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A COMPARISON OF CORROSION RATES DETERMINED BY
POLARIZATION RESISTANCE MEASUREMENTS FOR ZINC AND
CADMIUM METAL IMMERSSED IN NONSTIRRED AQUEOUS PORTLAND CEMENT SOLUTION

BY

WILLIAM JAMES MOORE, JR.
B.S.E., Florida Technological University, 1973

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Engineering
in the Graduate Studies Program of
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Orlando, Florida
1975

156684

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I wish to express my personal thanks to the many people concerned with the completion of my Master's Degree and thesis.

Special thanks are extended to Dr. Vaniah H. Baldwin who, as my thesis director, gave his time to many helpful discussions and who has greatly contributed to my understanding and knowledge of corrosion engineering. Many thanks to the other members of the committee in charge; Drs. Ronald D. Evans, David R. Jenkins and William F. Smith, for their helpful advice and encouragement.

ABSTRACT

The effect of nonstirred aqueous portland cement solution on the corrosion rates of zinc and cadmium metal using Tafel extropolation and linear polarization measurements has been investigated.

Results indicate that for the corrosion systems under investigation, zinc metal has a higher corrosion potential and lower corrosion rate than cadmium metal.

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CHAPTER I

INTRODUCTION

The most reliable method to determine the effect of corrosion on a metal is to expose the metal to the environment under its service conditions and evaluate the corrosion by weight-loss measurements. But the most reliable method is usually the slowest and most costly. It thus becomes desirable to find an alternative method of obtaining ageing data so that the results acquired in a few minutes can be used to predict the service life in years.

Because corrosion involves the destructive attack of a metal by a chemical reaction with its environment, electrochemical techniques may be used to obtain ageing data by measuring the extremely small voltage and current changes that occur over a short period of time. The data obtained can be used to measure the corrosion rate of metals in specific environments and the oxidizing power (i.e., potential) of the environment.

In the early 1960's, investigators began to use these polarization techniques in a variety of systems. Polarization methods were stimulated by the publications of Stern and Weisert¹, Stern²⁻⁴, Stern and Geary⁵, Stern and Roth⁶, Pourbaix and Vandervelden⁷, and Makrides⁸.

CHAPTER II

RESEARCH OBJECTIVE

The purpose of the conducted research was to examine the varied effects of controlled alkaline solutions on the corrosion rate of zinc and cadmium metal using the potentiostatic linear polarization and Tafel extrapolation techniques.

The results obtained are to be used to determine which of the tested metals are most desirable for use as a protective coating on steel reinforcement rods immersed in aqueous alkaline portland cement.

CHAPTER III

THEORY

Fundamentals of Polarization Measurements

The two main polarization techniques used in measuring the corrosion process are the Tafel Extrapolation and the Linear Polarization methods. Both methods are used to study metals which corrode electrochemically in a conducting solution.

Three electrodes are normally used for making polarization measurements (for a comparison of the two and three electrode systems, see Jones and Bandyopahya⁹ and Townsend¹⁰). One is called the reference electrode; the second, the sample electrode; and the third, the power electrode. The reference electrode is used as an invariant half-cell in the potential measuring circuit. The sample electrode is the electrode which undergoes corrosion. The power electrode is used to complete the current circuit in the electrolyte under test.

As the metal undergoes corrosion in an electrolyte it produces current. Electrons are freed at anodes and flow to cathodes. At the cathode surfaces the electrons are taken up by electron acceptors. Current continues to flow as long as there is a corroding metal, a conducting solution, and a continuous path for current flow.

The electrons which flow through the metal between the local anodes and cathodes constitute the corrosion current. It is impractical to insert an ammeter into this circuit and directly measure the corrosion current, but it is possible to do so indirectly by taking advantage of

the fact that there is a measurable relationship between the corrosion current and the effect of an externally applied current on the metal surface. This indirect method is the basis of the polarization technique.

In making a polarization measurement, a source of current is connected between the power electrode and the sample electrode so that the current flows through the electrolyte between the two electrodes. This current is added to the corrosion current and slightly alters the corrosion potential of the metal surface. The process of altering the surface conditions is called "polarization", and the sample electrode is said to be slightly polarized. In order to compute the amount of alteration due to the polarizing current, the sample electrode is compared to the reference electrode, which is unpolarized and at equilibrium. The comparison is made by measuring the potential of the sample electrode versus the reference electrode during the time the polarizing current is flowing between the power and sample electrodes.

In electrochemical corrosion, a high corrosion rate produces a high corrosion current, while a low rate produces a small current. Consequently, it takes a large amount of polarizing current to alter the corrosion conditions for a high corrosion rate and a smaller amount for a low corrosion rate. The total polarizing current which must be supplied by the external current source is large for large electrode areas and small for small areas. In short, the amount of polarizing current required is proportional to the amount of alteration of corrosion conditions to the surface area exposed and to the natural

corrosion rate of the sample electrode in the particular electrolyte in which measurements are taken¹¹.

Tafel Extrapolation Technique

The Tafel Extrapolation Technique is an effective electrochemical method for measuring instantaneous corrosion rates and has been used to verify the mixed-potential theory developed by Wagner and Traud¹². Stern and Geary⁵ have provided a theoretical mathematical approach which indicates that the method is fundamentally sound from an electrochemical viewpoint and is suitable for both anodic and cathodic polarization measurements¹³.

A review of the Tafel method has been provided by many authors¹³⁻¹⁵ and is based on the Tafel equation¹⁶:

$$\eta = \frac{+}{-} \beta \log \frac{i}{i_0} \quad (1)$$

In this equation η is the activation polarization caused by the slow electrode reaction; β and i_0 are constants for a given metal and environment and are both dependent on temperature; and i is the current density. The exchange current, i_0 , represents the current density equivalent to the equal forward and reverse reactions at the electrode at equilibrium. The larger the value of i_0 or the smaller the value of β , the smaller is the corresponding overvoltage¹⁷.

If the polarization voltage is plotted against the logarithm of the current density, a graph similar to Fig. 1 is observed. After a polarization of about 50 millivolts, either positive or negative, both the

