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Research and Development Report

### Effect of High Flow on Calcareous Deposits and Cathodic Protection Current Density

by  
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DTRC/SME-87/82 Effect of High Flow on Calcareous Deposits and Cathodic Protection Current Density



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## ABSTRACT

The effect of flowing seawater on cathodic protection current demand was studied by using a modified rotating cylinder electrode. HY-80 steel, nickel-aluminum bronze, and alloy 625 were evaluated at velocities of up to 90 ft/s. Measurements were made of the current required to polarize these specimens to -800 mV versus saturated calomel electrode with and without calcareous deposits preformed under quiescent conditions. Bronze and alloy 625 exhibited a two order of magnitude decrease in current when calcareous deposits were present. The steel exhibited less of a decrease, probably because a calcareous deposit formed on the bare surface during the exposure. High rotation speeds did not remove the calcareous deposits. Cathodic polarization curves were developed for material with calcareous deposits at 45 ft/s.

## ADMINISTRATIVE INFORMATION

The work described herein was performed under Work Unit 1-1508-011-73 under NAVSEA SSN 21 propulsor task program element 63561N, task area S1266001. The task leader is Mr. W. Palko and DTRC project manager is Mr. R. Boswell. The work was conducted in the Marine Corrosion Branch under the supervision of Mr. A.G.S. Morton.

## INTRODUCTION

Determination of the optimum design criteria for cathodic protection of marine structures subjected to high flow, such as pumps, piping, and ship appendages, is not as straightforward as for stationary structures. Flow affects the rate of diffusion of dissolved oxygen through the seawater to the protected metal, which influences the cathodic current demand. Calcareous deposits can be formed on the metal when the pH near the protected surface is raised by the generation of hydroxyl ions by the cathodic reaction, thus allowing certain hydroxides and carbonates of calcium and magnesium to become supersaturated and precipitate onto the metal surface. Flow past the surface affects the pH, which in turn affects the rate of

formation and type of calcareous deposits. This can change the degree to which they are capable of limiting the cathodic current.

Initial investigations<sup>1</sup> indicated that cathodic current density under flowing conditions can be predicted accurately from boundary layer diffusion theory only when calcareous deposits are not present. Calcareous deposits were found to lower the required current, in some cases to as low as 10  $\mu\text{A}/\text{cm}^2$ . Velocity effects were masked by data scatter of up to an order of magnitude between 5 and 30 days. This scatter could be due to variation in seawater chemistry, biological activity, or inherent variability in the rate of the reactions as precipitation occurs. The present work is a follow-on study to investigate the formation and effect of calcareous deposits under high flow conditions more thoroughly, and to quantify the effect of velocity by minimizing test time in order to reduce scatter.

The two principle objectives of the work reported herein were to determine the cathodic protection current demand on a structure with calcareous deposits under high flow conditions, and to find the conditions under which calcareous deposits might exist on such a structure.

#### MATERIALS

The materials tested included HY-80 steel, nickel-aluminum bronze, alloy 625, and anode grade zinc (MIL-SPEC-18001J). The chemical compositions of these materials are listed in table 1.

#### APPARATUS

Measuring electrochemical parameters under high flow conditions up to 10,000 RPM required the construction of two specially modified rotating disk apparatus. The apparatus shown in figure 1 used a Pine Instruments Company model AFASR rotator. A specially designed baffle plate was inserted at the top of the cell several inches

above the test specimen to alleviate the inherent problem of excessive splashing or air entrainment resulting from a vortex formed around the specimen, while having a minimal effect on the hydrodynamics at the specimen. The specimen holder consisted of a specially machined titanium rod, tapered on one end and with 1/2" - 20 (class 3) threads on the other, as shown in figure 2. Electrical contact to the 1 inch diameter, 1 inch high cylindrical specimen was made through the rotor and a carbon brush contact. The specimen was mounted between two roulon spacers fitted with o-ring seals to prevent seawater contacting the titanium rod. The counter electrode was a platinized screen positioned concentrically to the test specimen, and a saturated calomel reference electrode was used along with a luggin capillary with a Vycor fritted tip positioned just above the plane of the specimen near the upper roulon spacer. The test cell was about 12 inches in diameter and 12 inches high, constructed of 1/4 inch Plexiglass.

The second apparatus, shown in figure 3, used a larger motor to drive a titanium shaft containing a 2 inch diameter by 1 inch high cylindrical specimen and two tapered roulon spacers with o-rings, as shown in figure 4. Electrical contact was made with a carbon brush as with the 1 inch diameter apparatus, and the counter electrode and reference electrode assemblies were similar, although reinforced with a bead of epoxy along the outer edges to handle the larger stresses created by fluid motion. The cell was also similar in construction, except that an elaborate set of baffles was needed to prevent air entrainment.

Potential, current, and rotation speed data for the long-term exposures were gathered using a computerized data acquisition system described previously.<sup>2</sup> Constant potentials were held using an E G and G PAR model 173 potentiostat or a multichannel potentiostat model 440 built by Scribner Associates, Inc.



The electrolyte for the tests was natural seawater from Bank's Channel near Wrightsville Beach, North Carolina. The water was filtered and then heated and aerated in a separate reservoir prior to its introduction into the test cell. The temperature was maintained at  $30 \pm 3^\circ\text{C}$  with an immersion heater in the makeup water reservoir.

#### EXPERIMENTAL PROCEDURE

The 1 inch diameter apparatus was used for the first test. Specimens of nickel-aluminum bronze and alloy 625 were held at  $-800\text{ mV}$  while rotating at 10,000 RPM (45 ft/s) and the current monitored for 30 days. Duplicate runs of both materials were made concurrently. Also, specimens of anode grade zinc were held at  $-1030\text{ mV}$  for the same length of time and the current measured. The former potential was chosen to represent a typical potential value reached on a cathodically protected surface, whereas the latter potential was chosen to represent a 50 mV displacement from the quiescent open-circuit potential of the zinc. At the conclusion of the test the weight gain of the bronze and alloy 625 specimens, probably due to calcareous deposit formation, was measured. Also, the weight loss of the zinc was measured.

The 2 inch diameter apparatus was used for the second test. Specimens of bronze, alloy 625, and steel were held at a potential of  $-800\text{ mV}$  versus saturated calomel for 32 days in quiescent seawater to develop a calcareous deposit. They were then transferred, one at a time, to a different test vessel for stepped velocity tests. In these tests, the current required to maintain a potential of  $-800\text{ mV}$  was measured as the rotation speed was stepped from 0 to 10,000 RPM and back to 0 RPM in 1000 RPM increments. Each rotation speed was held for 5 minutes to allow the current to stabilize. In addition, specimens which had not been

exposed to build up a calcareous deposit were also tested in the rotator at the same set of rotation speeds. This allowed the effect of the calcareous deposit to be separated, as well as giving data for a comparison of theoretical currents based on boundary layer diffusion with actual currents.

The 2 inch diameter apparatus was also used for the third test. A specimen each of bronze, alloy 625, and steel were held at a potential of -1000 mV versus saturated calomel for 30 days in quiescent seawater to develop a calcareous deposits. They were then transferred, one at a time, to a different test vessel for high velocity polarization tests. In these tests, the specimen was rotated at 5000 RPM (45 ft/s) until the current was stable, then the potential was scanned from -1000 mV to the corrosion potential at 0.1 mV per second.

## RESULTS AND DISCUSSION

### First Test

Currents for the nickel-aluminum bronze 1 inch diameter specimens at 10,000 RPM (45 ft/s) and -800 mV are plotted in figures 5 and 6. Currents for alloy 625 are in figures 7 and 8. Currents for zinc at -1030 mV are plotted in figure 9.

The Pine rotators had difficulty maintaining 10,000 RPM on these 1 inch specimens reliably over the full 30 day test period. Occasional problems, the most frequent being broken drive belts, caused shutdown of the rotation on individual units for anywhere from a few minutes to a few days. The beginning point of each period where rotation had stopped is noted on figures 5-9. Some of the data scatter was caused by problems in maintaining rotation, and the rest could be due to the factors listed earlier: variability in seawater chemistry or biological activity, or inherent variability in the reaction rates.

When the cathodic current is limited by the oxygen reduction reaction, and when oxygen diffusion through a fluid boundary layer limits the supply of oxygen

at the specimen surface, the current can be calculated for a rotating cylindrical electrode based on the theory of fluid flow as follows:<sup>3</sup>

$$i_L = 0.0791 n F C_o V (V d_1 / v)^{-0.30} (v / D)^{-0.644}$$

where:  $i_L$  = diffusion limited current density

$n$  = number of electrons transferred per mole

$F$  = Faraday's constant

$C_o$  = bulk concentration of oxygen

$V$  = tangential velocity of specimen surface

$d_1$  = diameter of specimen

$v$  = kinematic viscosity

$D$  = diffusivity of oxygen in seawater

For a 1 inch diameter cylinder rotating at 10,000 RPM in seawater, the calculation becomes:

$$n = 4 \text{ eq/mo}$$

$$F = 96487 \text{ C/eq}$$

$$C_o = 2.5 \times 10^{-7} \text{ mo/cm}^3$$

$$V = \pi \times 2.54 \times 10000 / 60 = 1330 \text{ cm/s}$$

$$d_1 = 2.54 \text{ cm}$$

$$v = .008 \text{ cm}$$

$$D = 1.9 \times 10^{-5} \text{ cm}^2/\text{s}$$

Therefore:

$$i_L = 4.25 \text{ mA/cm}^2$$

Within the limits of the data scatter, the nickel-aluminum bronze in figures 5 and 6 require a current close to this value, around  $3 \text{ mA/cm}^2$  for the first day, indicating that the cathodic reaction is operating under control by diffusion of dissolved oxygen. During the test shown in figure 5, the current drops somewhat

to about 1 mA/cm<sup>2</sup>, but increases to its original level after about 15 days. Thus the cathodic reaction on this specimen remains essentially under diffusion control throughout the test. Thus, either calcareous deposit formation is minimal, or the deposits that do form don't limit the cathodic reaction.

