1	0.6	2	-257	-280
		30	6.6		-103	
		60	10.1		-92	
		90	6.8		-96	
		120	5.9		-94	
		150	6.2		-80	
		180	7.8		-100	
HY80	Gr/Epoxy – As-Fabricated (CAR)*	1	0.6	0.09	-715	-550
		30	2.3		-692	
		60	8.7		-649	
		90	7.1		-639	
		120	1.4		-635	
		150	0.1		-635	
		180	0.1		-627	
HY80	Gr/Epoxy – One Face Machine Sanded (COFM)*	1	19.9	20	-651	-550
		30	20.4		-669	
		60	13.4		-682	
		90	3.4		-677	
		120	2.1		-678	
		150	2.1		-657	
		180	1.4		-657	

*Note: CAR – No graphite fibers initially exposed to environment.
COFM – Minimum 68% graphite fibers on composite surface initially exposed to environment.
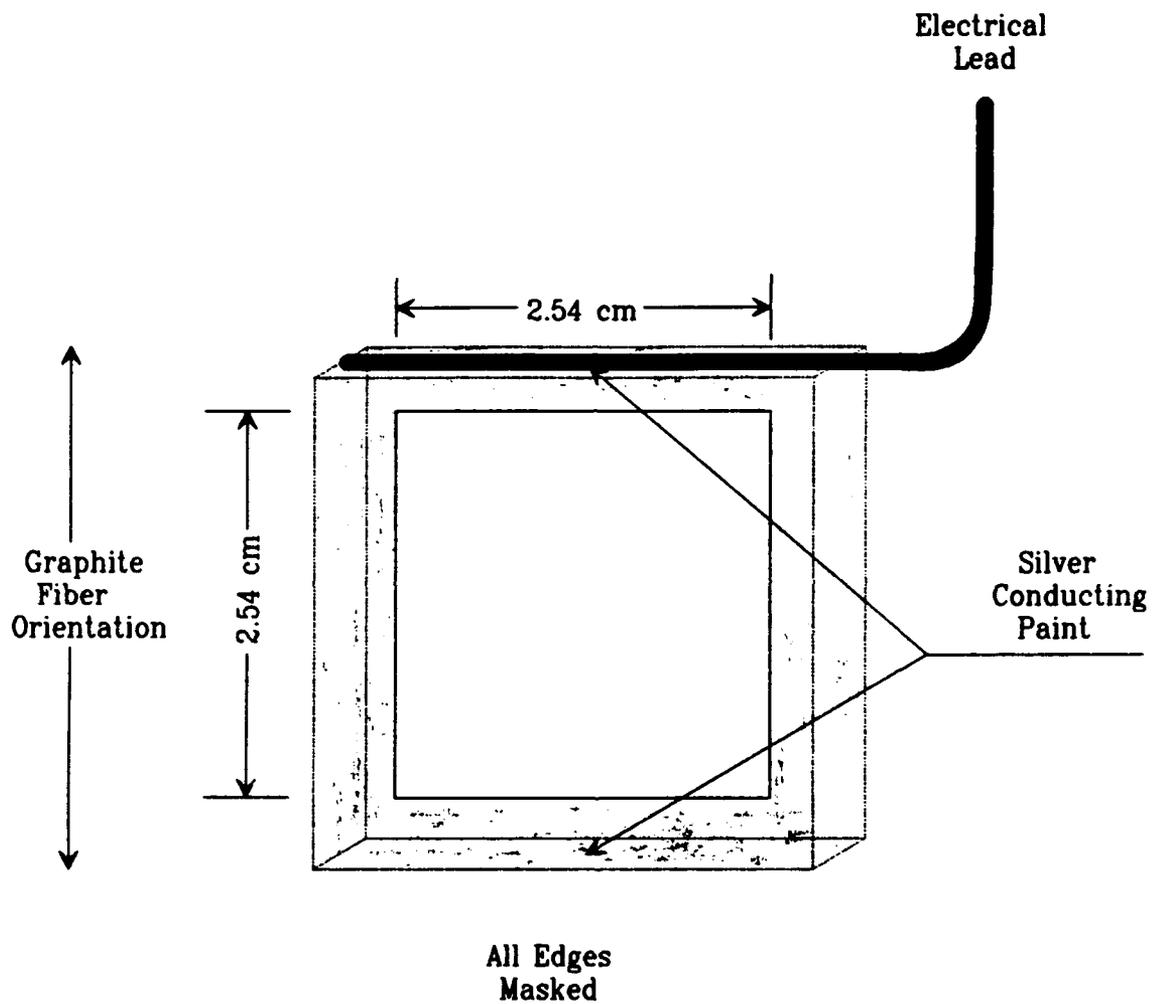
33