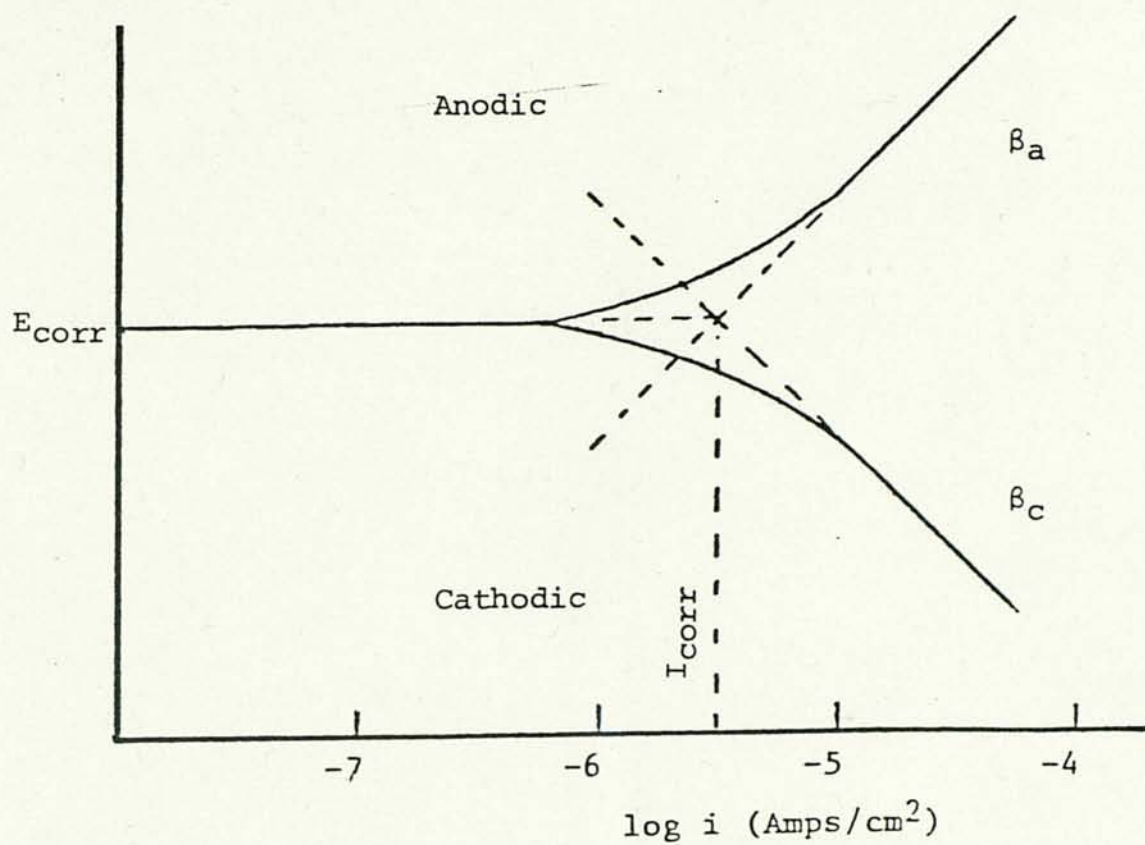


Figure 1 . Example of a Tafel plot.

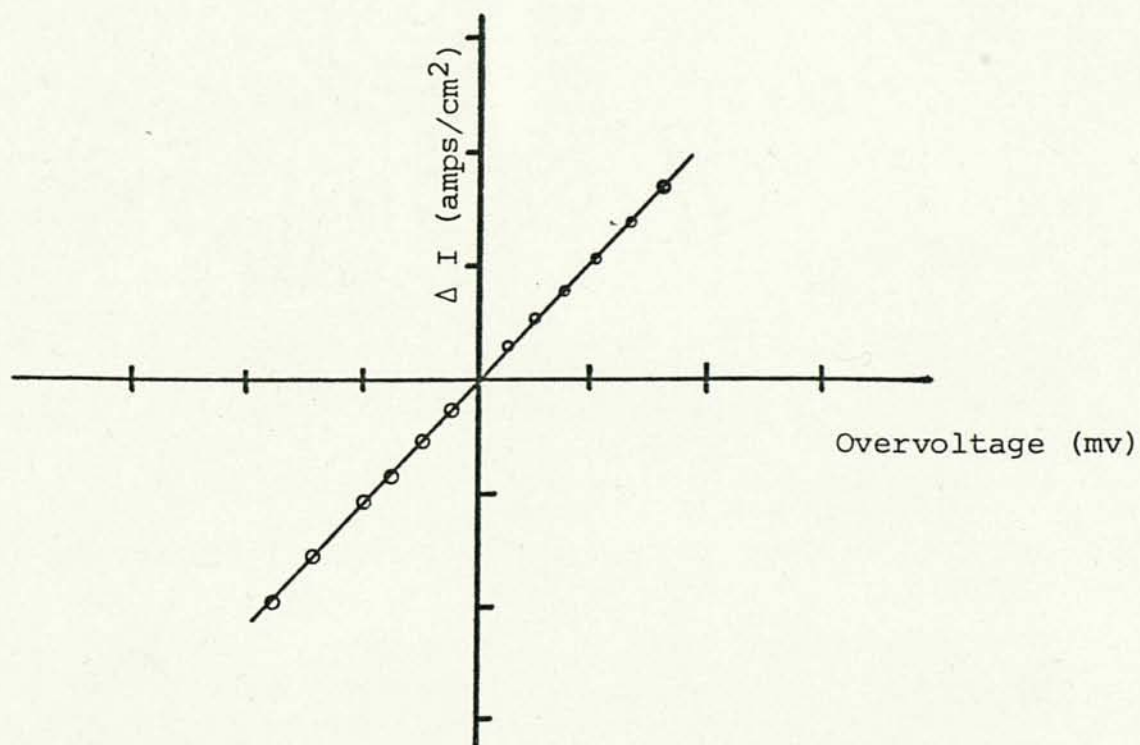


Figure 2 . Example of a linear polarization curve.

anodic and cathodic curves become straight lines in accordance with Eq. 1. The linear portion of the plot is called the Tafel Region and the slope of the line is called the Tafel Constant¹³.

The length of this straight-line segment of Tafel curves can vary from essentially nothing to three decades. The deviation from linearity at higher current densities is generally due to concentration or resistance effects⁵. Since the instantaneous corrosion rate (measured in $\mu\text{A}/\text{cm}^2$) at the corrosion potential is determined by extrapolating the Tafel line back to E_{corr} , experimental efforts are made to maximize the linear behavior. In the case of concentration polarization, stirred or flowing electrolyte tends to minimize concentration effects¹⁸.

Tafel constants are constants only for a particular system and do not vary widely from one system to another. Most systems show β_a to vary between 0.06 and 0.12 volt/decade while β_c remains essentially constant at 0.12 volt/decade¹³.

There are two main disadvantages with the Tafel extrapolation technique. First, a number of hours are required for each test. Second, the process requires that the tested sample be polarized several hundred millivolts. This extreme polarization will disturb and distort the sample electrode so that the same electrode cannot be expected to yield reliable results^{13,18}.

To ensure reasonable accuracy of the Tafel method, the slope should extend over a current range of at least one logarithmic decade. Furthermore, the method can only be applied to systems containing one

reduction process, since the Tafel region is usually distorted if more than one reduction process occurs. These difficulties can be avoided with the application of linear polarization measurements¹⁹.

Linear Polarization Technique

The disadvantages of the Tafel extrapolation method can be overcome by using the linear polarization technique. This method has provided a reliable and simple method for the determination of instantaneous corrosion rates^{5,14}.

Many successful applications have been recorded using the linear polarization method. They have included the study of inhibitors in solution²⁰ and localized corrosion²¹. Measurements have been taken in soils²², in nuclear reactor environments²³, in food products²⁴, in sea water condenser tubing²⁵, in automotive engine cooling systems²⁶, and with orthopedic implants in living tissue²⁷.

The linear polarization technique is based on the theory that within 10 to 20 millivolts of the corrosion potential, small changes in the potential of a freely corroding electrode have a linear relationship with current change and so is proportional to the corrosion current (Fig. 2). The equations which form the basis of the linear polarization theory were derived by Stern and Geary⁵ and is based on the following relationship:

$$\frac{\Delta E}{\Delta I} = \frac{1}{2.3 I_{\text{corr}}} \left(\frac{\beta_a \beta_c}{\beta_a + \beta_c} \right) \quad (2)$$

In this equation ΔE is the overvoltage of the corroding electrode produced by the polarizing current ΔI ; $\frac{\Delta E}{\Delta I}$ is the slope of the polarization curve (termed "polarization resistance"); β_a and β_c are the slopes

of the anodic and cathodic polarization curves in the Tafel region; and I_{corr} is the corrosion current. The ratio $\frac{\Delta I}{\Delta E}$ (termed "polarization admittance" by Annand²⁸) is used since this ratio is directly proportional to the corrosion current as indicated below¹⁸:

$$\frac{\Delta I}{\Delta E} = 2.3 I_{\text{corr}} \left(\frac{\beta_a + \beta_c}{\beta_a \beta_c} \right) \quad (3)$$

The theory upon which the equations are based assumes that²⁹:

1. The reaction obeys the equations derived from electrochemical kinetics for an activation-controlled process;
2. There is only a single electrochemical reaction;
3. The corrosion potential is not close to the reversible potentials of either partial reaction, so that the reverse reactions of each can be neglected;
4. Concentration polarization and ohmic voltage drops are absent or eliminated;
5. A uniform current density increases monotonically with an increase in current.