The situation is somewhat different for the duplicate test shown in figure 6. Here the rotation stopped several times. During the first of these times, the current decreased to approximately 10-20  $\mu$ A/cm<sup>2</sup>, a value shown previously<sup>2</sup> to be typical for low flow in this environment when calcareous deposits are present and limit the cathodic reaction. It is therefore reasonable to assume that during the shutdown period, calcareous deposits formed on this specimen. Once the rotator was repaired, the current required did not increase, indicating that the velocity experienced at the specimen surface (roughly 45 ft/s) was not sufficient to remove this deposit.

The Alloy 625 specimens shown in figures 7 and 8 behaved similarly. Both had currents that remained in the 1-3 mA/cm<sup>2</sup> range while rotating. The specimen in figure 7 apparently did not experience a shutdown of sufficient duration for calcareous deposits to form, and the current remained high. The duplicate specimen, in figure 8, experienced a one day period without rotation starting at day 18 which was apparently sufficient to allow the deposit to develop. As with the bronze, subsequent return to full rotation was insufficient to remove the deposit and return the current to initial levels.

Polarization currents for zinc at -1030 mV are shown in figure 9. Although the zinc would be expected to be anodically polarized at this potential based on quiescent freely-corroding potential data, some period of time was actually spent where the set potential was cathodic to the freely-corroding potential under flowing conditions. This resulted in brief periods of time when the zinc was cathodically protected.

The above results on bronze and alloy 625 illustrate the importance that calcareous deposit formation can have in the reduction of cathodic current density. The deposit reduced the current required by two orders of magnitude, however it did not appear to form unless rotation was stopped, and would not come off when rotation was resumed. Since many applications of these materials involve operation under intermittent flow, the deposit could be present in service. It is important to understand whether this deposit can be removed by the highest flow encountered in service, and how the current density changes as a function of flow for material already covered with the deposit. To this end, the two-inch diameter specimen data were generated and will be discussed.

#### Second Test

Figure 10 illustrates the theoretical current density for a rotating cylinder operating under conditions of pure boundary layer diffusion control as a function of rotation speed. Also in the figure are the measured current densities for freshly exposed bronze, alloy 625, and steel. The measured values for each material have two points for each rotation speed, one taken as the speed was incremented upwards, and one as it was incremented downwards. Both the bronze and the alloy 625 show currents close to the theoretical values for diffusion control, indicating that the cathodic reaction is not blocked by the presence of calcareous deposits and that the baffle plate had minimal effect on the hydrodynamic conditions at the specimen surface. The steel shows some departure from the theoretical value for diffusion control, possibly due to the rapid formation of calcareous deposits during the brief period of the test. This would be in agreement with earlier work which showed rapid formation of calcareous deposits on steel, but not on bronze or titanium.<sup>1</sup>

Figure 11 compares the data from freshly exposed material to that of material which was previously exposed for 30 days in quiescent seawater at -800 mV to develop

a calcareous deposit. The deposit developed by preexposure resulted in current densities two orders of magnitude less for bronze and alloy 625 than for freshly exposed material. Deposits on steel showed only a factor of 2 or 3 decrease in current density from freshly exposed material, although the currents were similar to those for pre-exposed bronze. The lesser decrease in current density for the steel is due to the lower currents for freshly exposed material, where some deposit had already been formed, not to higher currents for preexposed material. Velocity dependence of the current was evident for material with a deposit. This dependence was less than an order of magnitude over the velocity range used in the previous study,<sup>1</sup> 0 to 1000 RPM (0-9 ft/s) for an equivalent flow, thus showing why the velocity dependence was lost in the order-of-magnitude scatter in the earlier work.

During the stepped velocity testing of material with pre-formed calcareous deposits, there was no visual evidence of removal of calcareous deposits on any specimen, even at the maximum rotation speed (equivalent to 90 ft/s). The current density data shows no significant increase of current during the period of test after the maximum velocity step, as would occur if some deposit had been removed. A weight gain was reported for all specimens, also indicating the presence of a deposit not removed by the high flow. It is possible that significantly longer exposure than 5 minutes at the higher flow might result in some removal of the deposit. Current densities at 1000 RPM for all three materials were at or slightly below 10  $\mu\text{A}/\text{cm}^2$ , in agreement with the value from the earlier work.<sup>1</sup>

### Third Test

Figures 12 through 14 present the polarization curves for bronze, alloy 625, and steel developed on specimens rotating at 5000 RPM (about 45 ft/s) with a calcareous deposit pre-formed in quiescent seawater for 30 days. The bronze in figure 12 shows classic diffusion-limited cathode kinetics near -1000 mV with no

evidence of the hydrogen reduction reaction. The alloy 625 in figure 13, aside from a current spike at about -700 mV, displays a cathodic Tafel slope of about 400 mV per decade, although the slope is not particularly linear over a sufficient range for accurate determination. The hydrogen reduction reaction may be contributing to the currents at the lowest potentials. The steel in figure 14 shows definite indication of the hydrogen reduction reaction at potentials of -900 mV or below. The three curves in figures 12 through 14 should be indicative of the cathodic protection current demand on a structure operated under intermittent high flow.

#### Additional Discussion

Calcareous deposits do not appear to form readily or adhere properly to nickel-aluminum bronze or alloy 625 in flowing seawater. Once formed in quiescent seawater, these deposits are not removed by short exposures to high velocity flow up to 90 ft/s, and they reduce cathodic current demand by two orders of magnitude over that for freshly exposed material. The current for freshly exposed material is roughly equal to the theoretical value for pure oxygen diffusion through a fluid boundary layer. Steel will still form a calcareous deposit under flowing conditions, although the rate of formation was not studied. The effect of velocity on current density of material with a deposit was well under an order of magnitude from 1000 to 10,000 RPM (9 to 90 ft/s).

Since most engineering materials are used under conditions of intermittent operation, either intentionally or due to startup or breakdowns, the lack of formation of calcareous deposits under high flow conditions should not be construed to mean that they will not be present in service. In fact, since they are likely to form during quiescent periods and may not be removed during subsequent operation, their presence in service is possible. The extent of formation of the deposits may

vary, depending on the service history and environment of the structure of interest. Some components on which flow is critical are periodically cleaned to remove fouling. This process may also remove the calcareous deposits. Thus the amount of reduction in current may not always be as great as in this study, and conservative design for a cathodic protection system for a periodically-cleaned structure or machinery component may necessitate not considering the effect of the deposits. In the environment of this investigation, the use of short-term laboratory data to predict current densities in seawater will lead to predictions which are high by two orders of magnitude due to insufficient time for calcareous deposit buildup. Similarly, high velocity testing should be conducted after an initial quiescent period to allow for formation of the deposits. Three curves developed in this manner were presented.

#### CONCLUSIONS

The first objective of this work, to determine the cathodic protection current demand on a structure with calcareous deposits under high flow conditions, was met with the data in figures 10-14. The deposits reduce cathodic current demand by two orders of magnitude over that for freshly exposed material. The effect of velocity on current density of material with a deposit was well under an order of magnitude from 1000 to 10,000 RPM (9 to 90 ft/s).

The second objective was to find the conditions under which calcareous deposits might exist on a structure under high flow. These conditions can be described as follows:

Although calcareous deposits do not appear to form readily or adhere properly to nickel-aluminum bronze or alloy 625 in flowing seawater, they can be easily formed under low flow. They will still form on steel however. Once formed, these deposits are not removed by short exposures to high velocity flow up to



90 ft/s. Even though materials may be used under conditions of intermittent operation, thus allowing the formation of the deposits, cleaning to remove fouling or prolonged high velocity operation may remove them. Thus for many applications under high flow, the presence of calcareous deposits cannot be relied on. Conservative design for a cathodic protection system for a periodically-cleaned structure or machinery component may necessitate not considering the effect of the deposits.

#### ACKNOWLEDGEMENTS

The authors wish to acknowledge the contributions of the staff at the LaQue Center for Corrosion Technology in the conduct of the experiments reported herein. The contributions of Mark Joseph, Marty McGowan, and Dennis Melton are particularly appreciated.

