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Marine Corrosion Studies

The Electrochemical Potential of High Purity Metals in Seawater

(Ninth Interim Report of Progress)

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M. H. PETERSON

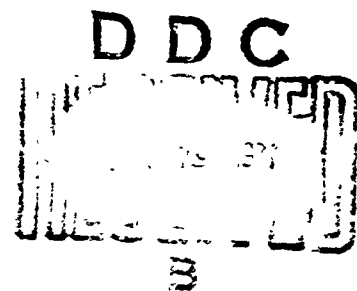
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Interim Report Series on Marine Corrosion

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ABSTRACT

A study has been conducted in which the electrochemical potentials of high purity metals were determined in quiescent seawater.

The data are presented as histograms and as potential time graphs. The electrochemical potentials of many of the metals varied over a broad range, and therefore it is impractical to assign a specific potential value to many of the metals. A galvanic series is included, however, based on the data obtained from the histograms.

Two of the metals, bismuth and tin, had relatively stable potentials in seawater, but further experimentation indicated their unsuitability as reference electrodes to monitor cathodic protection systems on ship hulls.

STATUS

This report completes one phase of the task; work is continuing on other phases.

AUTHORIZATION

NRL Problem M04-02
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INTRODUCTION

The design of Navy instrument packages and other submerged structures requires knowledge on the corrosion compatibility of the less-common metals and the usual structural alloys in seawater. One of the basic parameters required to estimate the compatibility of different metals coupled in seawater is the electrochemical potential of each metal of the structure. In addition, if the use of cathodic protection to mitigate corrosion is anticipated, a knowledge of the potential of the metals to be protected is a prerequisite to the design of the system.

An experiment was initiated at NRL's Marine Corrosion Research Laboratory, Key West, Florida, to study the electrochemical potentials of 16 different metals in seawater. The experiment included high purity specimens of the less-common metals and some of the more common metals of higher purity than have heretofore been studied in this manner.

PROCEDURES

The Specimens

Most of the metals were exposed as rods with diameters ranging from 0.1 to 0.3 inches. The platinum specimen was a wire with a diameter of 0.020 inches, and the bismuth specimen was triangular shaped.

All specimens were washed with fresh water and slightly abraded using nylon mesh. Specimens were dried with acetone and allowed to stand in the laboratory for one day prior to initiating the experiment.

Experimental Technique

All specimens were totally immersed in individual glass cell containers of 80 ml capacity. The details of the experimental technique used for specimen immersion and the determination of the electrochemical potentials during the 69-day exposure period are shown in Fig. 1.

The electrical connection to each specimen was above the solution level and was sealed with a water resistant putty and vinyl electrical tape. To eliminate waterline

effects from the potential data, the specimens were positioned in the individual cells so that the untaped area was completely immersed and well below the solution level.

Seawater temperature during the exposure period ranged from 19 to 24° C (66 to 75° F). A flow rate sufficient to renew the seawater in each container every 2 minutes was maintained. This flow rate was equivalent to a velocity of less than 0.005 ft/sec. A strainer filled with nylon mesh and a filter tube (60-70 micron) was used to remove any suspended matter that may have been in the seawater.

Electrochemical potentials were measured with a high impedance data acquisition system with a saturated calomel electrode (SCE) as the reference electrode.

DATA AND DISCUSSION

Histograms of the electrochemical potential of each metal are shown in Fig. 2. Graphs of the potentials as a function of time are shown in Fig. 3. Table 1 is a galvanic series for the metals based on the histograms.

High purity iron, aluminum, molybdenum, and tantalum exhibited potentials having ranges of 0.1 volt or less. The comparatively negative potential of the high purity aluminum may be of interest, because a relatively high potential galvanic anode could possibly be developed that would offer the weight advantages of aluminum. However, considerable detailed study would be required to develop and exploit the economical usefulness of such an anode for seawater cathodic protection systems.

The electrochemical potential data also show that the two tantalum specimens had grossly different potentials and potential ranges. The high purity (99.99+) zone refined tantalum showed a negative potential with a range of less than 0.1 volt, whereas the less pure tantalum showed a positive potential with a range of approximately 0.3 volt.