If β values of 0.12 volt/decade are assumed to represent the average of all corrosion systems, then Eq. 3 reduces to:

$$\frac{\Delta I}{\Delta E} = I_{\text{corr}} / .026 \quad (4)$$

This equation may be used to calculate the approximate corrosion rate of a system without the knowledge of its electrode-kinetic parameters. It can be applied to systems with activation or diffusion controlled ($\beta_c = \infty$) reduction reactions and yields corrosion rates differing by no more than a factor of three from the actual rates^{1,19}.

To obtain the corrosion rate in meaningful units, the current density, I_{corr} , is substituted into the following equation³⁰:

$$\text{Corrosion Rate (in mpy)} = \frac{(.129) (I_{\text{corr}}) (\text{gram eq. wt.})}{(\text{density of metal})} \quad (5)$$

Linear polarization measurements can be made even though there is a small current flowing when the electrodes are at a starting potential. The amount of current that is flowing under these conditions is considered the zero point and the change of current density from this point, when the voltage is changed ± 10 millivolts, is considered ΔI ⁹.

The linear polarization theory states that the anodic and cathodic slopes are equal. However a number of investigators³¹⁻³⁴ have found that the two slopes are not equal. The direction (cathodic or anodic) in which the linear polarization should be run has not yet been completely resolved and generally no mention is made of this in papers discussing the technique. The general impression is that the slopes should be the same¹⁸.

Values for the Tafel slopes are needed in using the linear polarization technique, but if they are unobtainable, they can be estimated. In the ASTM subcommittee tests¹⁸, a value of 0.10 for both constants was suggested. The error will usually be about 30% or less, as established by Stern and Weisert¹.

The main advantages of the linear polarization method are obvious. It permits rapid corrosion rate measurements and does not, because of the small polarization involved, disturb the corrosion system. It may be used to measure very low corrosion rates and can be used on structures which cannot be subjected to weight-loss tests^{19,35}.

CHAPTER IV

LABORATORY APPARATUS

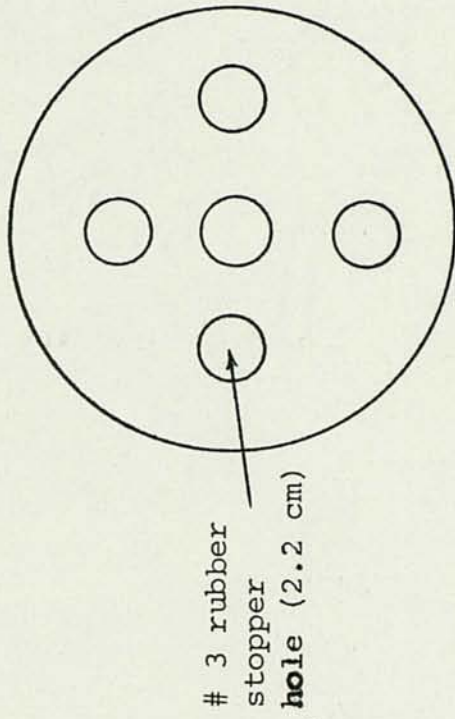
Special equipment was required in order to conduct polarization experiments. Instrumentation included the acquisition of a potentiostat, potentiometer, electrometer, digital multimeter, and construction of a polarization cell, electrode holders, and electrodes. The important characteristics of these instruments are described and discussed in Greene's³⁶ handbook on electrode kinetics.

Polarization Cell

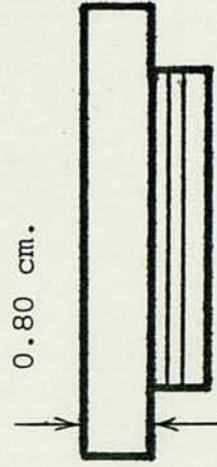
The polarization cell described within and illustrated in Fig. 3 is based on a design by Greene³⁶. Many laboratories use homemade polarization cells¹⁸ and this simple design was utilized because of its low construction cost and its ability to be used in electrochemical studies involving an alkaline media.

The constructed polarization cell was essentially a modified glass jar. The top of the jar's metal lid was removed and replaced with a plastic disk. Five symmetrical holes were drilled through the plastic disk and the electrode assembly was inserted through the holes in the disk by means of a #3 rubber stopper.

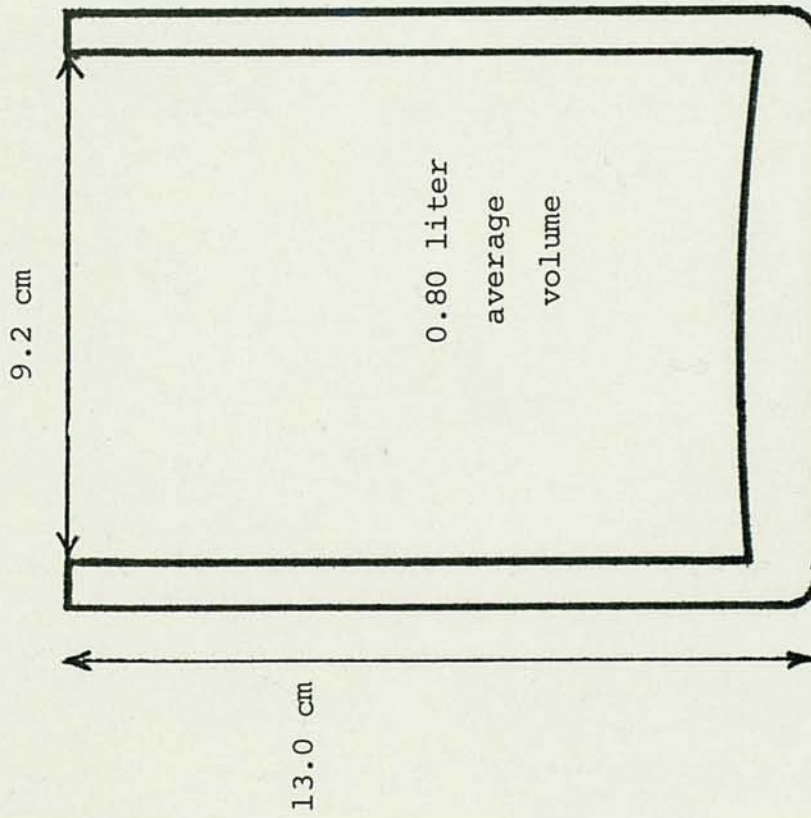
Sample electrodes were attached to a 4-40 threaded steel rod through a plastic holder and a neoprene compression gasket. Attachment was accomplished by drilling and tapping the sample electrode so that the 4-40 mounting rod made electrical contact with the electrode. Mounting



Top view of jar cover



Side view of jar cover



Side view of glass jar

Figure 3. Diagram of a polarization cell.

was accomplished by compressing the electrode against the gasket by means of an upper nut and washer assembly. Sufficient compression was applied to cause deformation of the gasket between the sample electrode and plastic holder to prevent electrolyte leakage. The easily assembled compression gasket mounting technique is a versatile electrode mounting procedure when properly assembled and has been used in a variety of specimen assemblies³⁶⁻⁴².