Figure 1. Gr/epoxy composite specimen used for galvanic corrosion testing.
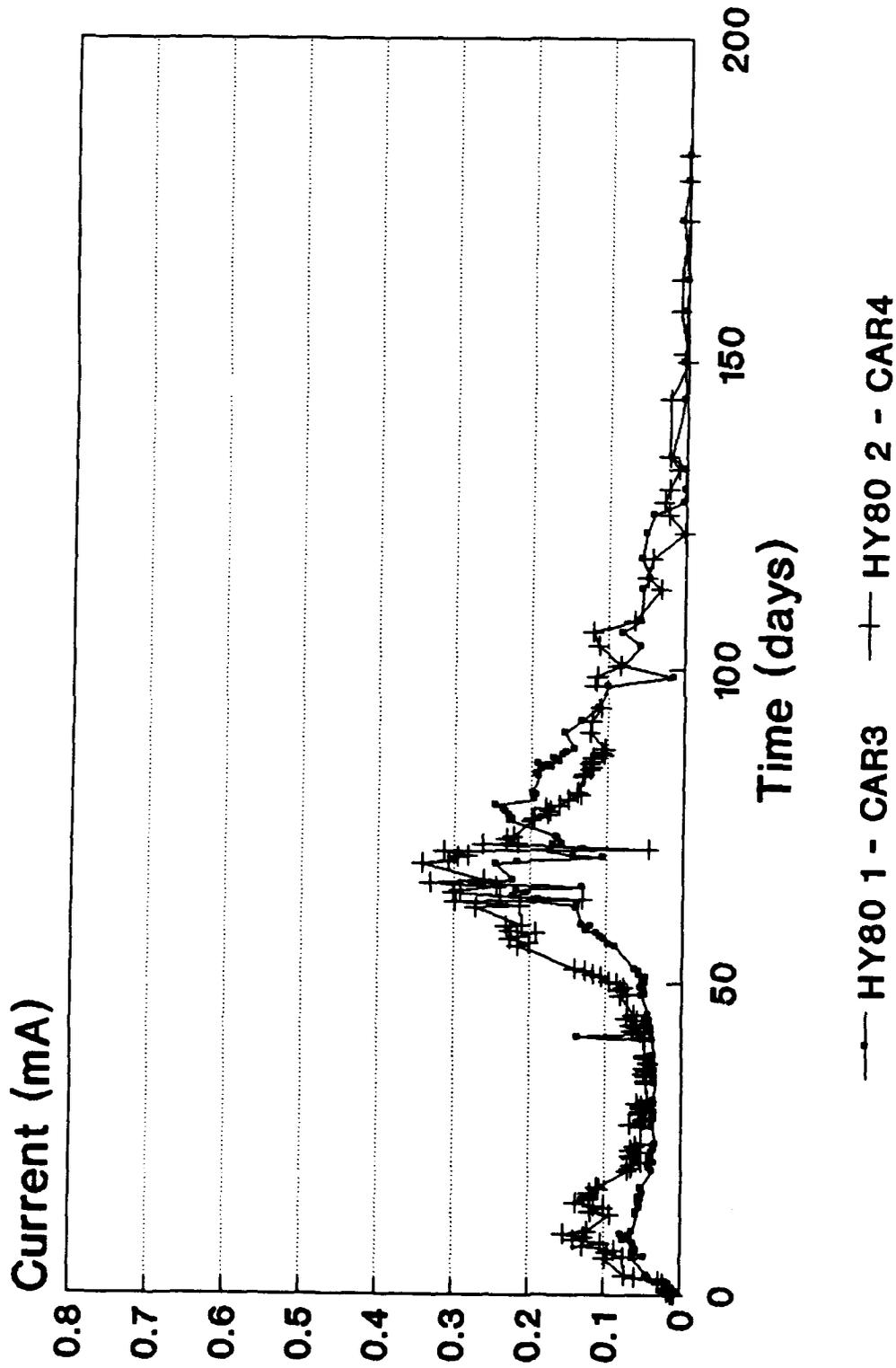
Figure 2. Galvanic current data for HY80 steel – CAR (Gr/epoxy composite with no graphite fibers initially exposed).
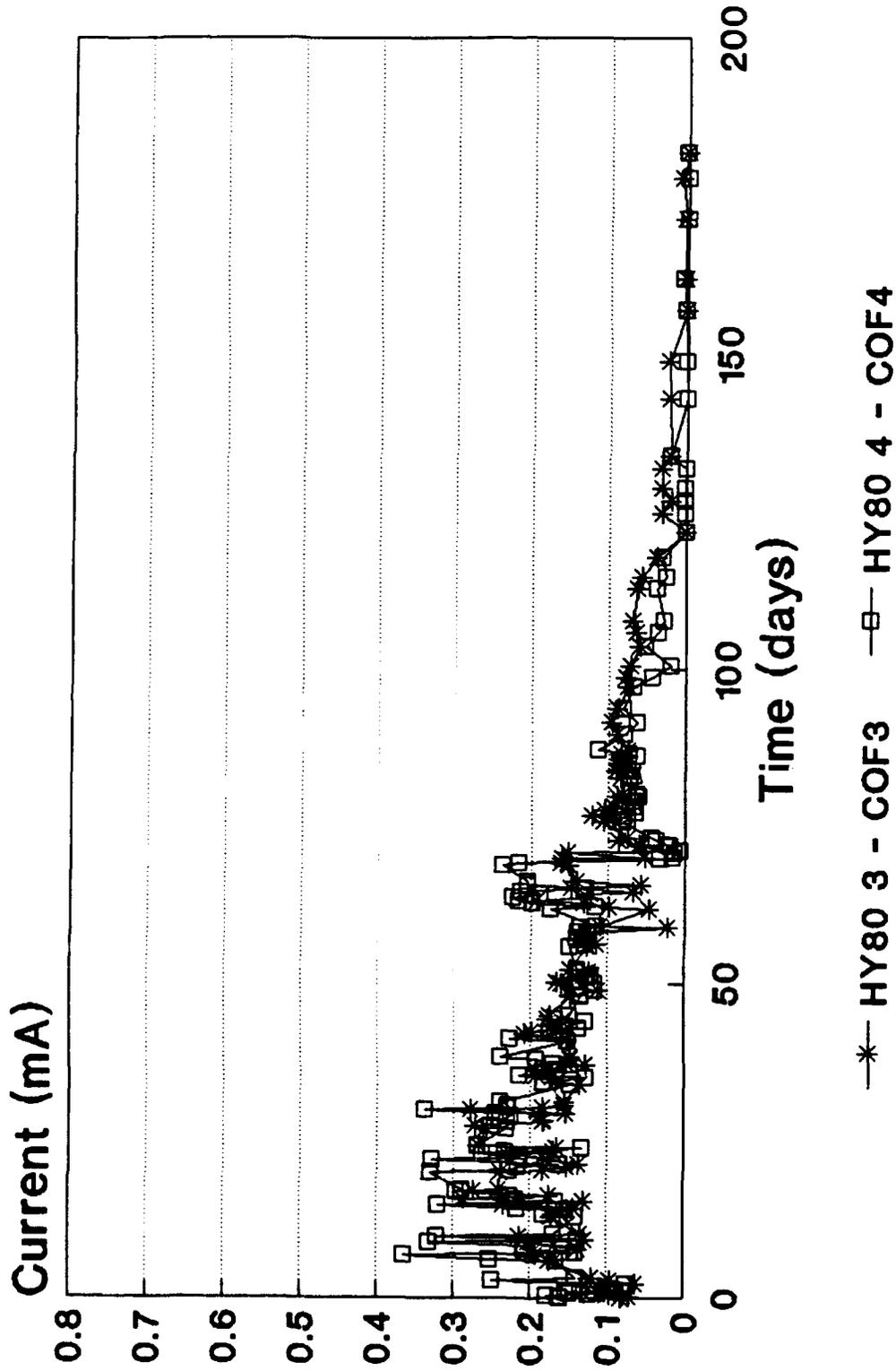
Figure 3. Galvanic current data for HY80 steel - COF (Gr/epoxy composite with one face hand sanded to initially expose a minimum 4% graphite fiber area on surface).