The histograms also illustrate one of the pitfalls inherent in the use of mean values and standard deviations to characterize a series of measurements. It is evident that the potentials of copper, nickel, and indium were

not normally distributed around the mean in the usual bell-shaped curve, but that there were in these instances two metastable potentials and that there was a strong tendency for the potential to stabilize at one of these values. For data of this type the reporting of a mean value and standard deviation is not only meaningless, but implies that the data was normally distributed.

Bismuth and tin had potentials with a spread of 0.025 volts or less. These relatively stable potentials indicated the possibility of bismuth and tin being used as reference electrodes to monitor cathodic protection systems such as are used on a ship's hull.

In order to study bismuth and tin for reference electrode use, the experiment was altered after 69 days to study the effect of seawater dilution on the potential of these electrodes. The effect of seawater dilution on the electrochemical potential of the bismuth and the tin electrodes is shown in Figs. 4 and 5, respectively.

Although the bismuth and the tin electrodes showed rather constant potentials in seawater during the initial 69-day period (Fig. 3), their potentials in diluted seawater varied considerably. In addition, after exposure to diluted seawater for approximately 72 hours (3 days), the potential of both electrodes returned to within 5 mv of the initial seawater value, but the recovery time was approximately one day. Variations of potential in diluted seawater and the relatively slow response time are undesirable characteristics for a reference electrode to monitor a cathodic protection system on a ship's hull that would at times be in full strength seawater and at other times be in diluted seawater. Based on these criteria, there would be no advantage in the use of bismuth or tin electrodes over the commonly used Ag/AgCl electrodes.

The other metals studied exhibited rather broad electrochemical potential ranges. It was, therefore, impractical to assign a particular potential to any of these metals.

To assist in estimating the relative activity of the metals studied, a galvanic series based on a subjective ranking of the histograms has been prepared and is shown in Table 1. Metals that have been grouped together in this series would be expected to be galvanically compatible,

but the anodic side of a galvanic couple within the group can not be predicted from the potential data. However, one would anticipate the more severe galvanic effects when metals in different groups were coupled, and the most severe effects from coupled metals that were widely spaced in the series shown.

SUMMARY

1. Electrochemical potential data in seawater are shown for many of the less-common metals and some of the more common high purity metals during 69-days continuous immersion in relatively quiescent seawater.
2. The data are presented as histograms and potential as a function of time graphs. A galvanic series of the metals studied is included.
3. The electrochemical potentials of many of the metals varied over a rather broad range, and therefore a specific potential value cannot be assigned to these metals.
4. The electrochemical potentials of bismuth and tin were relatively stable indicating that they might be useful as reference electrodes, but subsequent experiments showed that the potential of these metals varied considerably in diluted seawater, and their response recovery time from diluted to full strength seawater was too long for further consideration as reference electrodes to monitor a cathodic protection system on a ship's hull.
5. The potential of high purity aluminum was observed to be quite negative, and there is a possibility that a high potential galvanic anode could be developed with the weight advantage of aluminum. This would, however, require a rather extensive development program to determine the value and economic feasibility of such an aluminum anode.