Table 1. Composition of alloys tested (%).

| Elements           | Alloy |          |            |          |
|--------------------|-------|----------|------------|----------|
|                    | HY-80 | Ni-Al-Br | Alloy 625* | Zn Anode |
| Iron               | Rem   | 3.93     | 5.0 max    | 0.0090   |
| Copper             | -     | 80.1     | -          | 0.0020   |
| Nickel             | 2.49  | 4.66     | 58.0 min   | < 0.0005 |
| Zinc               | -     | 0.44     | -          | 99.8     |
| Aluminum           | -     | 9.44     | 0.40 max   | 0.166    |
| Cadmium            | -     | -        | -          | 0.411    |
| Manganese          | 0.30  | 1.55     | 0.50 max   | -        |
| Carbon             | 0.132 | -        | 0.10 max   | -        |
| Silicon            | 0.20  | 0.092    | 0.50 max   | -        |
| Sulfur             | 0.017 | -        | 0.015 max  | -        |
| Tin                | -     | 0.077    | -          | -        |
| Cobalt             | -     | 0.014    | -          | -        |
| Chromium           | 1.72  | 0.007    | 20.0-23.0  | -        |
| Molybdenum         | 0.41  | -        | 8.0-10.0   | -        |
| Niobium + Tantalum | -     | -        | 3.15-4.15  | -        |
| Titanium           | -     | -        | 0.40 max   | -        |
| Phosphorus         | 0.011 | -        | 0.015 max  | -        |

\*Nominal

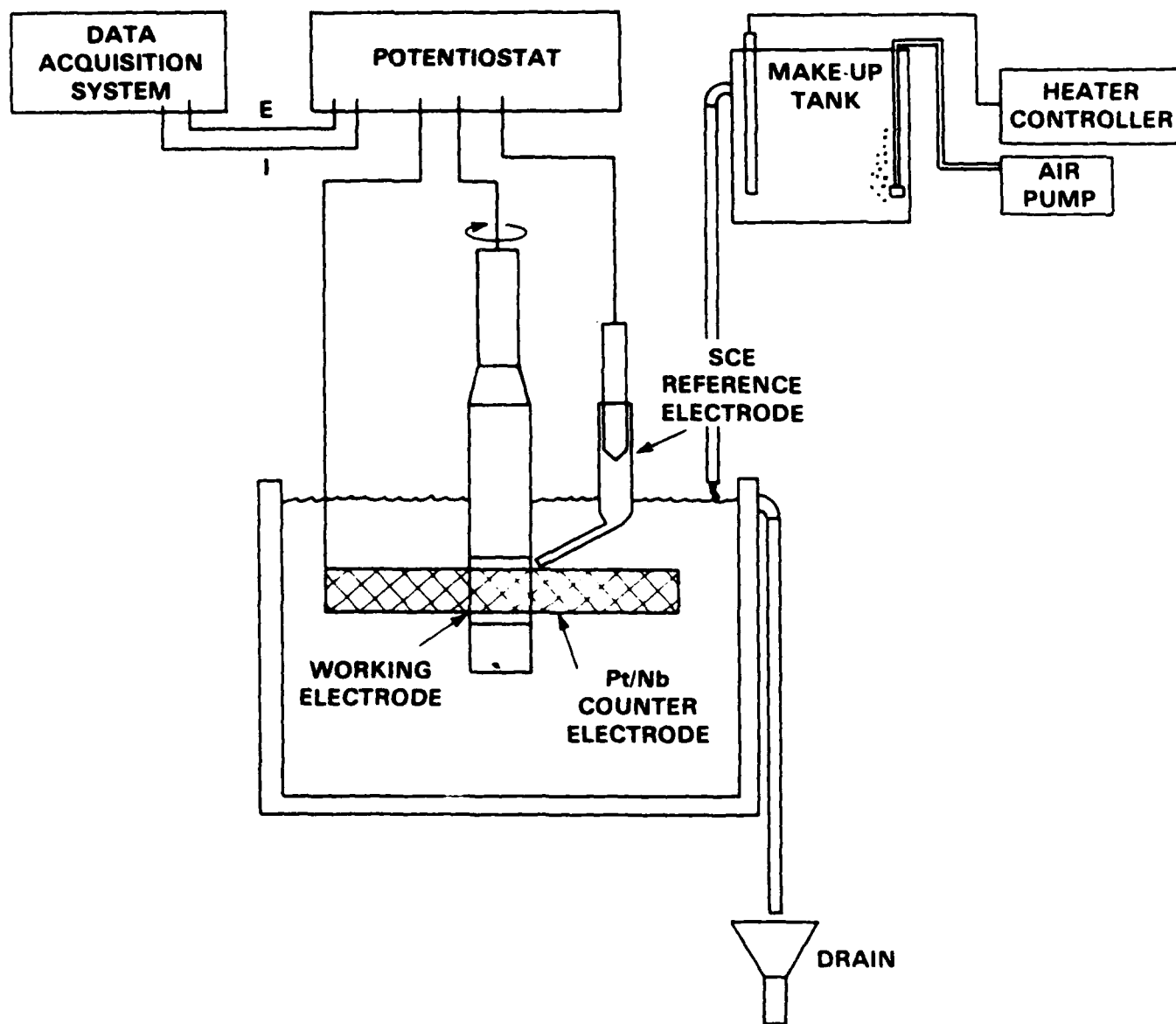


Fig. 1. One-inch rotating cylinder apparatus.

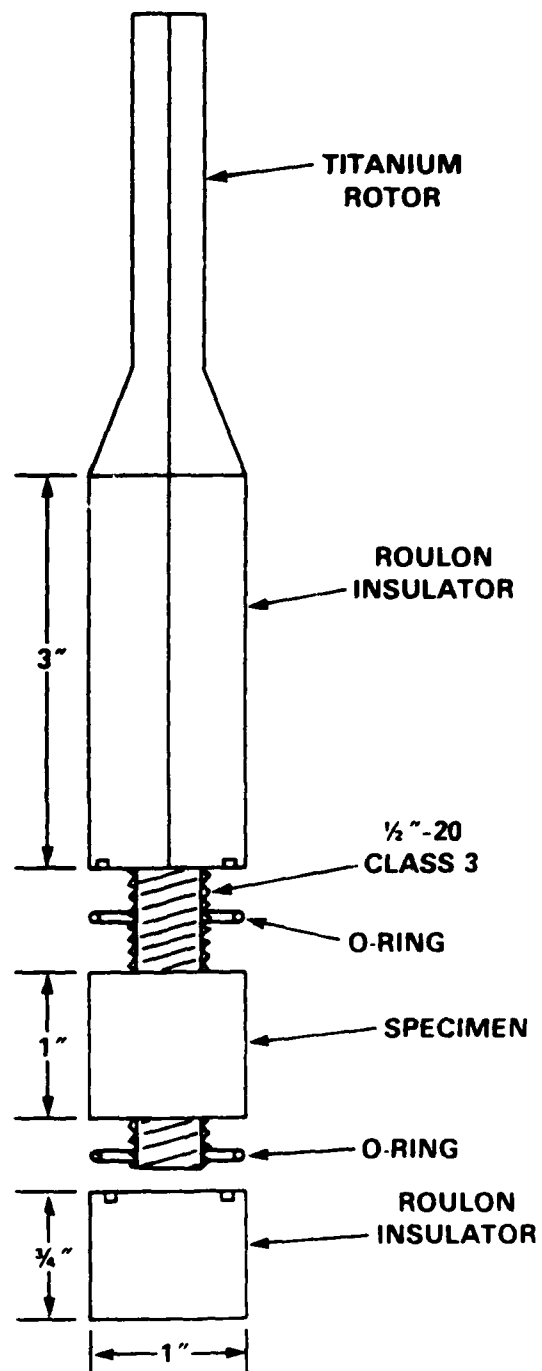


Fig. 2. Detail of one-inch specimen mounting.