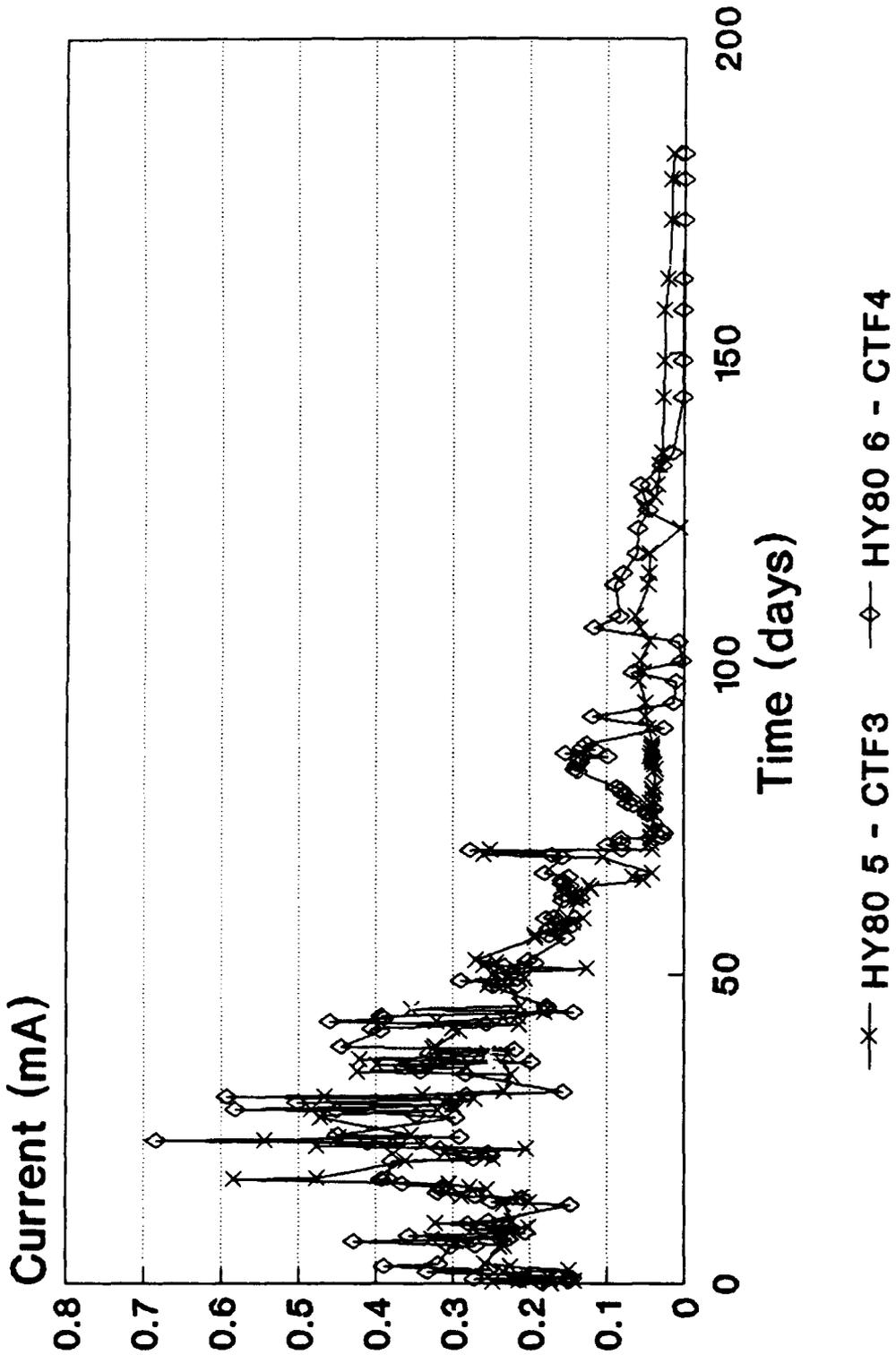
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Figure 4. Galvanic current data for HY80 steel - CTF (Gr/epoxy composite with two faces hand sanded to initially expose a minimum 8% graphite fiber area on surface).
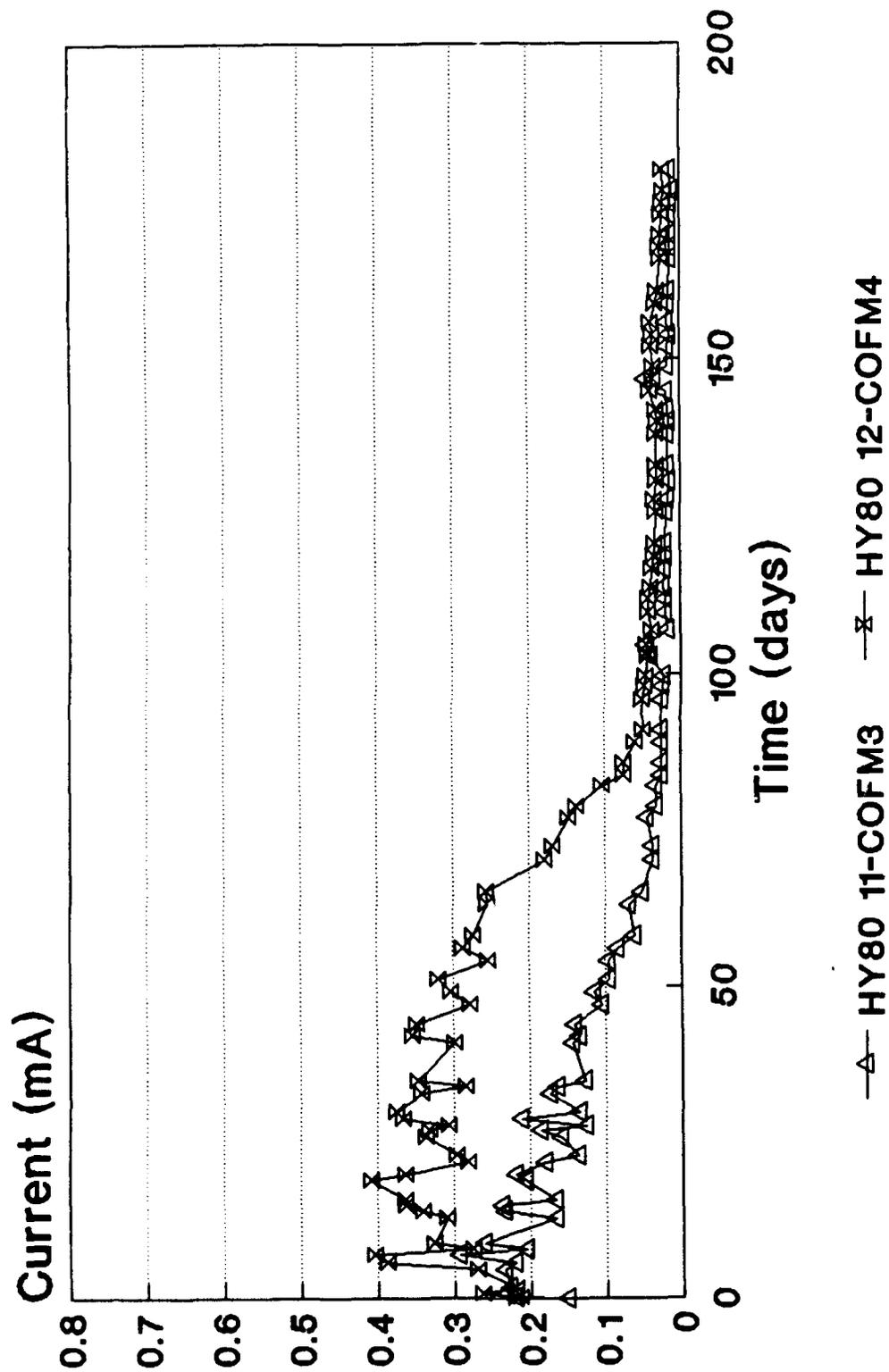
Figure 5.   Galvanic current data for HY80 steel – COFM (Gr/epoxy composite with one face machine sanded to initially expose a minimum 68% graphite fiber area on surface).