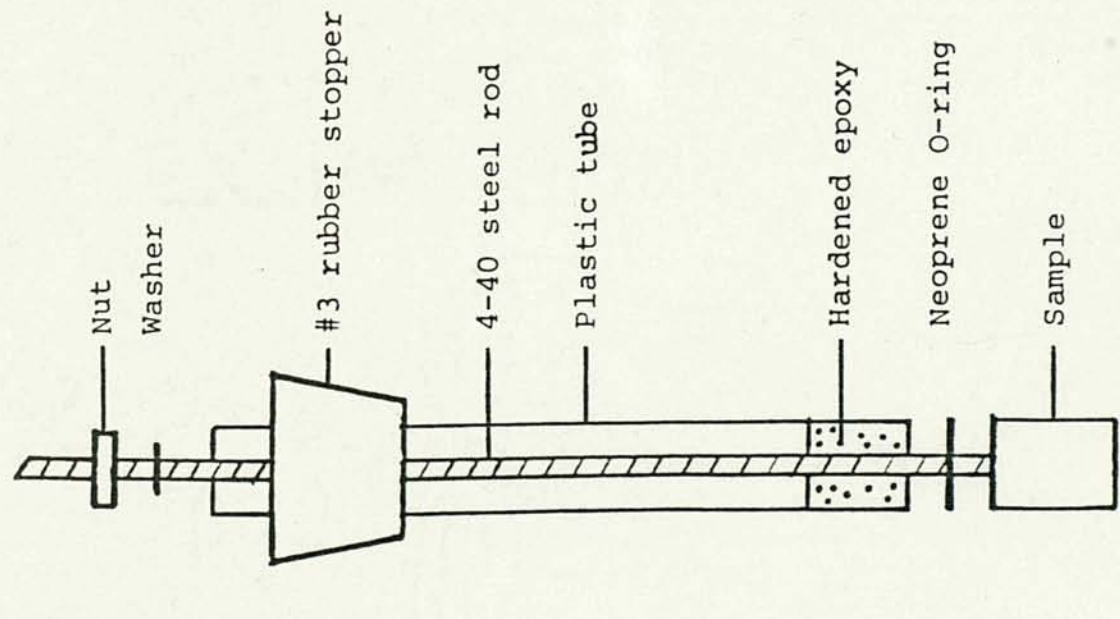
The cell atmosphere was controlled by a system of gas inlet and outlet tubes inserted through #3 rubber stoppers. If hydrogen gas was used, it was admitted continuously through the inlet tube and dispersed throughout the electrolyte by means of a fritted glass cylinder. If gas was not used, the gas inlet tube was replaced with a rubber stopper. The outlet tube was used continuously and vented directly into an exhaust fan.

Auxiliary Electrodes

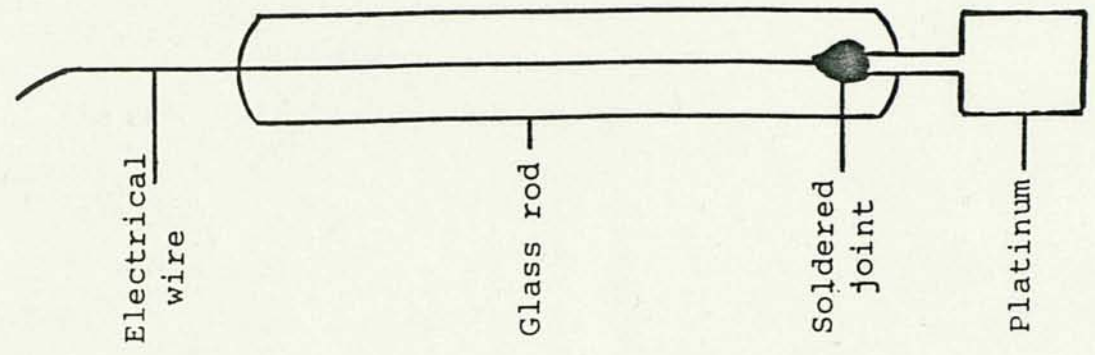
Two electrodes were constructed for use in the alkaline electrolyte. A mercury-mercuric oxide electrode was used as the reference electrode and a platinum electrode as the power electrode.

Mercury-Mercuric Oxide Electrode. This electrode was chosen because of its advantages of having a highly reproducible standard state for the metallic phase and complete freedom from any disturbing effects due to variable valency of oxide. This rugged and well behaved electrode was unlikely to disturb the pH and was confined to alkaline solutions.

No special precautions, except those needed to secure components of reasonable purity, were needed in constructing this electrode⁴³.



Sample Electrode



Platinum Electrode

Figure 4. Diagram of Sample and Platinum electrodes.

Platinum Electrode, A platinum electrode was used because of its inertness in all types of electrolytes during polarization of the sample electrode⁴³.

Sample Electrodes

Two electrodes were constructed to undergo experimentation: zinc and cadmium metal. Each metal was melted and poured into a graphite mold and upon cooling, was machined, drilled, and then tapped for insertion onto the electrode holders. Before immersion into the polarization cell, each sample electrode underwent fine grinding and polishing to remove any corrosion products built up during the test. This was followed by an etching consisting of dilute HCl and nitric acid. After rinsing in distilled water, the electrodes were placed in the polarization cell.

Zinc, Zinc was chosen as a test metal because it is one of the major metals used in combating corrosion due to its ability to galvanically protect steel and other metals. It has good resistance to attack by corrosive atmospheres, natural waters, and sea water.

The relation of impurities, crystal orientation, and pH (Fig. 5-8) on zinc to corrosion behavior has been observed in some environments and large differences in behavior in one environment have disappeared completely in another. There is a general feeling, however, that the corrosion resistance of a metal increases with increasing purity^{17,29,44-48,58}.

Cadmium. Cadmium was used because, like zinc, it is used as a protective coating. It is less resistant to town and industrial atmospheres than zinc. It is pH dependent (Fig. 9-11) and is considerably more resistant to sea

Table 1

Chemical Analysis of Samples Used *

a) Zinc

<u>As</u>	<u>Fe</u>	<u>Pb</u>
0.0000003%	0.005%	0.002%

b) Cadmium

<u>Cu</u>	<u>Pb</u>	<u>Fe</u>	<u>Zn</u>
0.001%	0.01%	0.002%	0.004%

* received from the Fisher Scientific Company ; all percentages in wt. % .