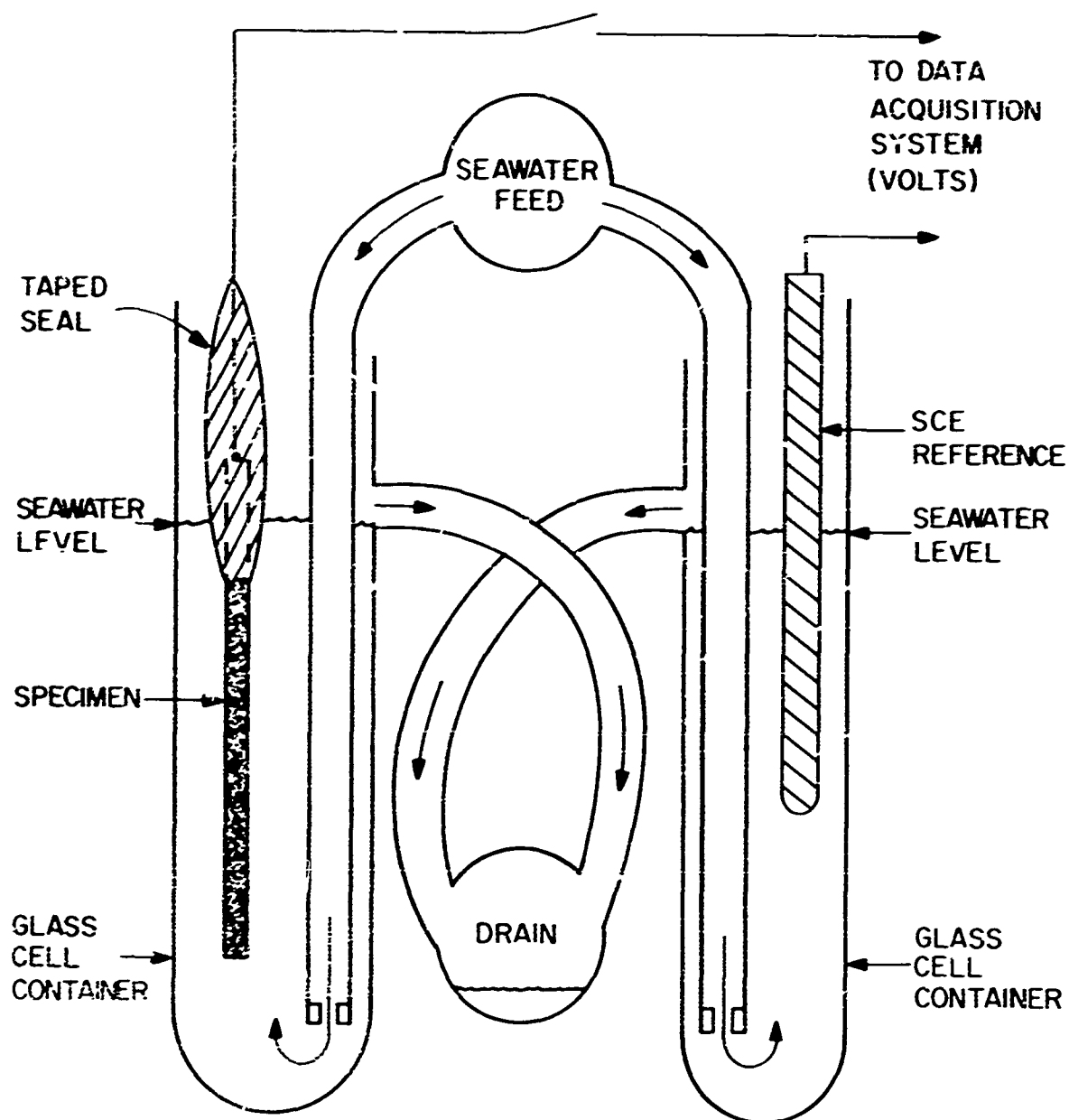
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The assistance of Mr. C. W. Billow of the NRL Marine Corrosion Research Laboratory is acknowledged for conducting much of the experimental study. This study was supported in part by the Naval Ship Systems Command.

Table 1

Galvanic Series of Less-Common and High Purity Common Metals
(69 Days in Seawater at Key West, Florida)