Gr/epoxy
(COF 3)

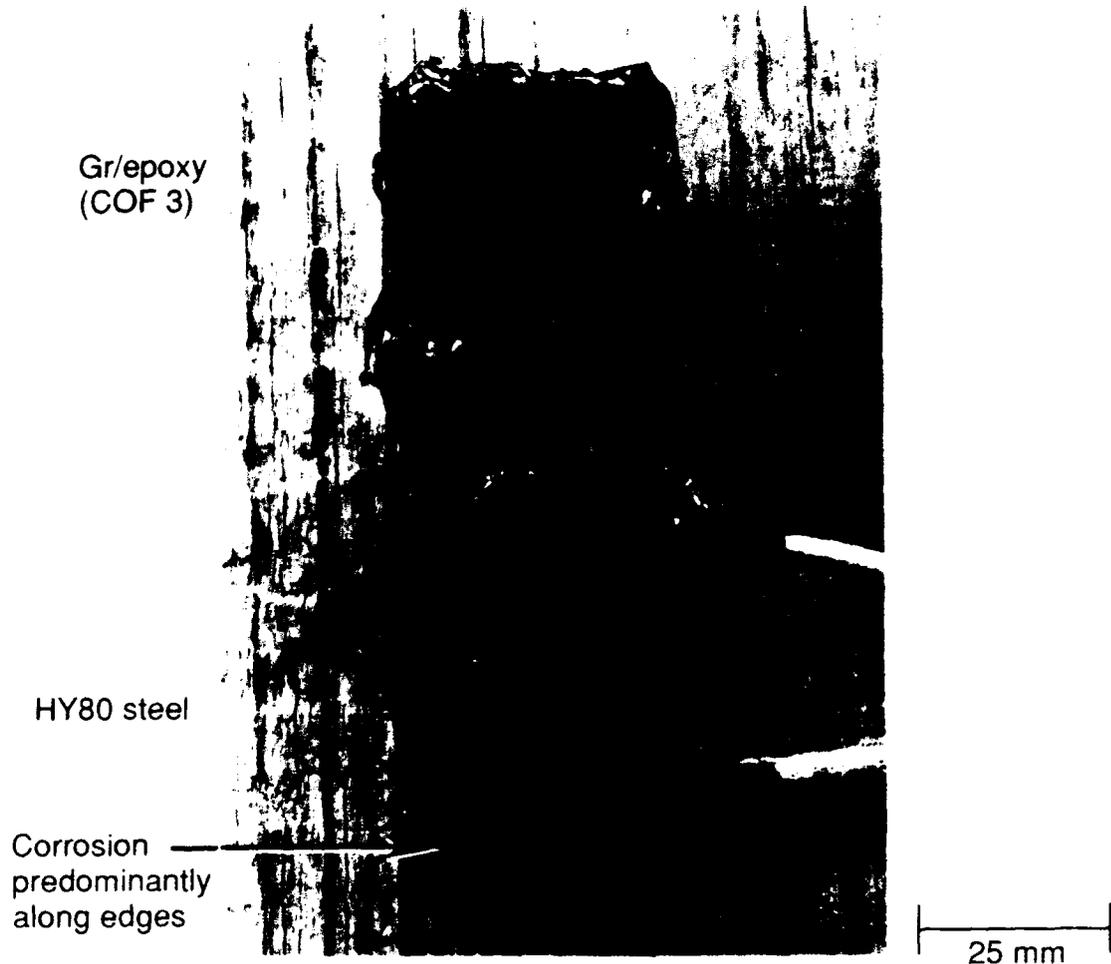HY80 steel

Corrosion
predominantly
along edges

25 mm

Figure 6. Representative photograph showing HY80 steel and Gr/epoxy galvanic
couple specimen surfaces after 180-day seawater exposure (specimen
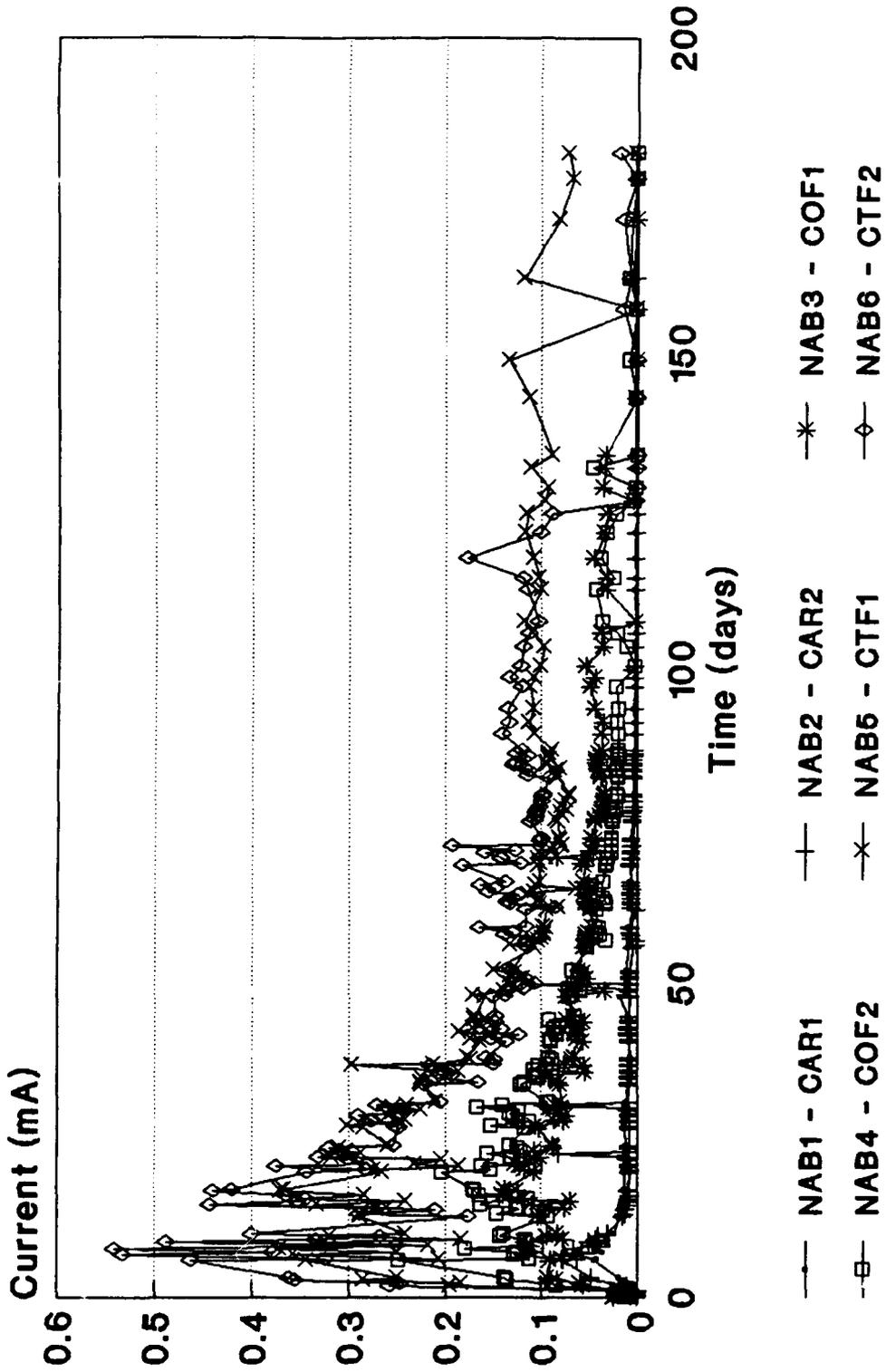surfaces were brush cleaned after testing).