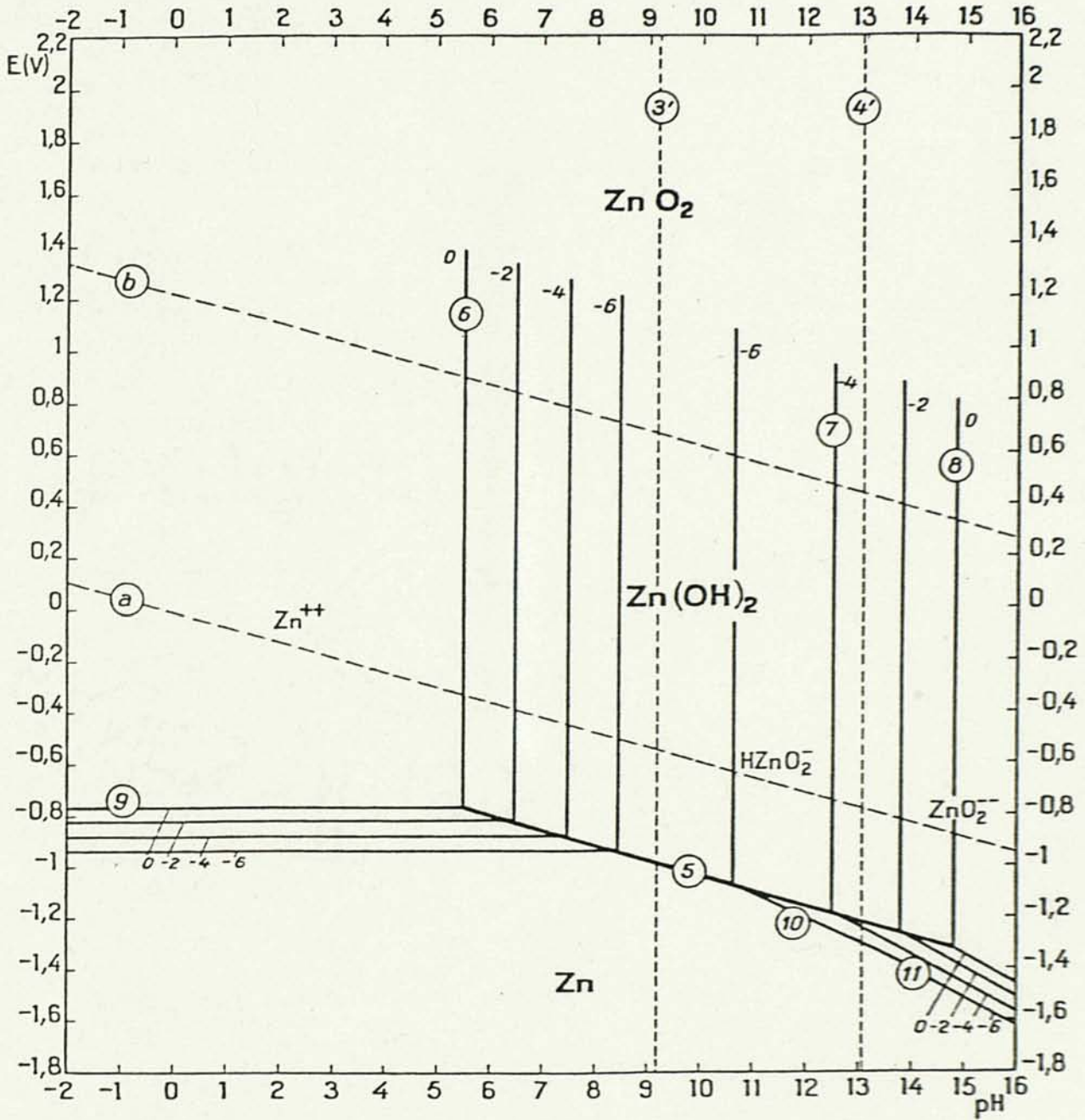


Figure 5 . Potential-pH equilibrium diagram for the system zinc-water at 25 °C [58].

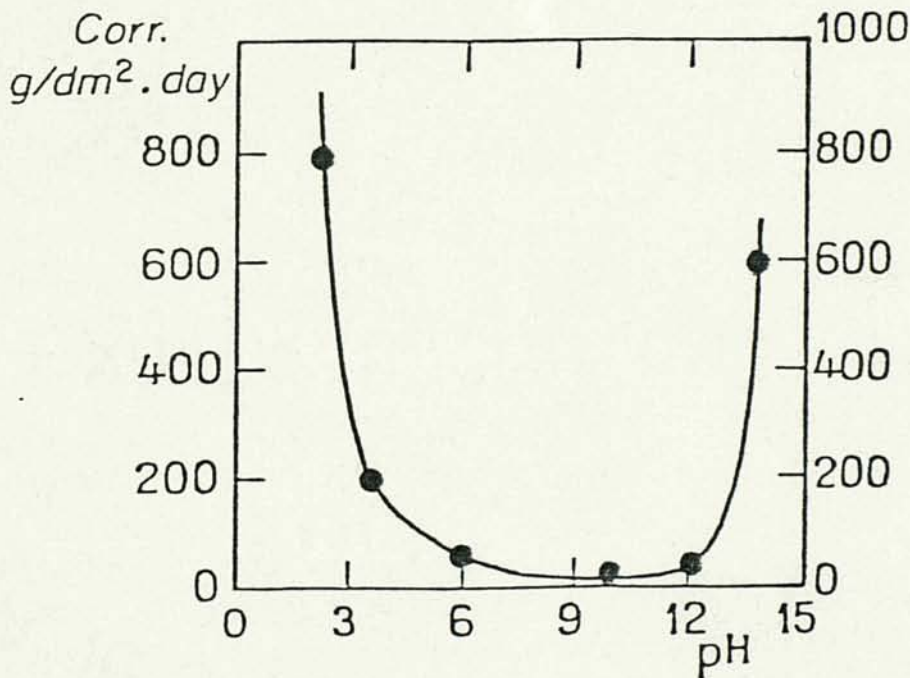
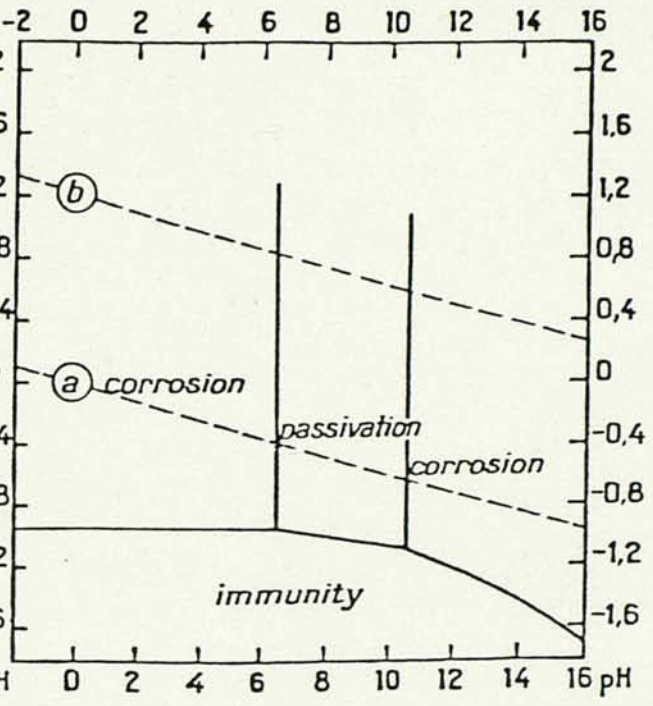
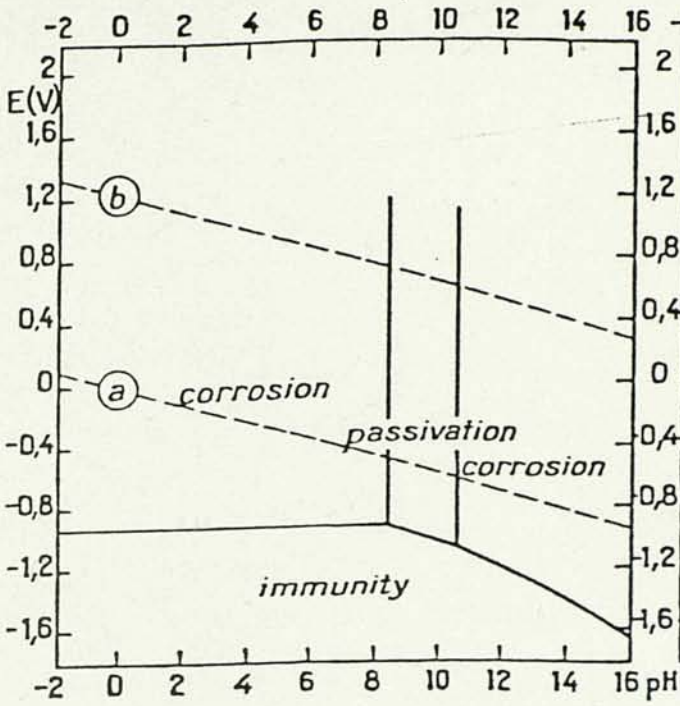


Figure 8 . Influence of pH on the corrosion rate of zinc [58].