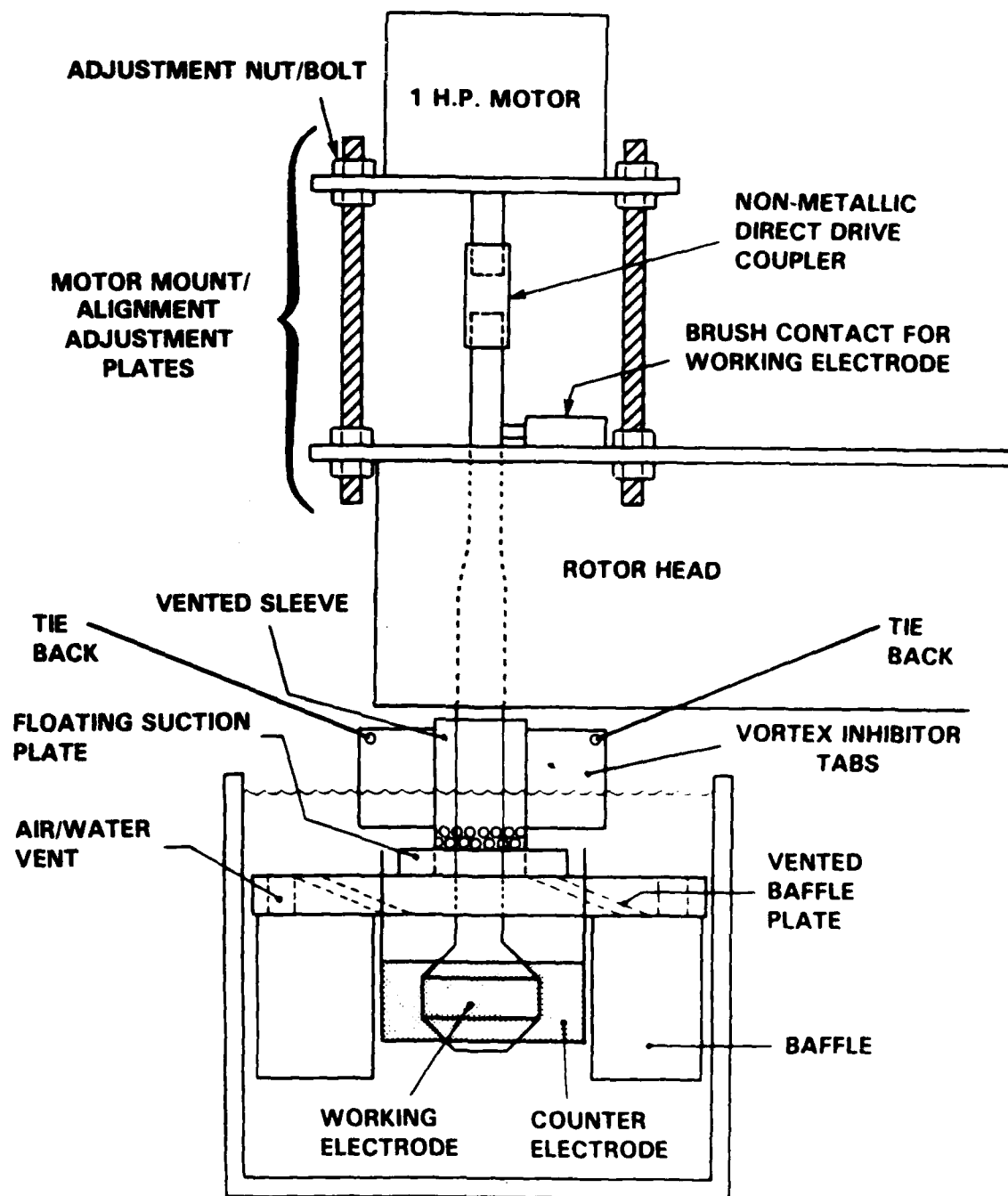


Fig. 3. Two-inch rotating cylinder apparatus.

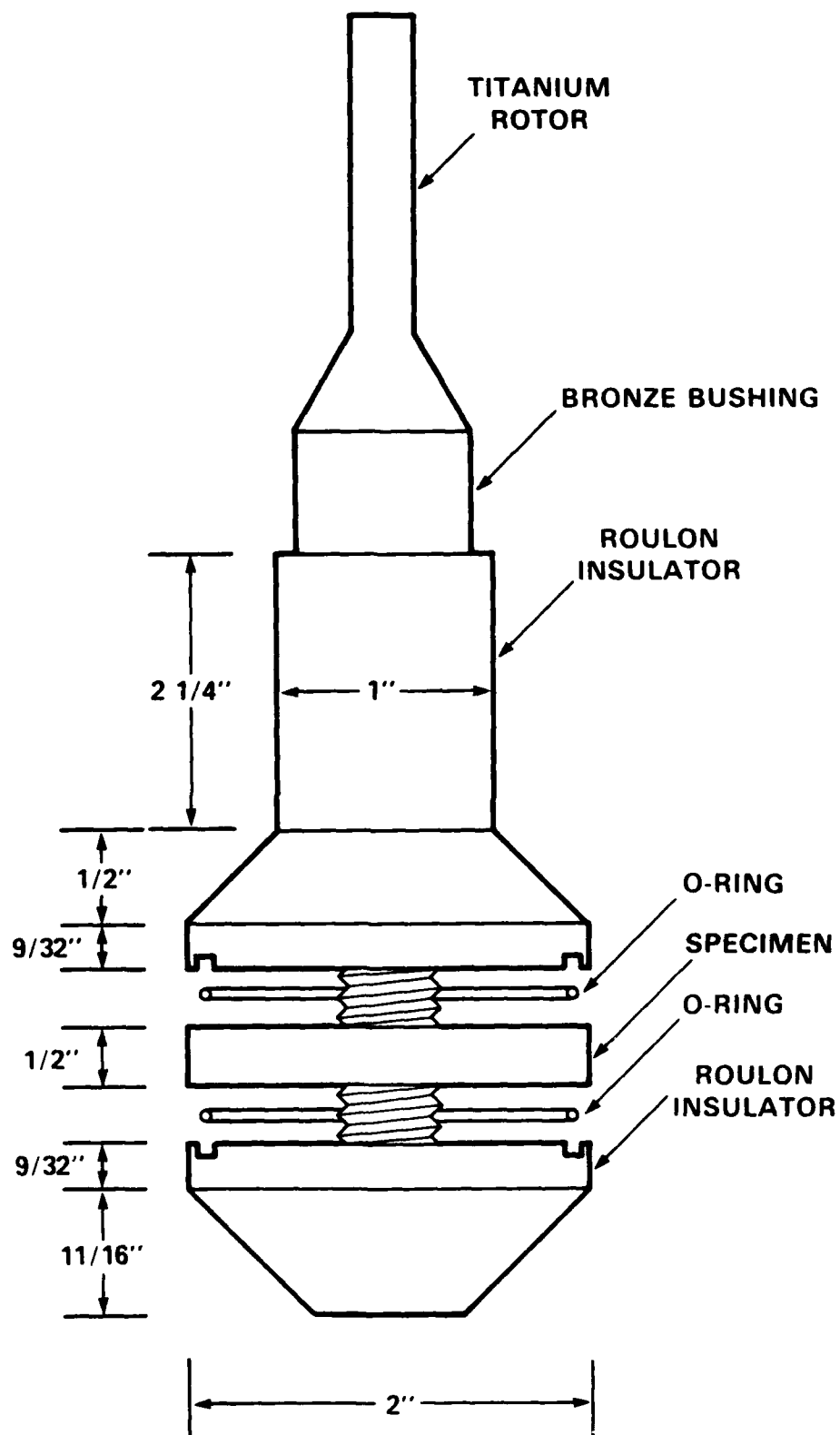


Fig. 4. Detail of two-inch specimen mounting.

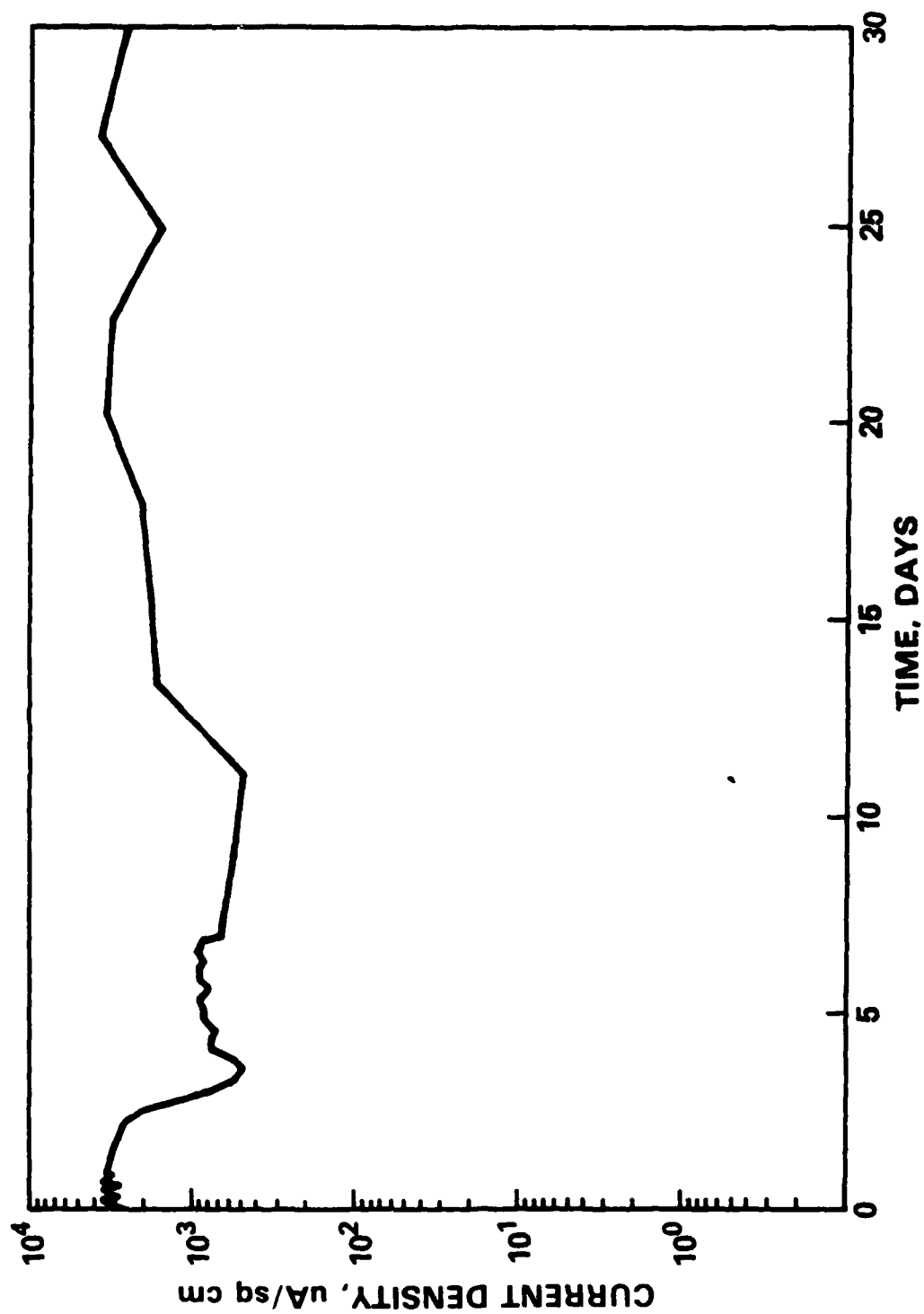


Fig. 5. Nickel-aluminum bronze specimen 1 at 50 ft/s and -800 mV vs. SCE in natural seawater.