Figure 7.   Galvanic current data for nickel aluminum bronze (NAB) coupled to Gr/epoxy composites labeled as CAR (no graphite fibers initially exposed), COF (minimum 4% graphite fiber area initially exposed), and CTF (minimum 8% graphite fiber area initially exposed).
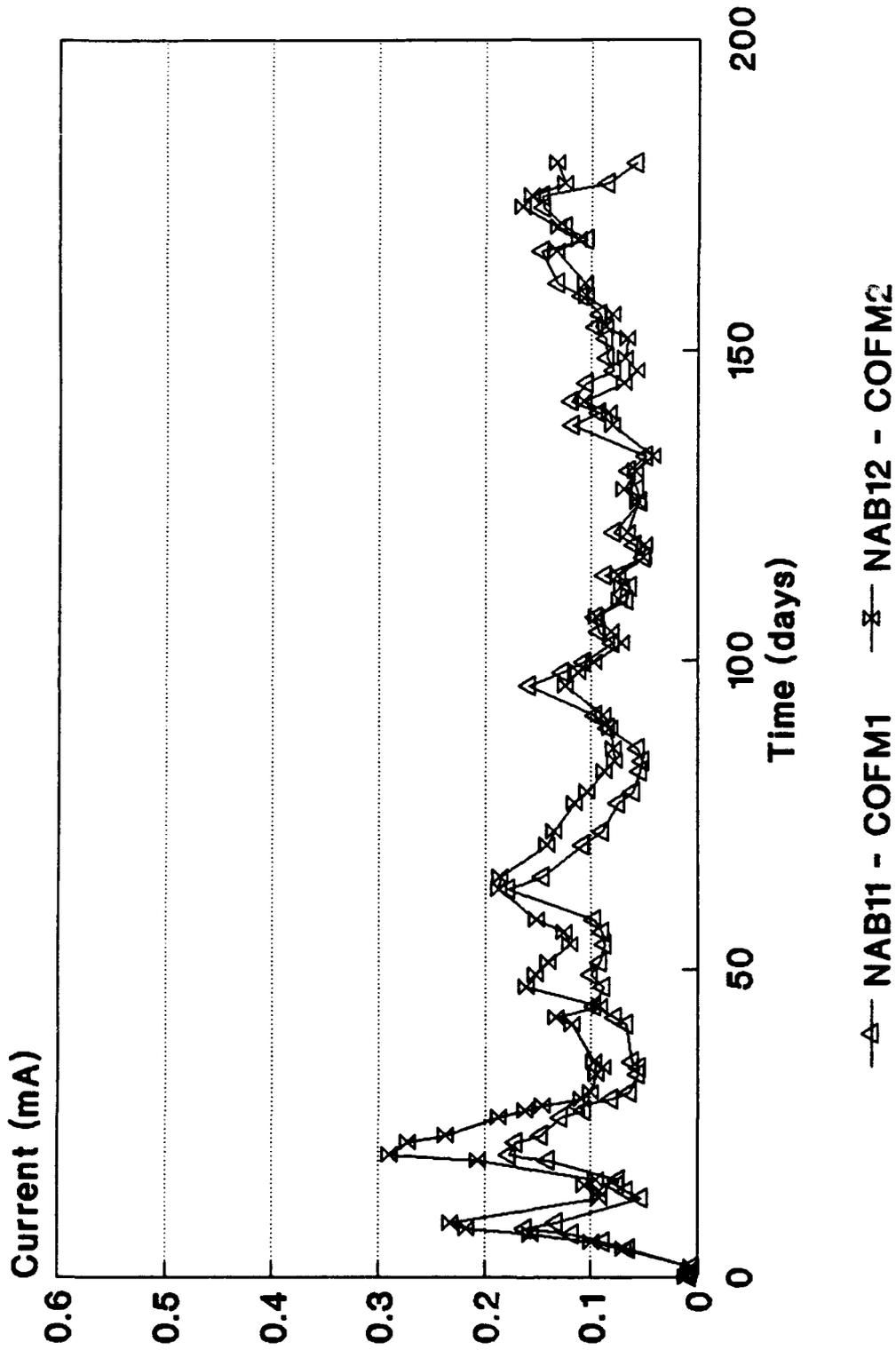
Figure 8. Galvanic current data for nickel aluminum bronze (NAB) – COFM (Gr/epoxy composite machine sanded to initially expose a minimum 68% graphite fiber area on surface).
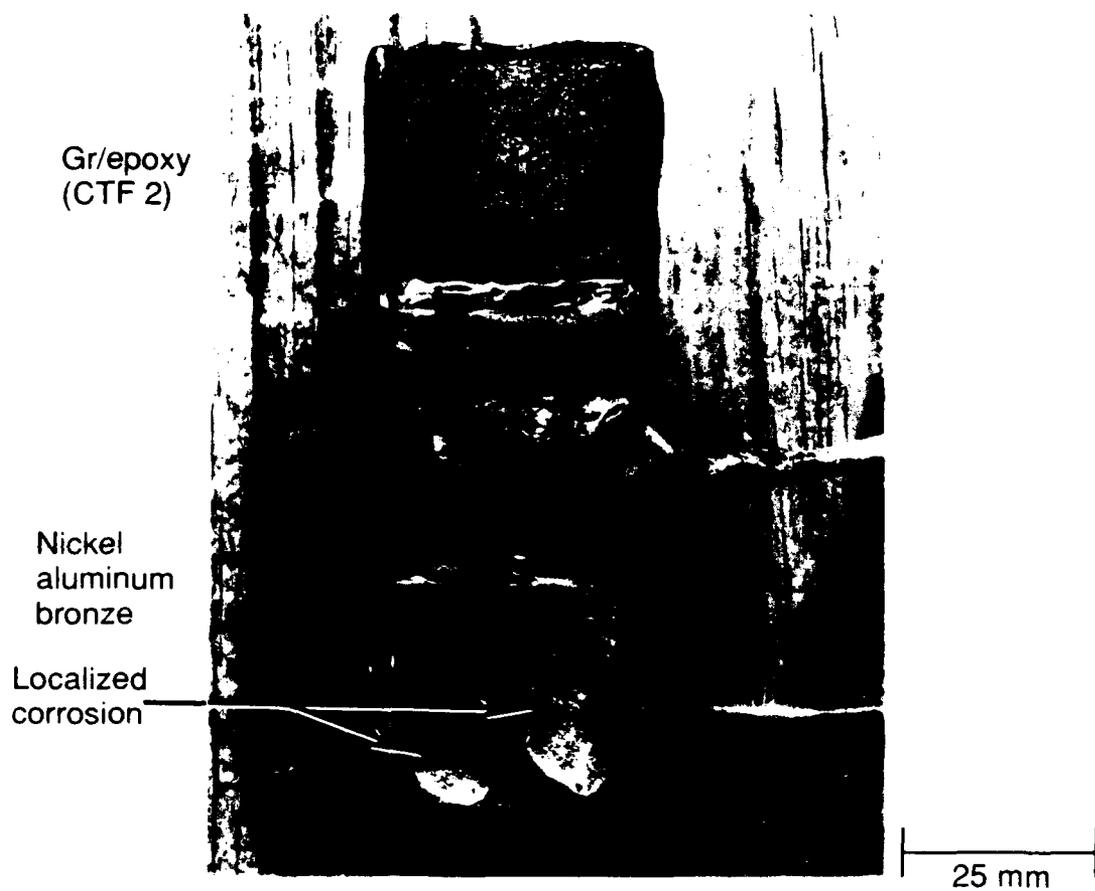
Figure 9. Nickel aluminum bronze – Gr/epoxy composite galvanic couple
specimens after 180-day seawater testing (NAB specimen is
representative of severe localized corrosion present on NAB
specimens coupled to COF, CTF, and COFM Gr/epoxy composites).
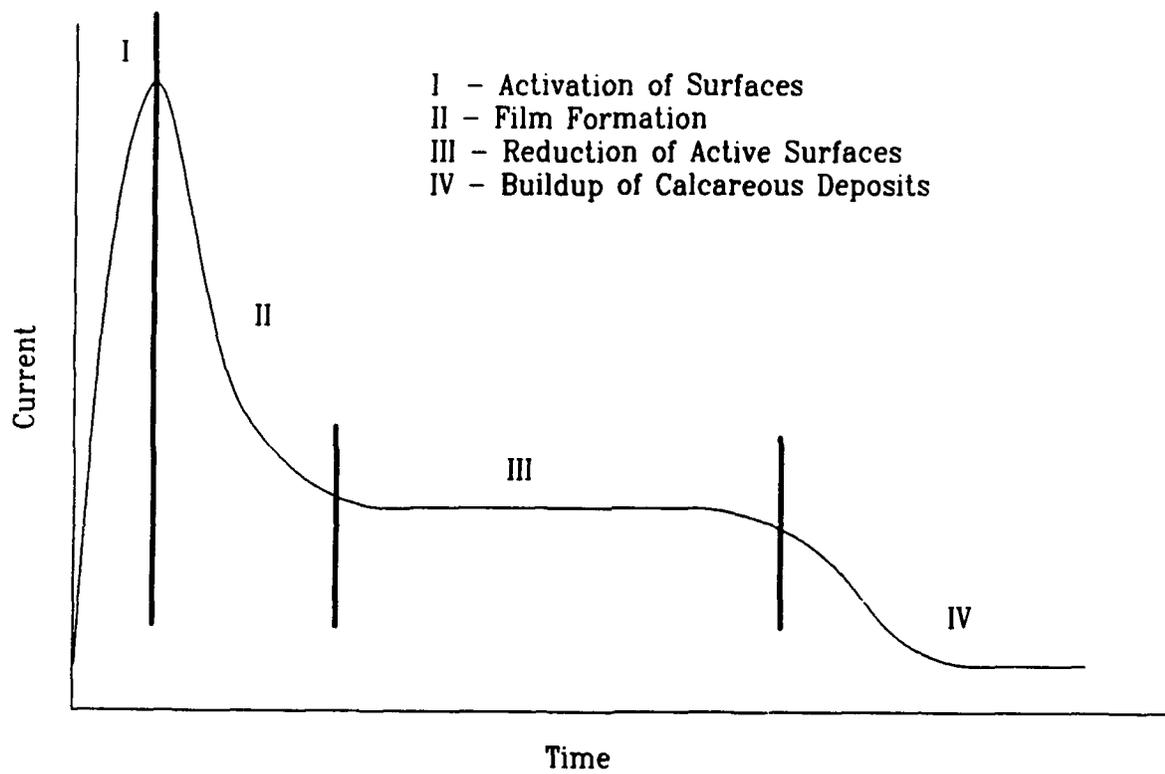
Figure 10.   Current trends as determined from the composite-metal galvanic couple testing.
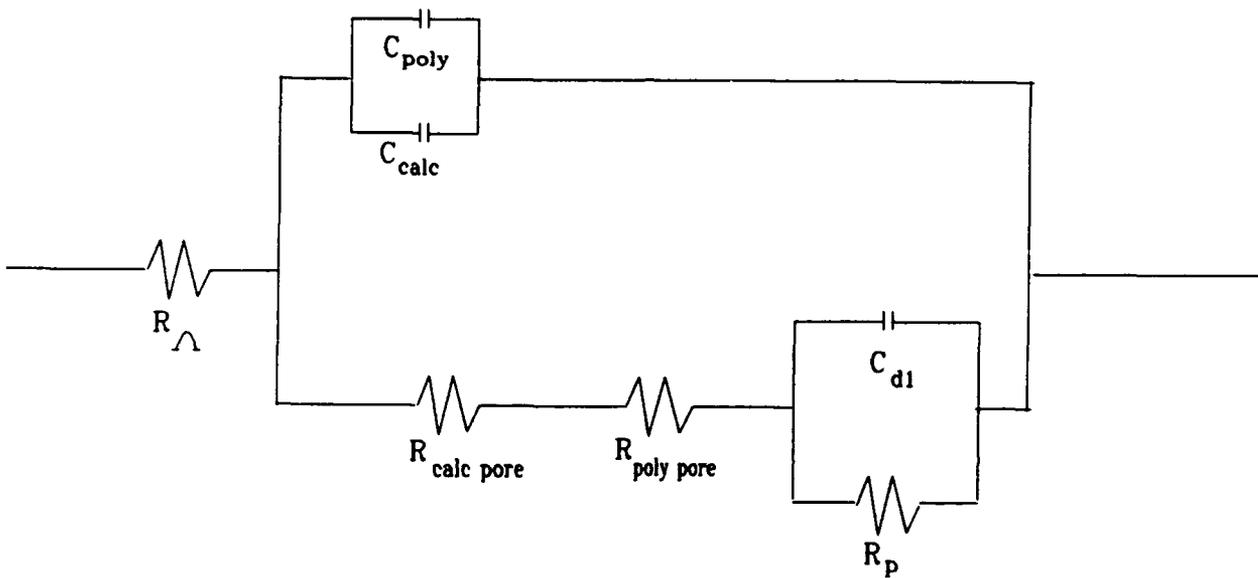
Figure 11.   Nested equivalent circuit for Gr/epoxy composite with
              calcareous deposit.