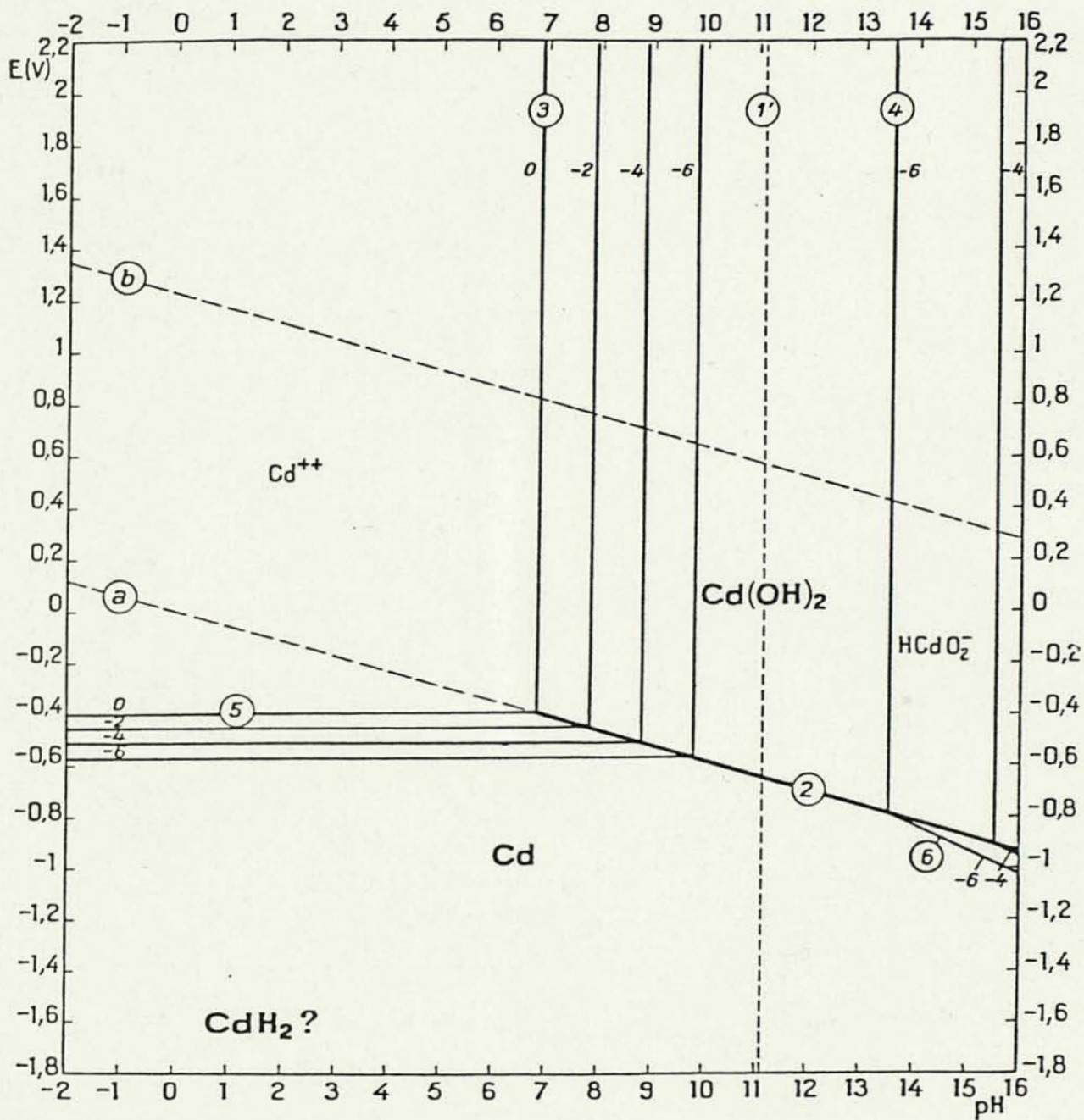


Figure 9. Potential-pH equilibrium diagram for the system cadmium-water at 25 °C [58].

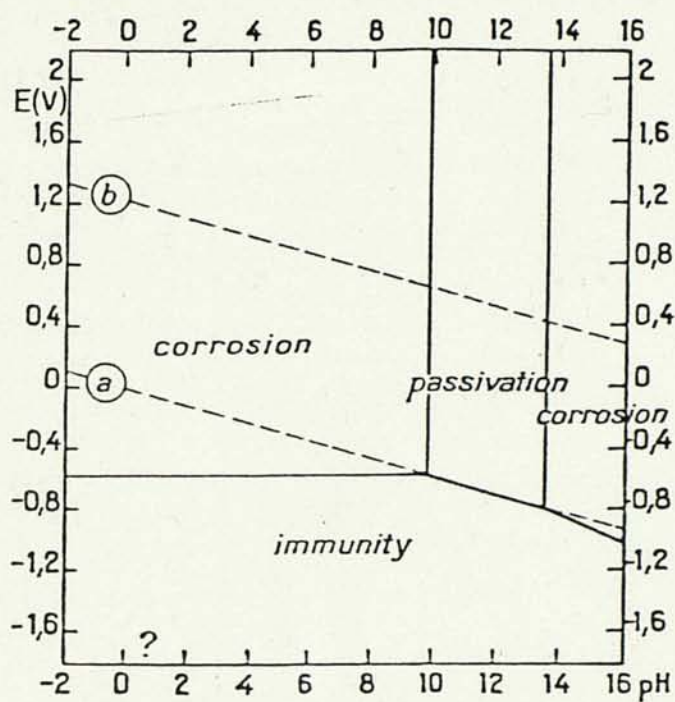


Figure 10. Theoretical conditions of corrosion, immunity, and passivation of cadmium at 25 °C [58].

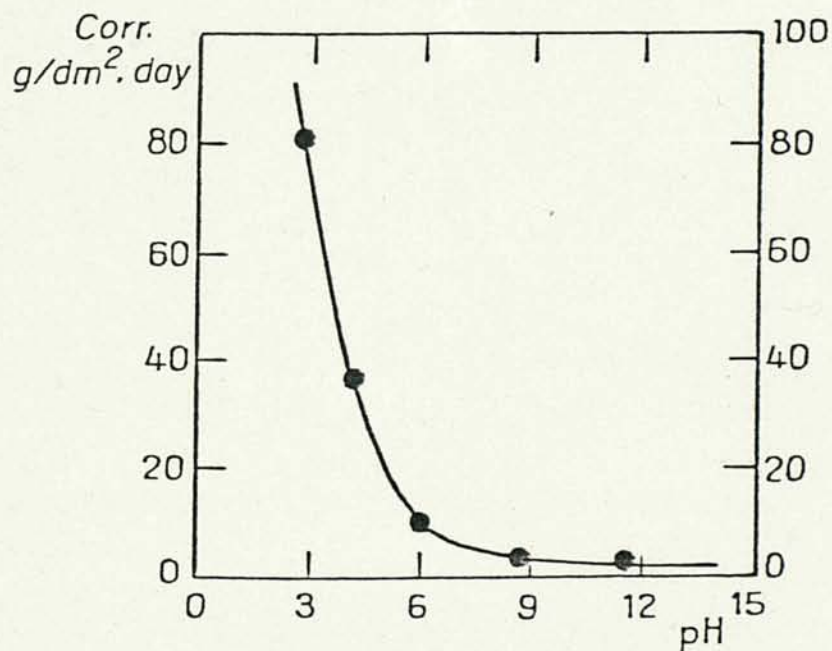


Figure 11. Influence of pH on the corrosion rate of cadmium [58].

water. In aqueous media cadmium, unlike zinc, resists attack by neutral and strong alkali solutions. This is due to the formation of a protective film of corrosion products, which unlike zinc, do not form soluble compounds with alkalis^{17,49,58}.