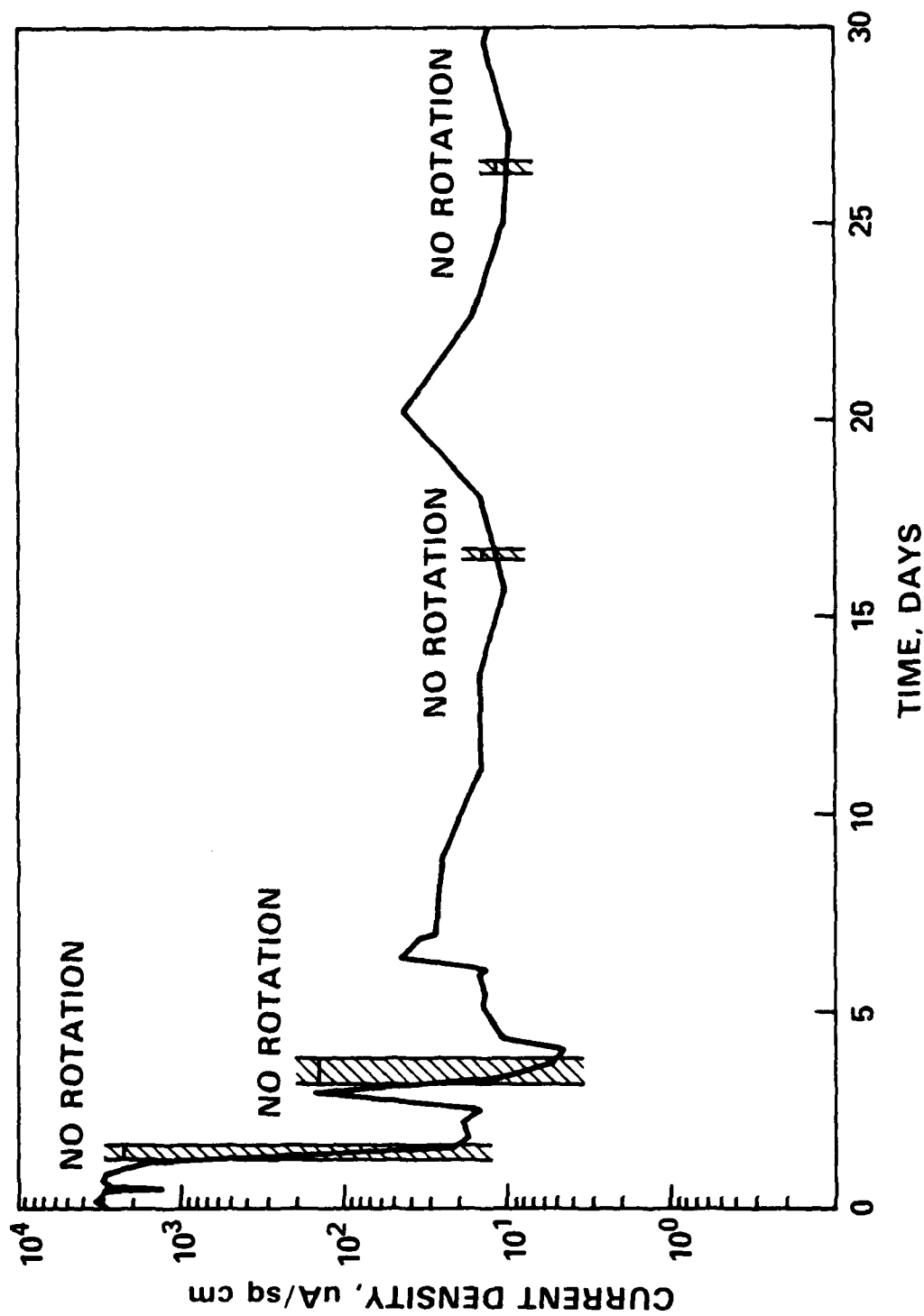


Fig. 6. Nickel-aluminum bronze specimen 2 at 50 ft/s and -800 mV vs. SCE in natural seawater.

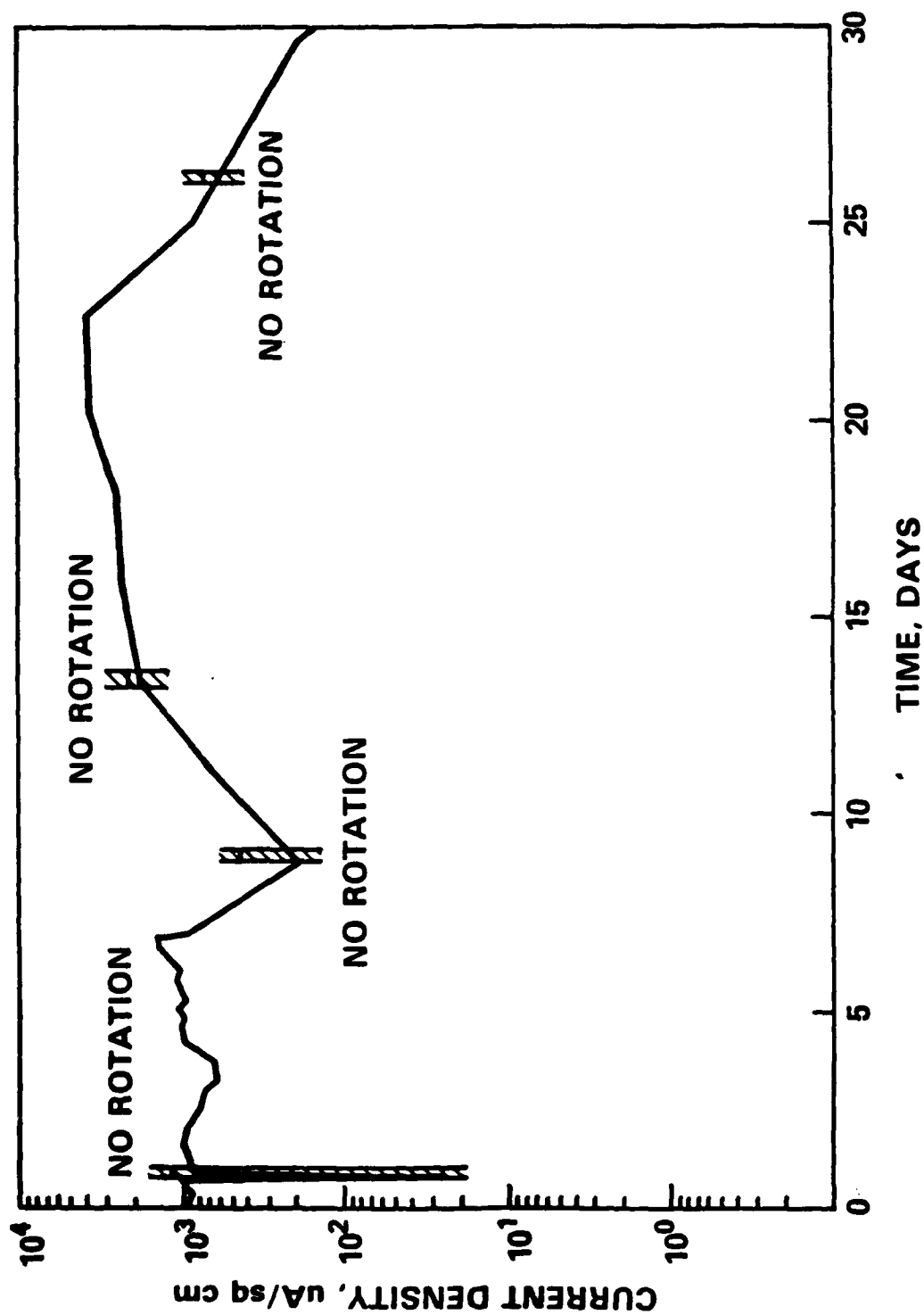


Fig. 7. Inconel 625 specimen 1 at 50 ft/s and -800 mV vs. SCE in natural seawater.