where C_{poly} = capacitance (polymer)
         C_{calc} = capacitance (calcareous deposit)
         $R\Omega$ = solution resistance
         $R_{calc\ pore}$ = resistance (pores in calcareous deposit)
         $R_{poly\ pore}$ = resistance (pores in polymer (Gr/epoxy composite))
         C_{dl} = double layer capacitance
         R_p = polarization resistance
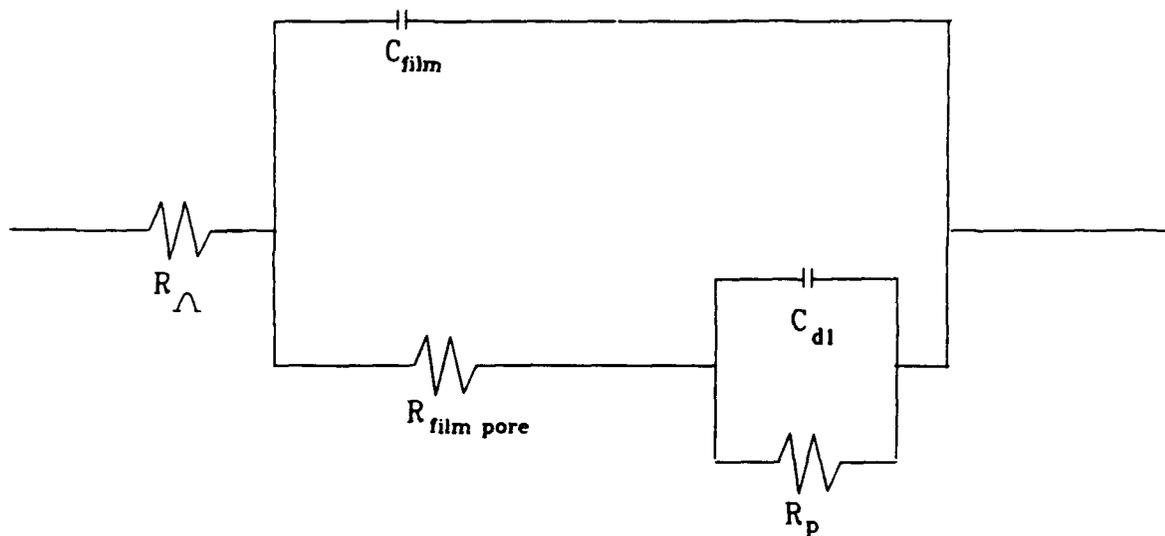
Figure 12. Simplified nested equivalent circuit for coupled Gr/epoxy composite with calcareous deposit.