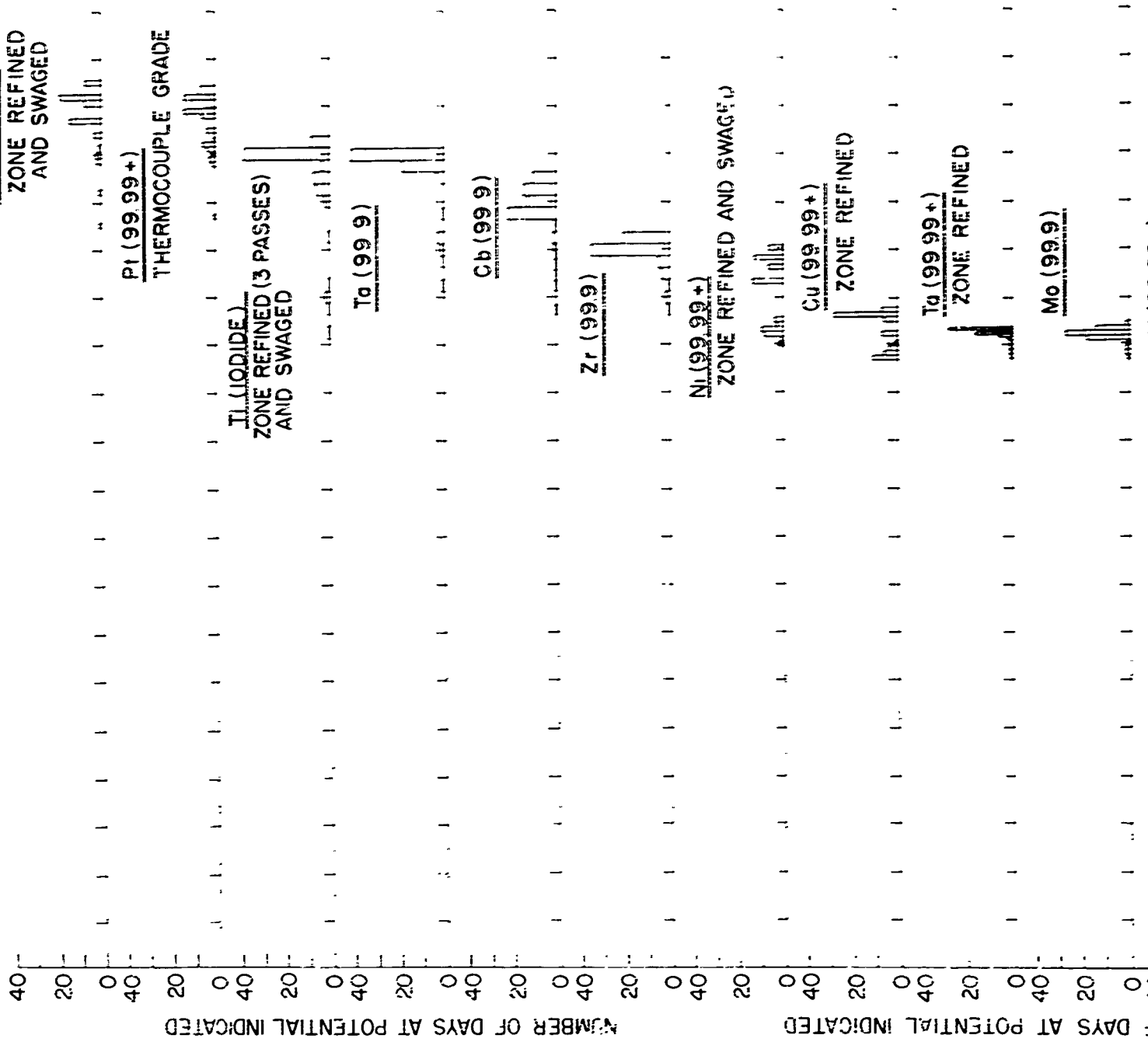
Metal		Metal Purity (percent)	Median Potential (Volts) SCE Reference
<u>Noble</u> (Cathodic)	Palladium	99.99+	+0.308
	Platinum	99.99+	+0.295
	Titanium	Iodide, (zone refined)	+0.200
	Tantalum	99.9	+0.195
	Columbium (Niobium)	99.9	+0.110
	Zirconium	99.9	+0.010
	Nickel	99.99+ (zone refined)	-0.038
	Nickel	99.99+ (zone refined)	-0.172
	Copper	99.99+ (zone refined)	-0.141
	Tantalum	99.99+ (zone refined)	-0.172
	Molybdenum	99.9	-0.173
	Vanadium	99.99+ (zone refined)	-0.209
	Tungsten	99.9	-0.240
	Bismuth	99.9	-0.248
<u>Ignoble</u> (Anodic)	Indium	99.999 (spectrographic grade)	-0.368
	Tin	99.999 (spectrographic grade)	-0.671
	Iron	99.9+ (electrolytic grade)	-0.749
	Aluminum	99.99+ (zone refined)	-1.472
		99.99+ (ingot)	-1.455
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Fig. 1 - Experimental technique used for specimen immersion and determination of electrochemical potentials.