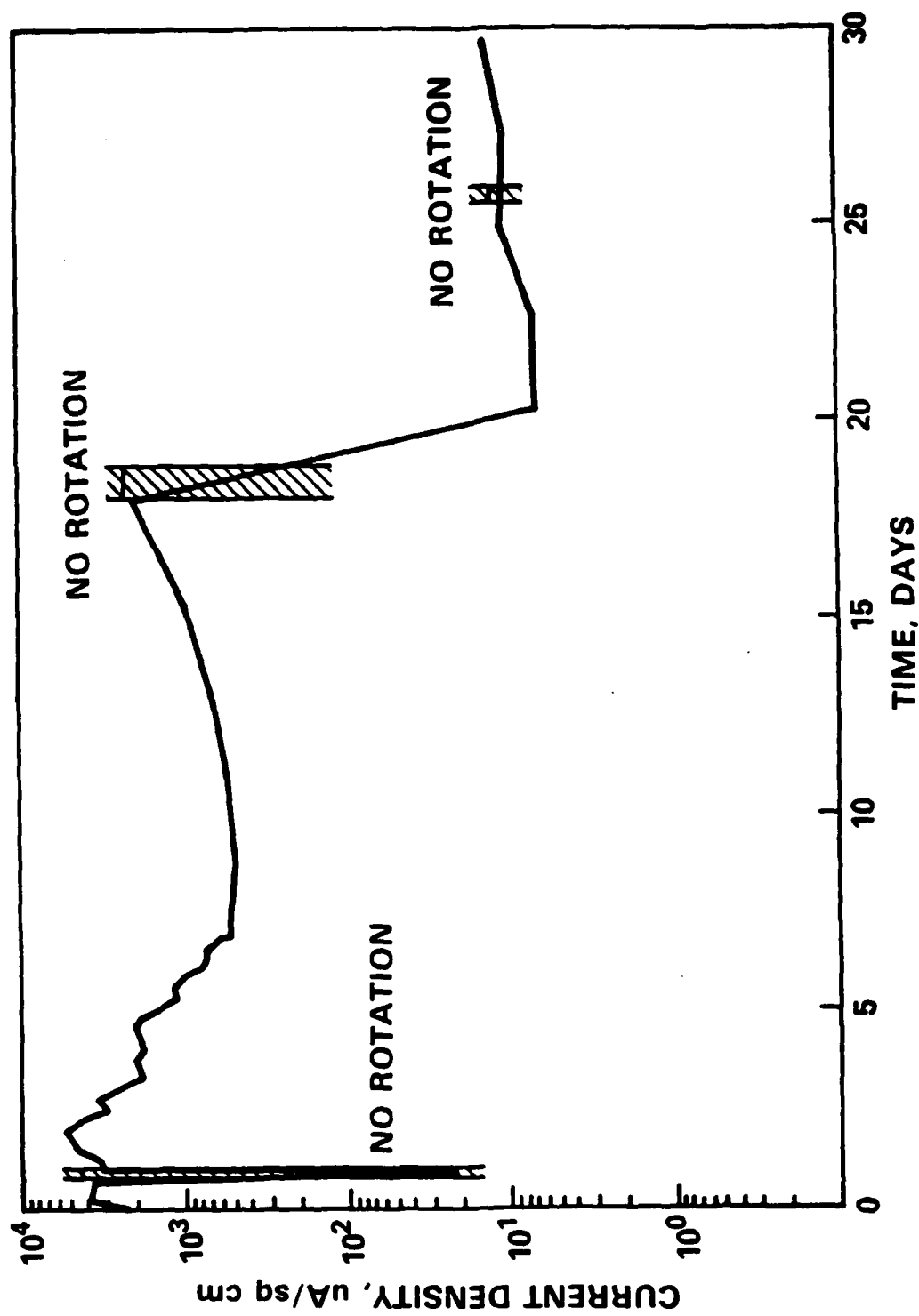


Fig. 8. Inconel 625 specimen 2 at 50 ft/s and -800 mV vs. SCE in natural seawater.

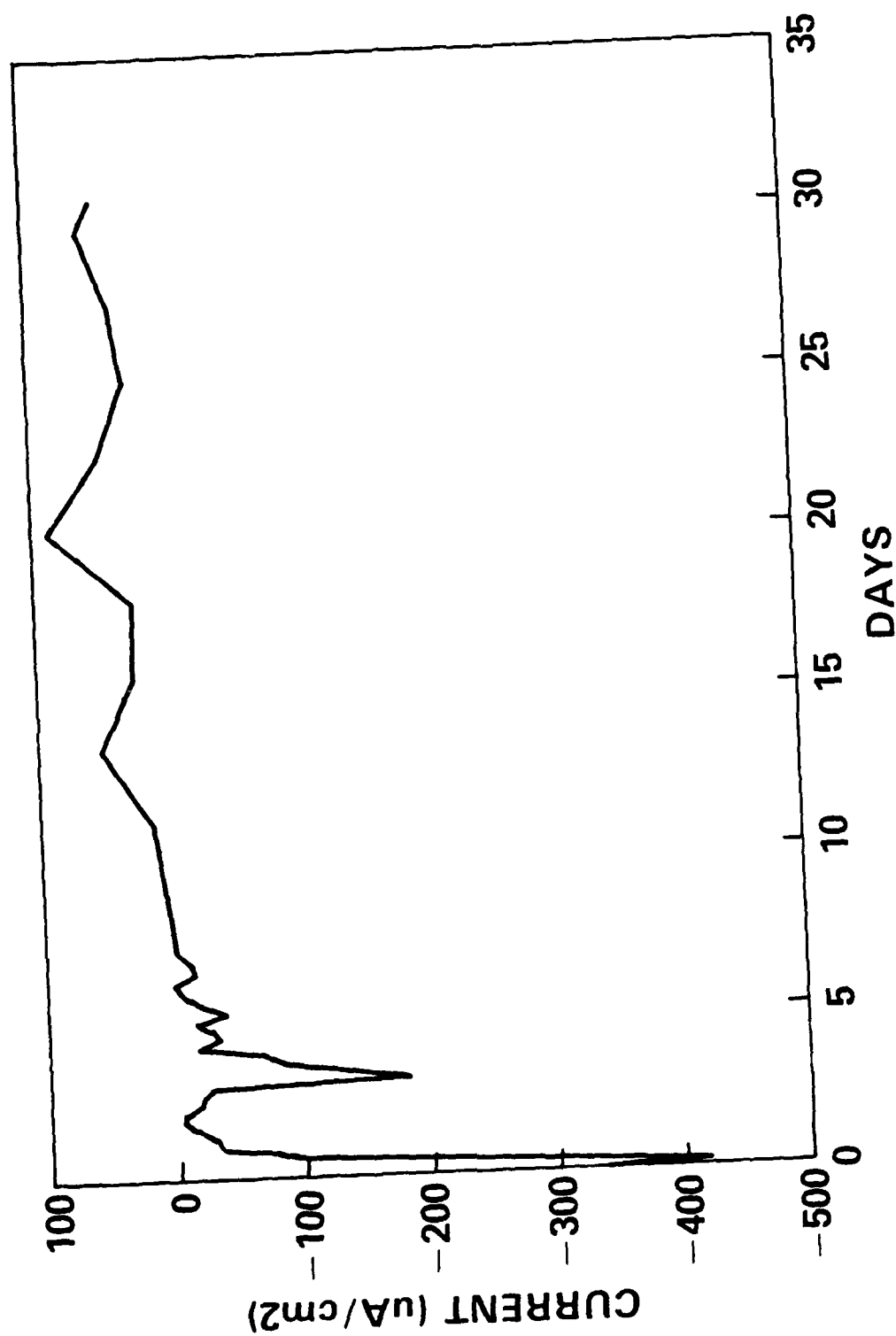


Fig. 9. Zinc at -1030 mV vs. SCE in natural seawater.