where C_{film} = film capacitance
$R\Omega$ = solution resistance
$R_{film\ pore}$ = resistance (pores in film)
C_{dl} = double layer capacitance
R_p = polarization resistance
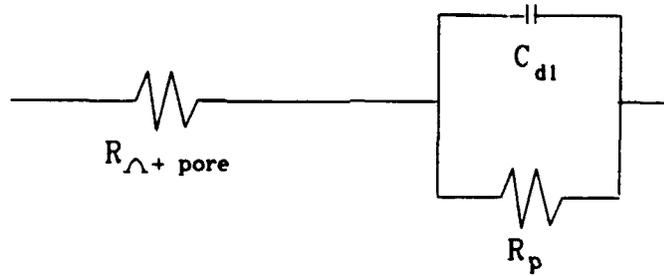
Figure 13.   Simplified nested equivalent circuit for uncoupled
             Gr/epoxy composite without calcareous deposit.

where C_{dl} = double layer capacitance
         R_p = polarization resistance
         $R_{\Omega + pore}$ = resistance (solution + pores in film)
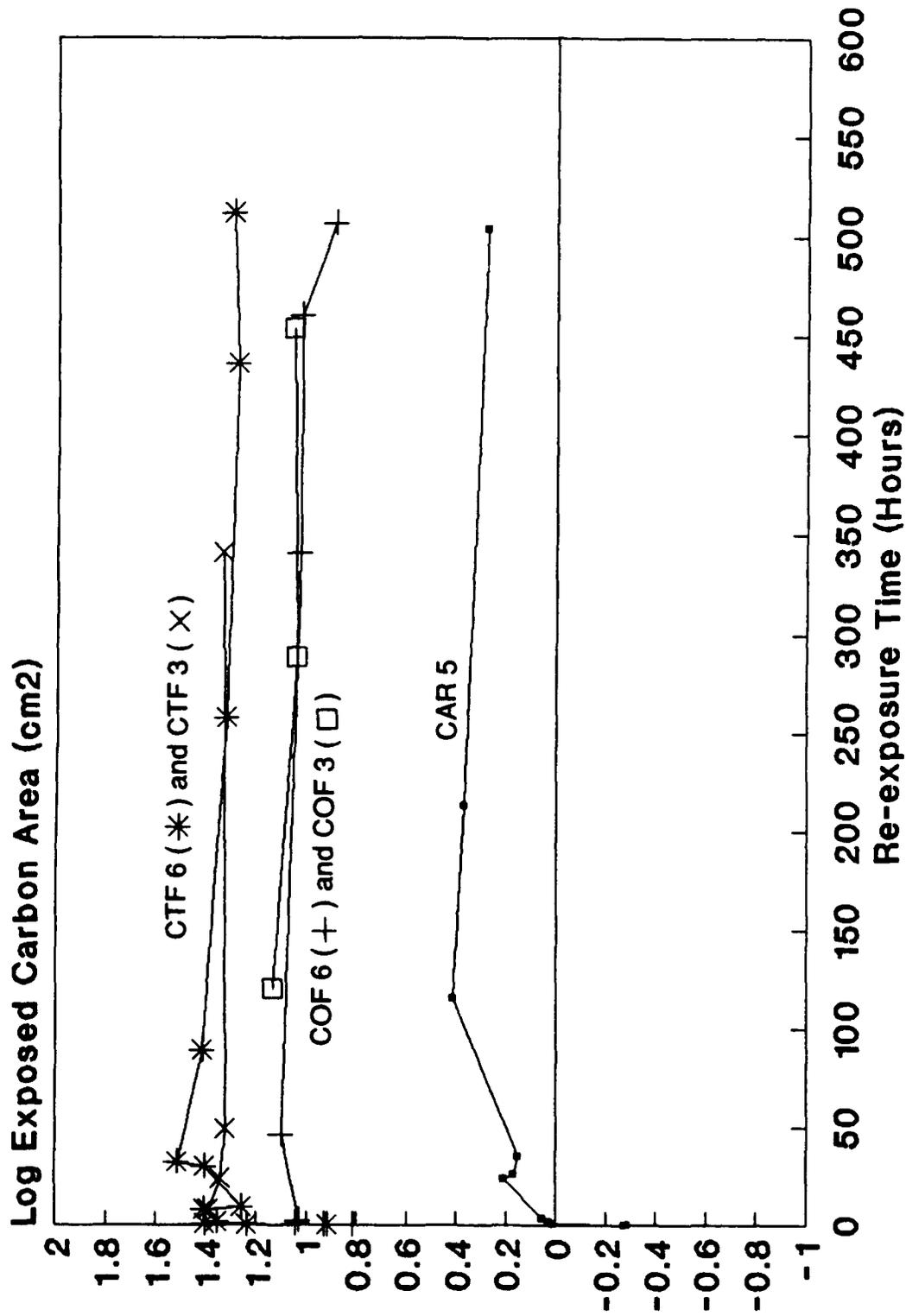
Figure 14. Exposed graphite fiber surface area versus re-exposure time for Gr/epoxy composite specimens (calculated from EIS data).
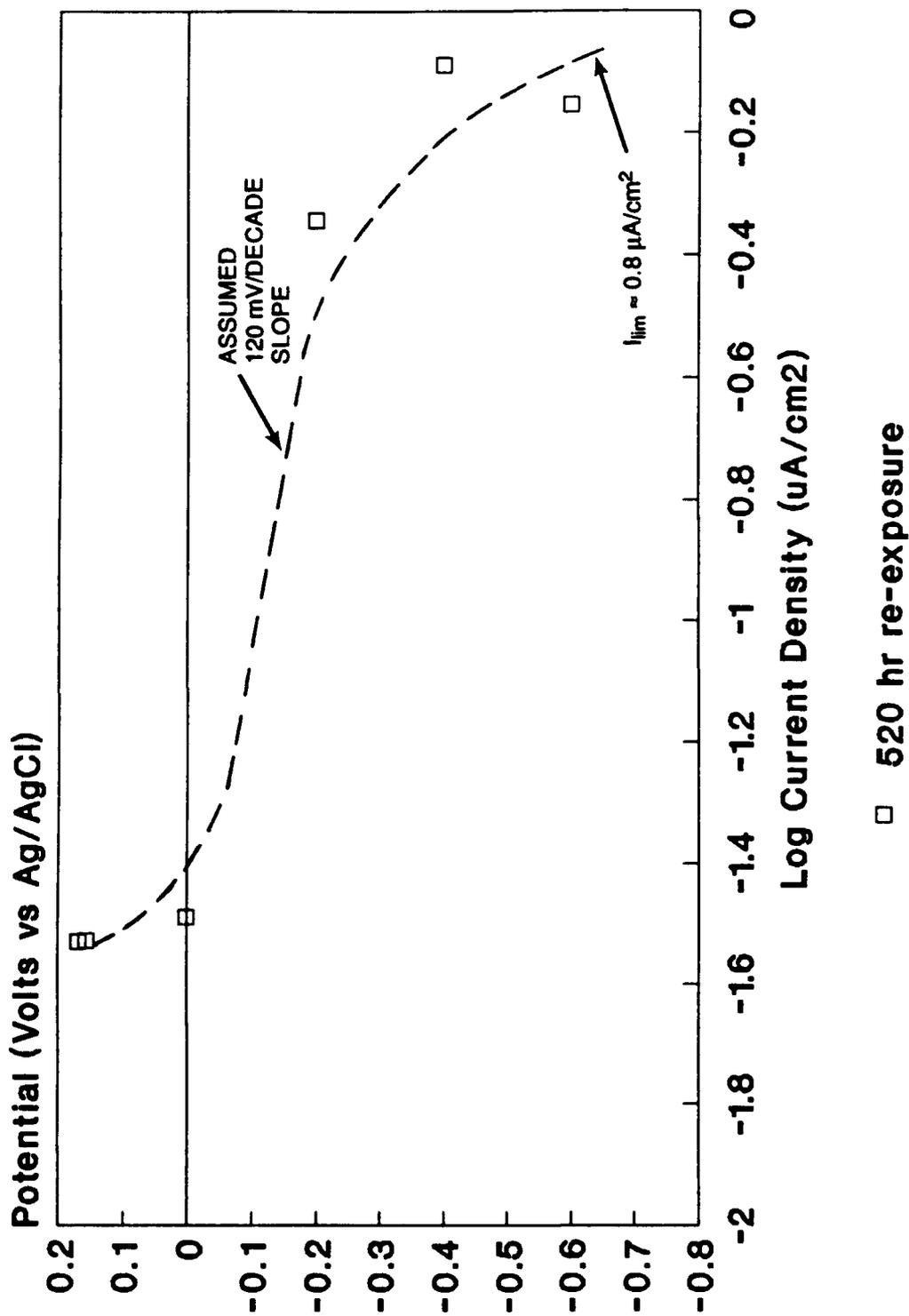
Figure 15. Cathodic behavior of Gr/epoxy composite specimen COF 6 (uncoupled specimen with one face as-fabricated) using electrochemical impedance spectroscopy at controlled potentials.