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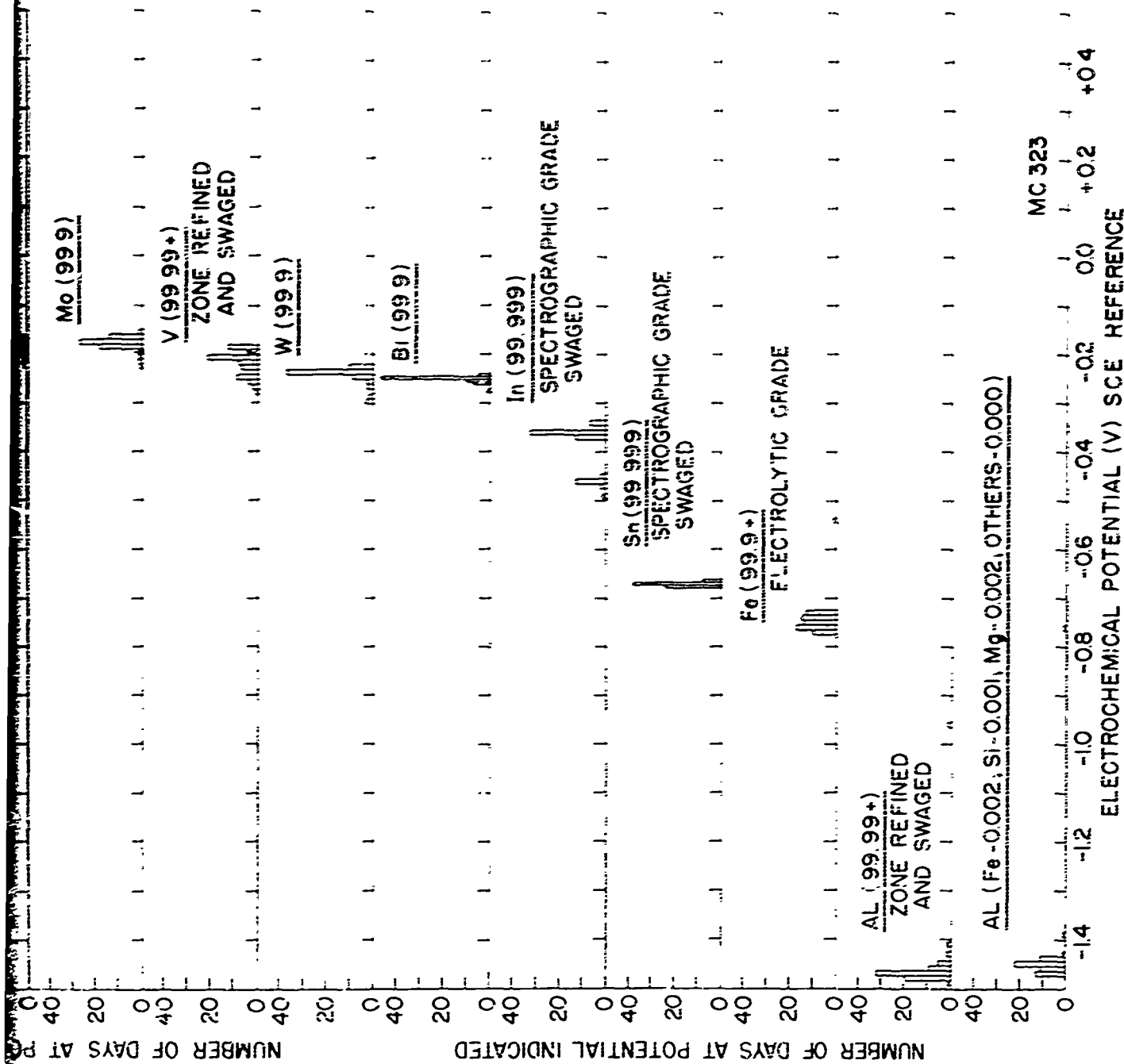


Fig. 2 - Histograms of the electrochemical potential for high purity metals. 69 days in quiescent seawater at Key West, Florida.