Cadmium is quite similar to zinc in its behavior as a corrosion resistant protective coating; however, several noteworthy differences depending on the particular environment have been reported^{18,50,51}. The protection cadmium affords steels and other materials more noble than itself depends on its sacrificial behavior^{47,52,53,59}.

Portland Cement

The majority of the electrolytes were composed of high alkaline (pH \geq 12.0) portland cement. The high alkalinity was due to the presence of calcium hydroxide and could be reduced by the addition of chlorides and by the diffusion of carbon dioxide and sulphur dioxide gas through the solution.

There are over 30 different raw materials used in the production of portland cement with each material having about five main oxide compositions. The raw materials comprising portland cement are divided into four components: lime, silica, alumina, and iron⁵⁴.

Reinforced concrete, based on portland cement, will resist corrosion of the steel reinforcement under normal service conditions, provided that the concrete is of low permeability and the steel to concrete interface is free from voids and discontinuities. When a structure is exposed to an aggressive environment, concrete will not provide adequate protection and the steel reinforcement will corrode⁵⁵.

Electrical Equipment

Because the polarization measurements were electrical in nature, precision electronic instruments had to be acquired and calibrated correctly. To eliminate drift, all electrical equipment was left running continuously during the investigation.

Potentiostat/Galvanostat. The Potentiostat/Galvanostat is a fast rise, high current instrument capable of maintaining a constant voltage across, or a constant current through, an electrochemical cell under a variety of conditions. It featured control by means of an internal control potential source as well as by an external control potential applied to two front panel inputs.

A buffer "electrometer" was attached to minimize loading on high impedance reference electrodes.

The instrument was designed to control either the current through or the potential across the polarization cell.

Electrometer. An electrometer is an electronic voltmeter with an extremely high impedance. It was used to measure the voltage between the sample and reference electrodes.

Potentiometer. A potentiometer is an accurate voltage source used to program the potentiostat when polarizing the sample electrode during linear polarization experiments.

Digital Multimeter. A digital multimeter is essentially a circuit analyzer and was used to measure the potential difference between the sample and reference electrodes.

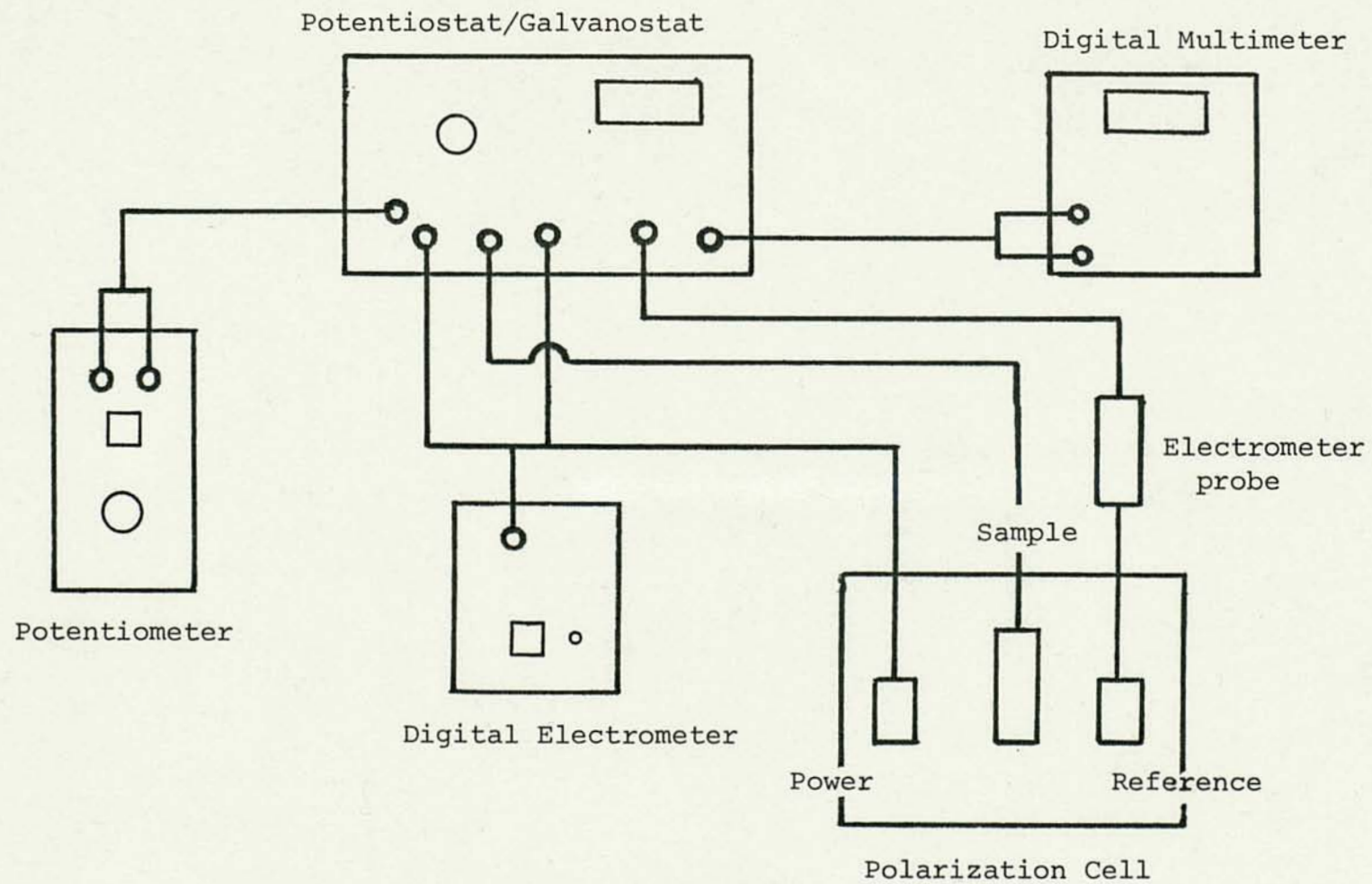


Figure 12. Schematic drawing of laboratory apparatus.

CHAPTER V

EXPERIMENTAL PROCEDURE

Since experimental procedure influences polarization characteristics^{56,57}, it was necessary to conform to a rigid procedure concerning system preparation and data recording to obtain reproducible results.

System Preparation

Cells. The polarization cell and its components were cleaned in diluted HCl and rinsed in distilled water after each experiment to remove any foreign residue.

Electrolytes. Four different types of aqueous saturated solutions were produced using calcium hydroxide or portland cement. Depending on the metal undergoing polarization, either zinc or cadmium ion (μM) was added to the solution. Unless otherwise stated, the pH of all solutions varied from 12.0 to 12.50. Cement solutions varied from 1 to 3 weeks in age. Solutions were used only once and then permanently removed from the system.