Figure 16. Potentiodynamic polarization behavior of Gr/epoxy composites and metals in seawater.
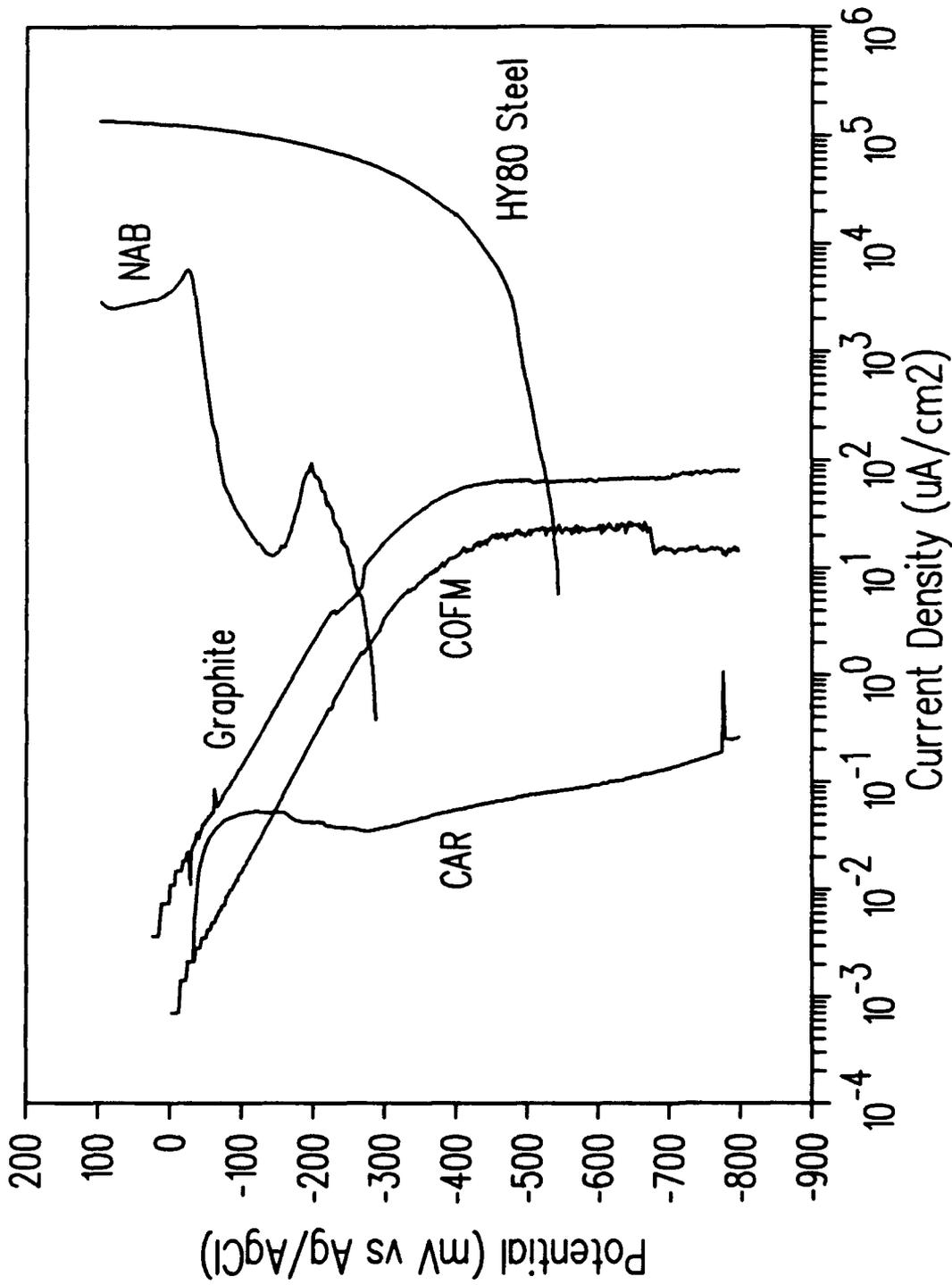
Note: CAR – As-fabricated Gr/epoxy (no graphite fibers initially exposed)
       COFM – Machine sanded Gr/epoxy (minimum 68% graphite fiber area initially exposed on surface)
       NAB – Nickel aluminum bronze

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE July 1992	3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE
The Effect of a Seawater Environment on the Galvanic
Corrosion Behavior of Graphite/Epoxy Composites Coupled
to Metals

5. FUNDING NUMBERS

1-2802-305-40

6. AUTHOR(S)

D.M. Aylor and J.N. Murray

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Surface Warfare Center, Carderock Division
Marine Corrosion Branch; Code 2813
Annapolis, Maryland 21402-5067

**8. PERFORMING ORGANIZATION
REPORT NUMBER**

SME/92-32

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

**10. SPONSORING/MONITORING
AGENCY REPORT NUMBER**

11. SUPPLEMENTARY NOTES

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12b. DISTRIBUTION CODE

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13. ABSTRACT (Maximum 200 words)

Galvanic compatibility between graphite/epoxy (Gr/epoxy) composites and metals (HY80 steel and nickel aluminum bronze (NAB)) was evaluated in 180-day seawater galvanic couple tests and laboratory electrochemical tests. Results indicate that significant galvanic corrosion of NAB and HY80 can occur when each material is coupled to a Gr/epoxy composite containing exposed graphite fibers, with the rate of the metallic corrosion increasing as the exposed graphite fiber area in the composite is increased. Galvanic corrosion can also occur between Gr/epoxy composites with no graphite fibers initially exposed to the environment and a metal as a result of moisture absorption through the epoxy outerlayer to the graphite fibers. The electrochemical impedance spectroscopy evaluation demonstrated that Gr/epoxy composites with no graphite fibers initially exposed to the environment can act as an effective cathode for oxygen reduction in seawater. It was estimated that after 200 days' seawater exposure, 15% of the planar area of this Gr/epoxy composite contained seawater-exposed graphite fibers. The potentiodynamic polarization results suggest that short-term electrochemical testing is not a reliable method for assessing long-term galvanic corrosion behavior of Gr/epoxy-metal couples but does indicate a sensitivity to graphite fiber area effects.

14. SUBJECT TERMS

graphite/epoxy, composites, metals, seawater, galvanic
corrosion

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	