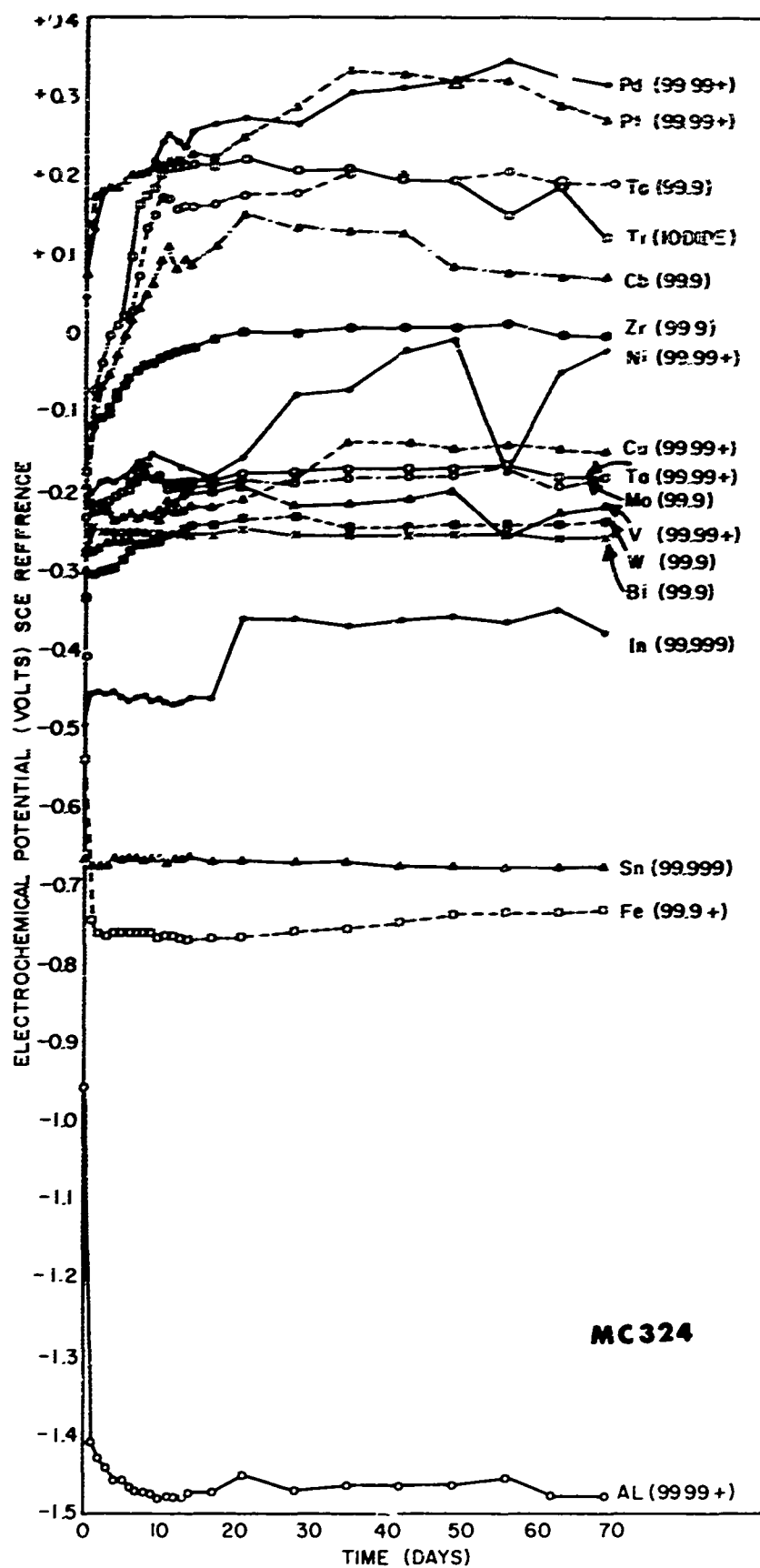


Fig. 3 - Electrochemical potential vs. time graphs for high purity metals. 69 days in quiescent seawater at Key West, Florida.