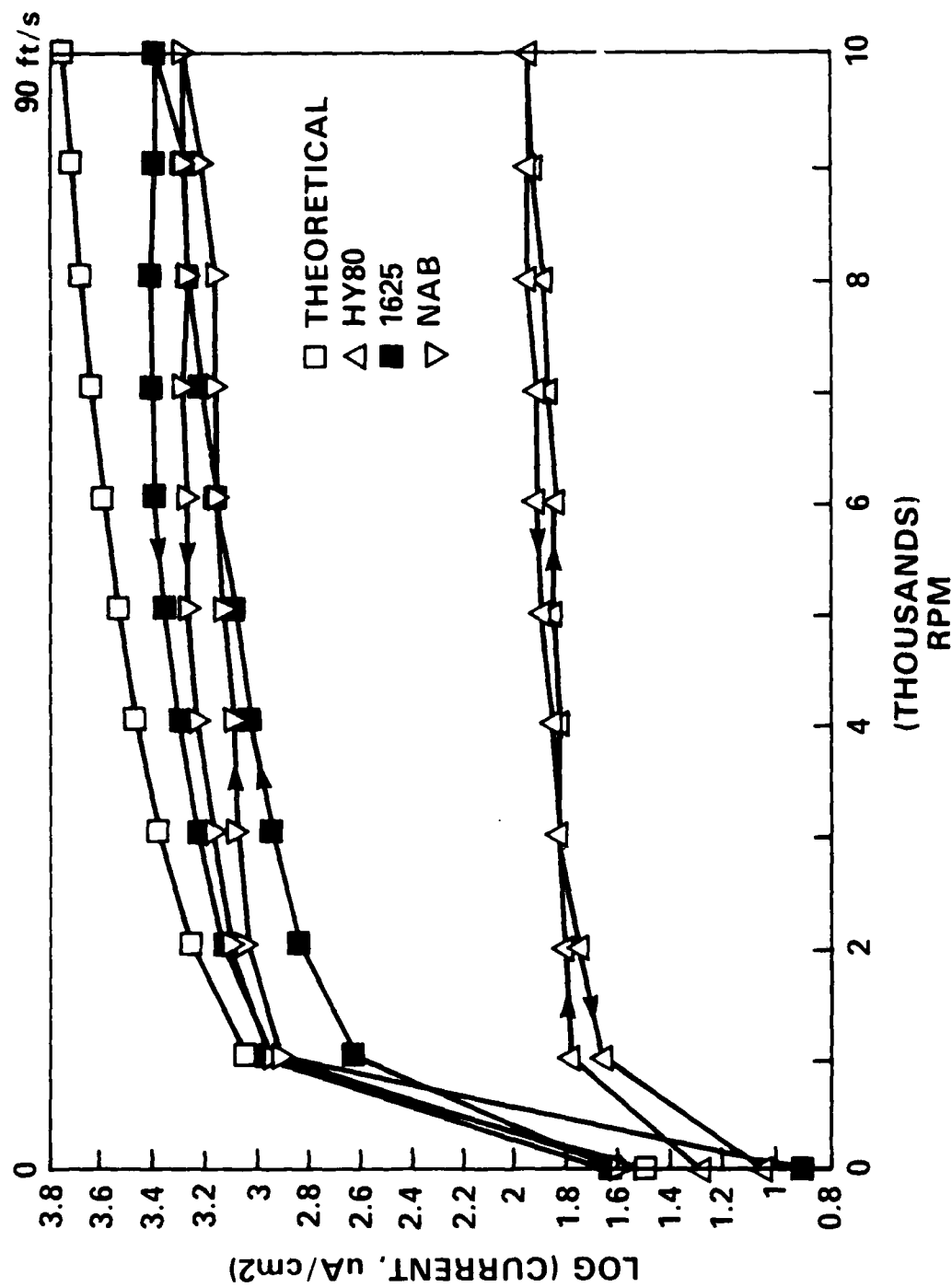


Fig. 10. Freshly exposed materials at -800 mV vs. SCE in natural seawater.

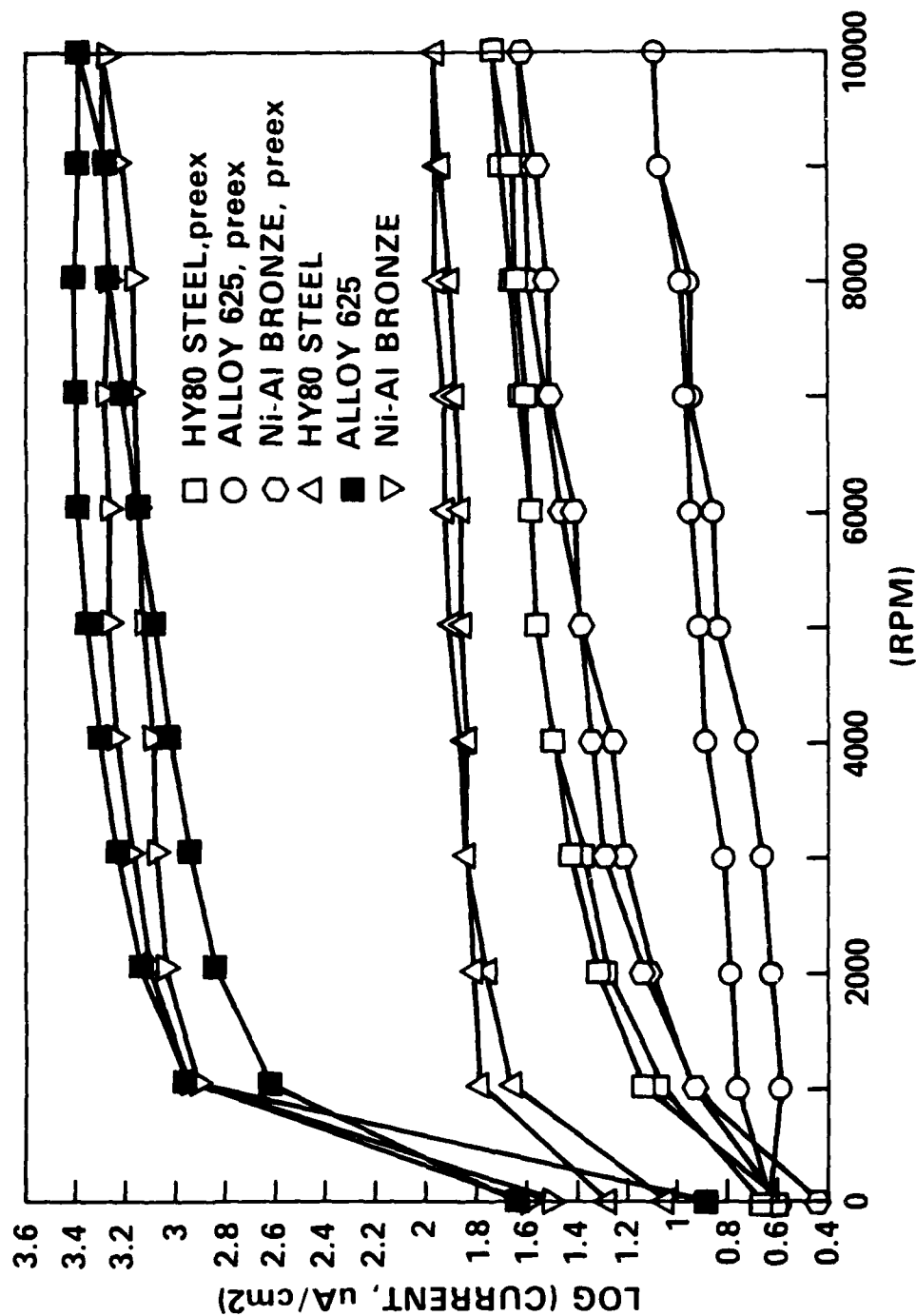


Fig. 11. Effect of 30 day quiescent pre-exposure at -800 mV vs. SCE in natural seawater.

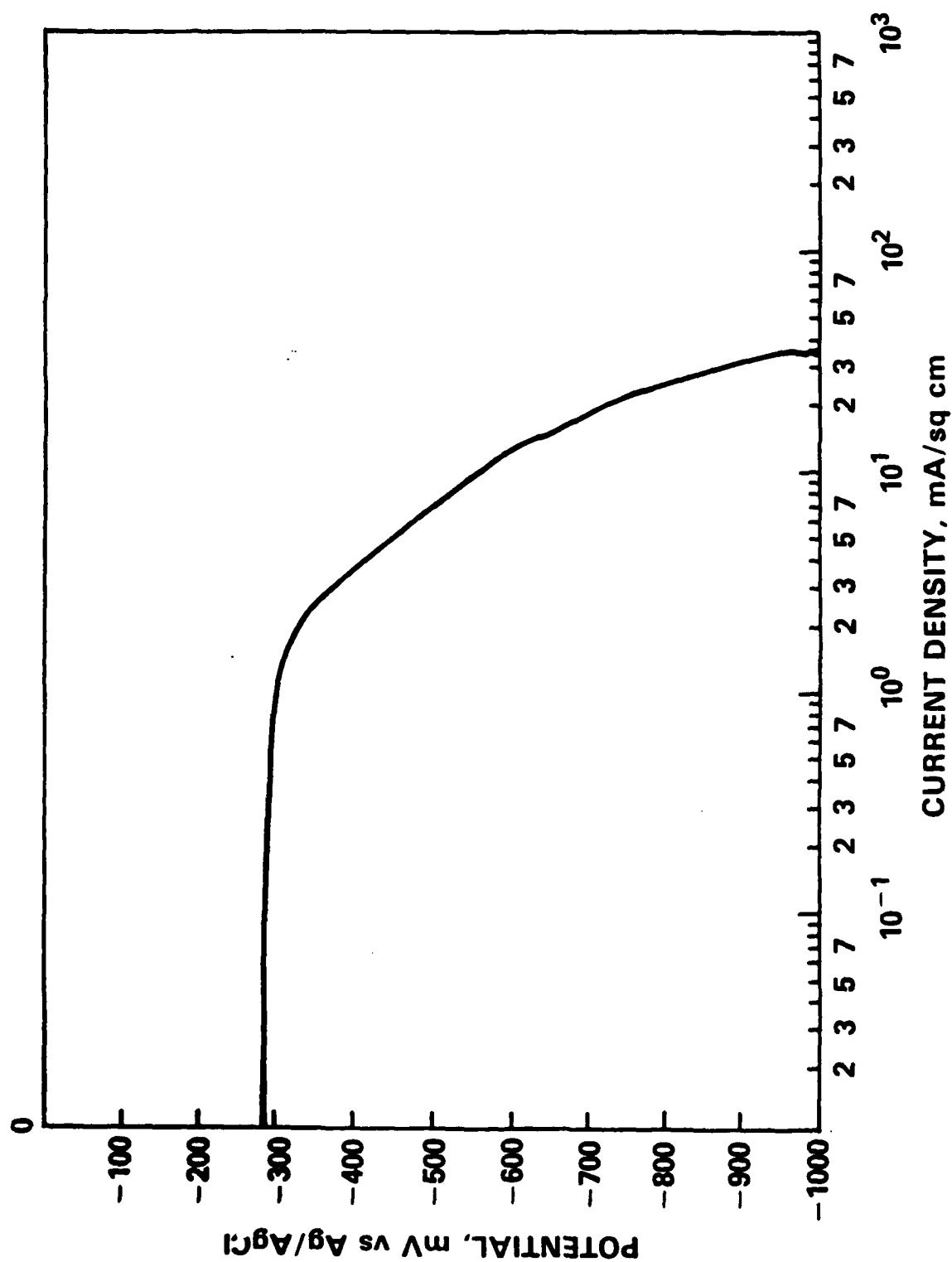


Fig. 12. Polarization of nickel-aluminum bronze at 45 ft/s in natural seawater.

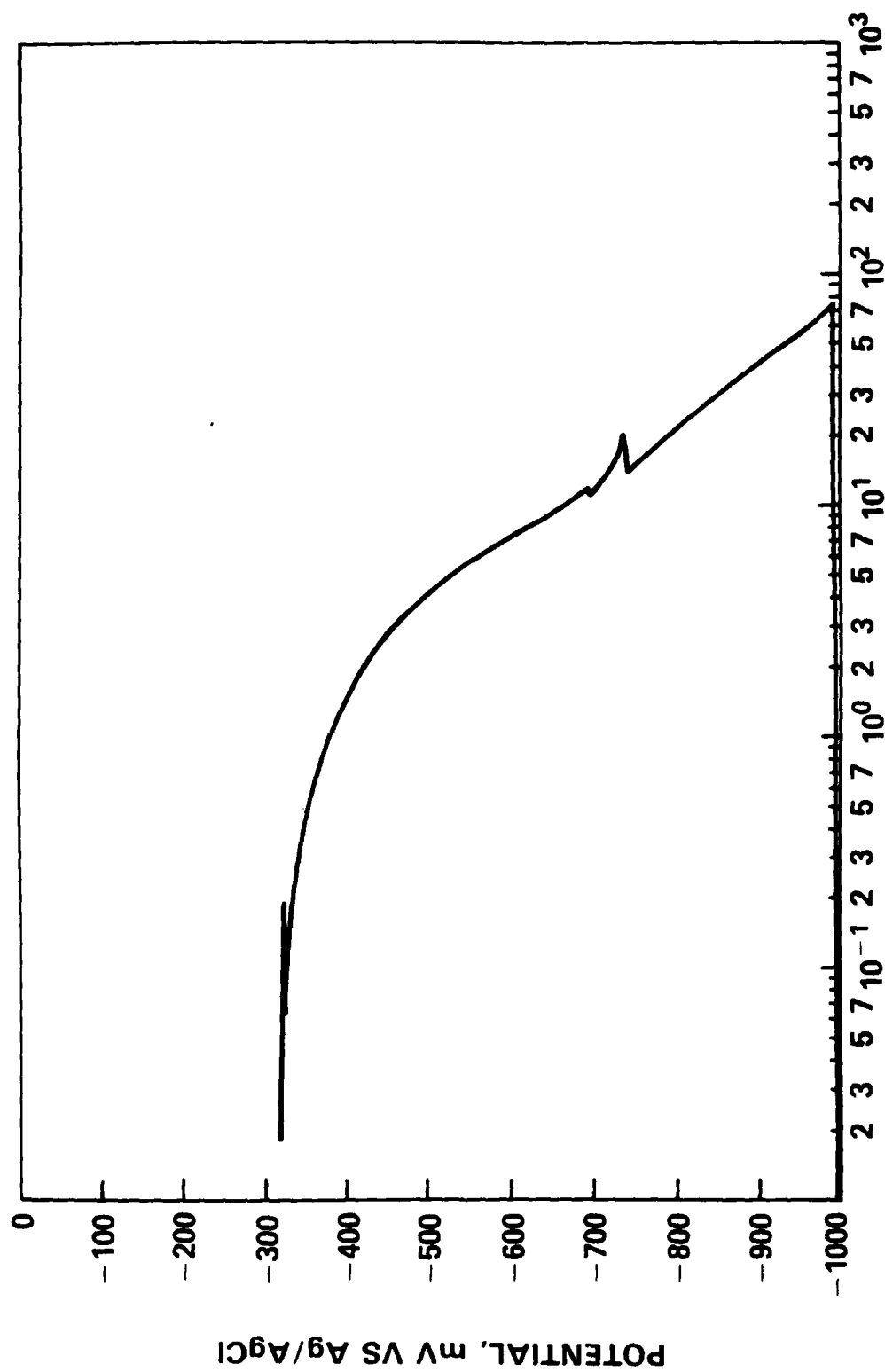


Fig. 13. Polarization of alloy 625 at 45 ft/s in natural seawater.

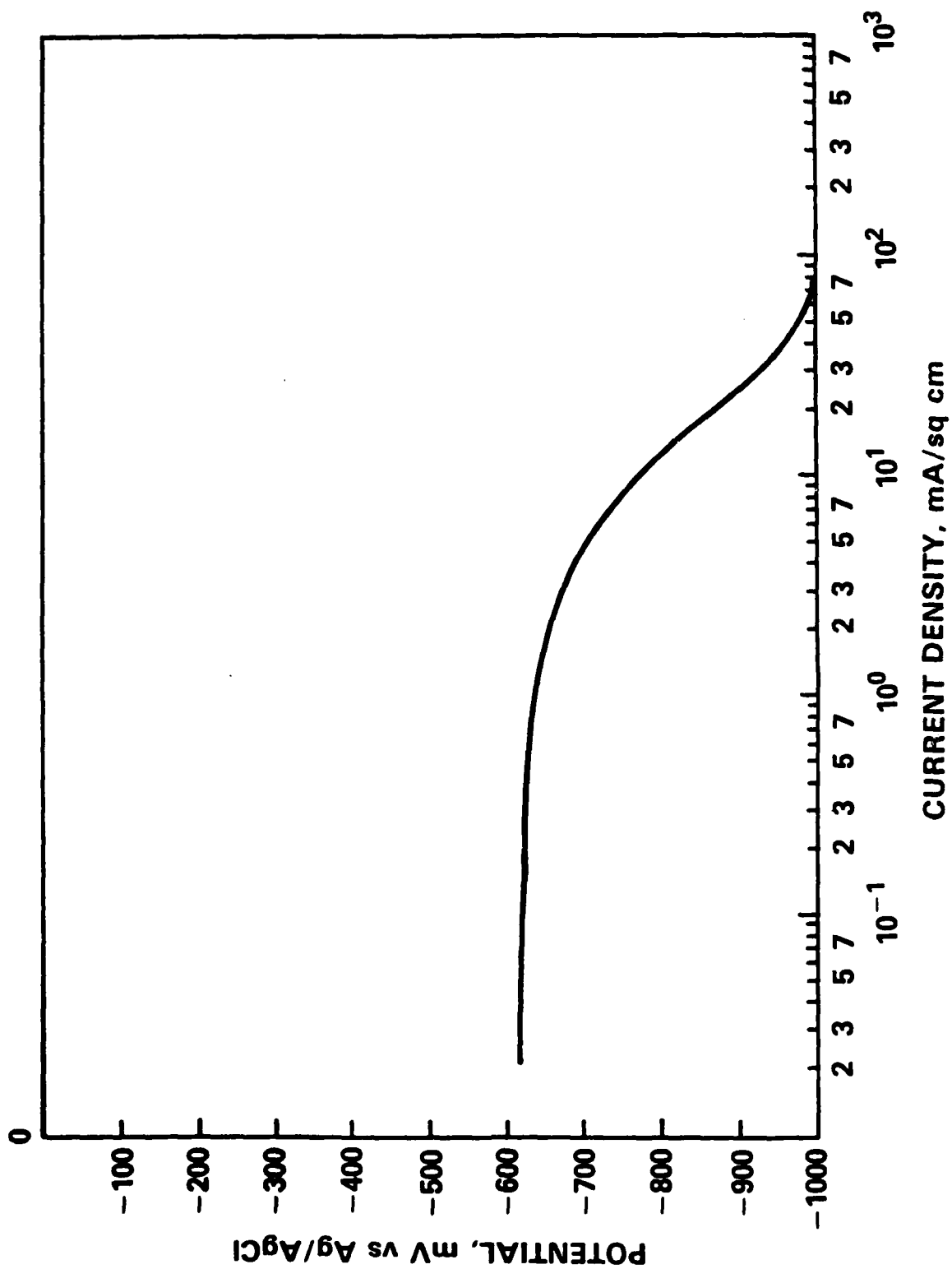


Fig. 14. Polarization of HY-80 steel at 45 ft/s in natural seawater.

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