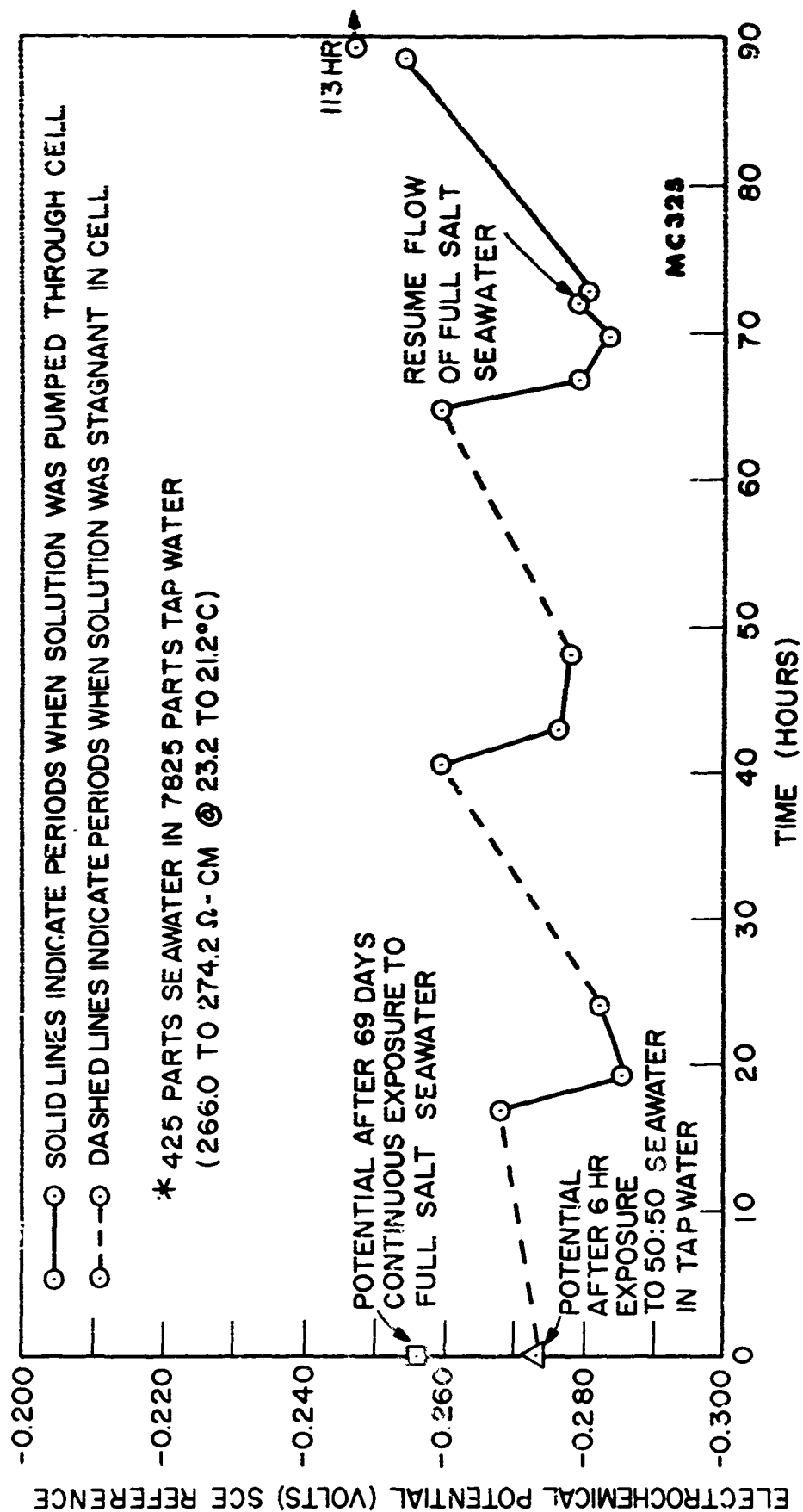


Fig. 4 - Effect of seawater dilution* on the potential of 99.9% blismuth.

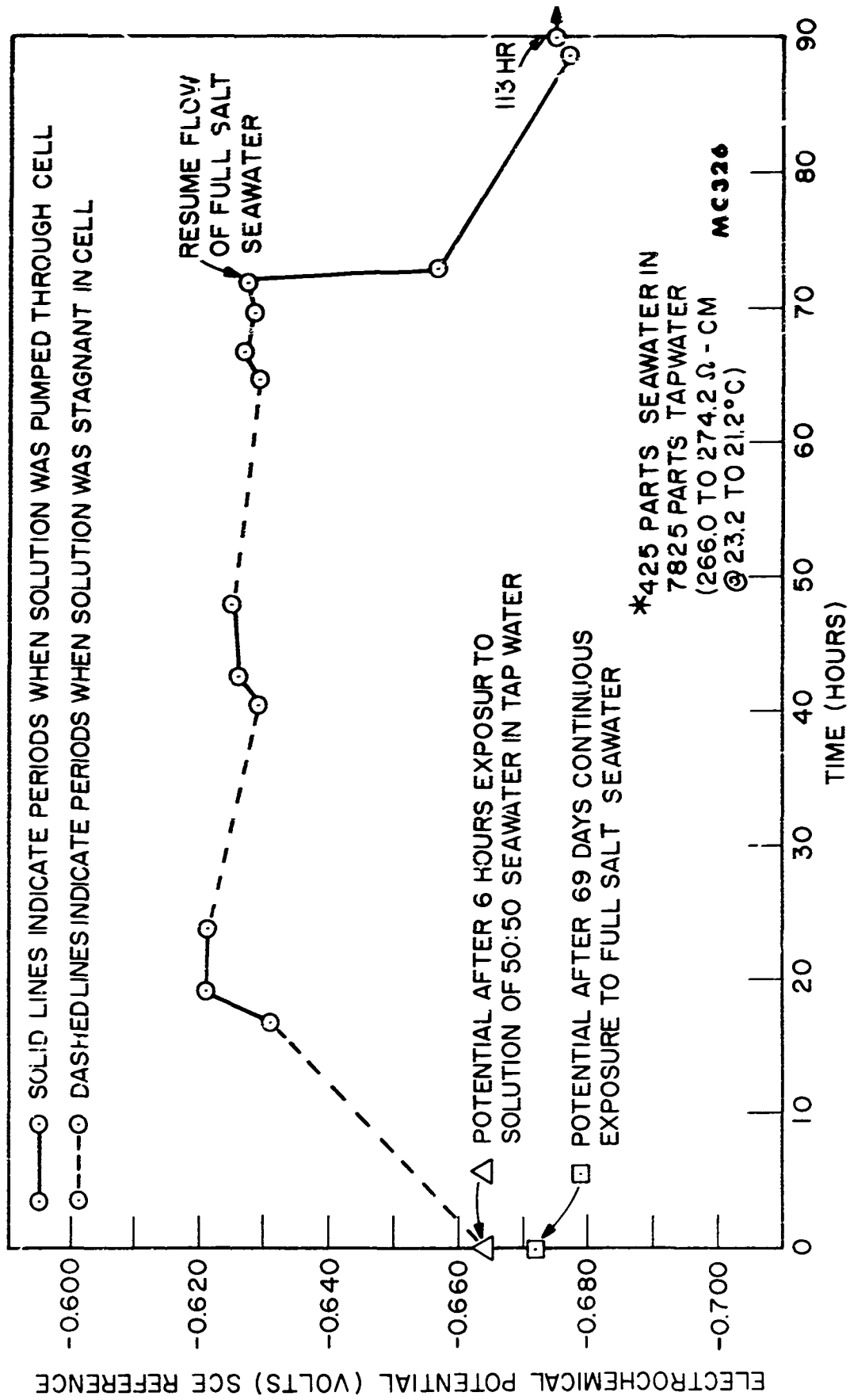


Fig. 5 - Effect of seawater dilution* on the potential of 99.999% tin.

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A study has been conducted in which the electrochemical potentials of high purity metals were determined in quiescent seawater. The data are presented as histograms and as potential time graphs. The electrochemical potentials of many of the metals varied over a broad range, and therefore it is impractical to assign a specific potential value to many of the metals. A galvanic series is included, however, based on the data obtained from the histograms. Two of the metals, bismuth and tin, had relatively stable potentials in seawater, but further experimentation indicated their unsuitability as reference electrodes to monitor cathodic protection systems on ship hulls.		

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High purity metals
Less common metals
Electrochemical potential
Histograms
Seawater
Diluted seawater
Galvanic series