Calcium Hydroxide Solution. Saturated $\text{Ca}(\text{OH})_2$ solution was prepared with boiled distilled water and stored in Pyrex glass containers. Since oxygen contributes one more redox system to the data analysis, it was removed by purging continuously for 24 hours with hydrogen.

Deaerated Cement Solution. Deaerated cement solution was prepared from distilled water and portland cement. The solution was constantly

stirred for over 24 hours, purged with hydrogen gas, and stored in a Pyrex glass container.

Aerated Cement Solution. Aerated cement solution was prepared in the same manner as that of the deaerated solution. It was then aerated continuously with oxygen gas for over 24 hours and stored in a polyethylene container.

Aerated Cl^- Cement Solution. Aerated Cl^- cement solution was prepared and stored in the same manner as that of the aerated cement solution with the exception of an addition of 0.325 wt-% Cl^- ions.

Data Recording

Before the potentiostatic polarization technique was applied the polarization cell assembly was connected into the electronic component system and left to equilibrate for 24 hours.

The linear polarization technique was applied anodically and then cathodically at a rate of 0.20 millivolts per 25 seconds for ± 5.0 millivolts.

After completion of the linear polarization method, the system was allowed to equilibrate for 24 hours before undergoing the Tafel extrapolation technique.

The Tafel extrapolation method was applied in the same manner as the linear polarization method at a rate of 20 millivolts per 25 seconds for ± 500 millivolts.

Constant stirring was applied continuously for the zinc immersed in calcium hydroxide and intermittently for the zinc in deaerated cement solution. The data was recorded manually.

CHAPTER VI
TEST CONDITIONS

The experimental tests were conducted under carefully controlled laboratory conditions in order to predict corrosion behavior under roughly similar circumstances. The results from these short term electrochemical corrosion tests do not represent or reproduce actual service conditions and therefore the conclusions based upon the experimental data are only qualitative and approximate.

Among the testing parameters under control were aeration time (24 hours), equilibration time (24 hours), test duration, temperature (25°C), velocity, and pressure of the gas above the electrolytes.

CHAPTER VII

TEST RESULTS AND DISCUSSION

The results of the completed tests on the forementioned corrosion systems are shown in Fig. 13 through 24 and are summarized in Table 2.

Zinc in Calcium Hydroxide Solution

The results of the Tafel plot of zinc immersed in stirred, deaerated calcium hydroxide solution are shown in Fig. 13. The corrosion potential (E_{corr}) was found to be -1.170 S.H.E. volts. A slope of 0.025 volts/decade was observed in the anodic region of the curve between 2.0×10^{-3} and 8.0×10^{-3} Amps/cm². A cathodic slope of 0.02 volts/decade was noticed between 3×10^{-5} and 2×10^{-4} Amps/cm². Passivation in the anodic region occurred at a value of +140 mV from the corrosion potential while cathodic passivation was observed -90 mV from E_{corr} and these passivation regions are in agreement with the 3' and 4' lines on Fig. 5, i.e., ZnO_2 and Zn(OH)_2 formation.

The linear polarization plot showed an average slope of 833.33 $\mu\text{A/volt-cm}^2$. A corrosion rate of 2.36 mpy was obtained with a maximum rate of 5.02 mpy occurring in a few samples.

Zinc in Deaerated Cement Solution

The polarization plots of zinc in nonstirred cement solution are shown in Fig. 15 and 16. This system showed the most unstable conditions of any cement system undergoing testing. It can be seen from the Tafel plot that the corrosion system hardly follows the Tafel equation. With

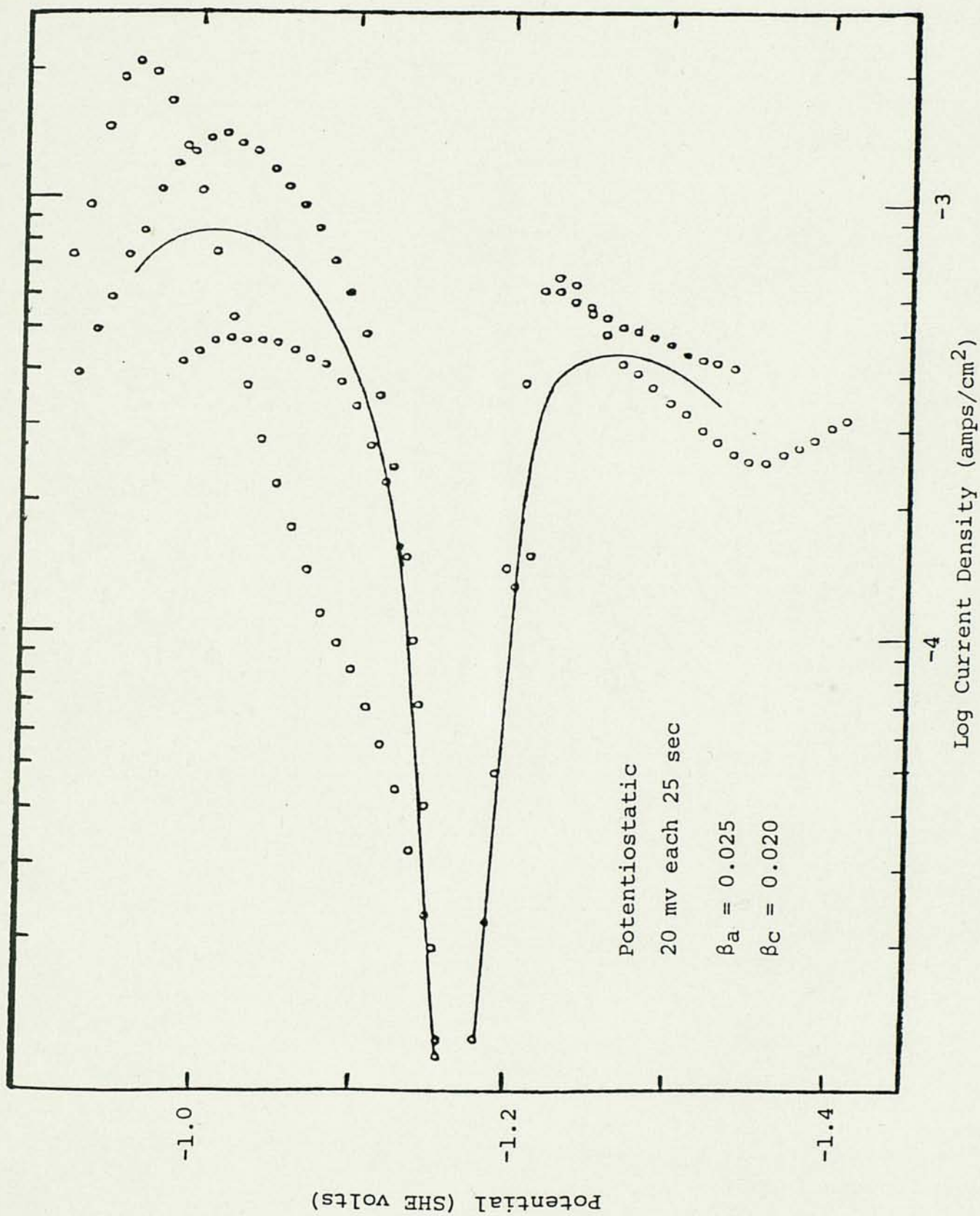


Figure 13 . Tafel plot of zinc in calcium hydroxide solution.

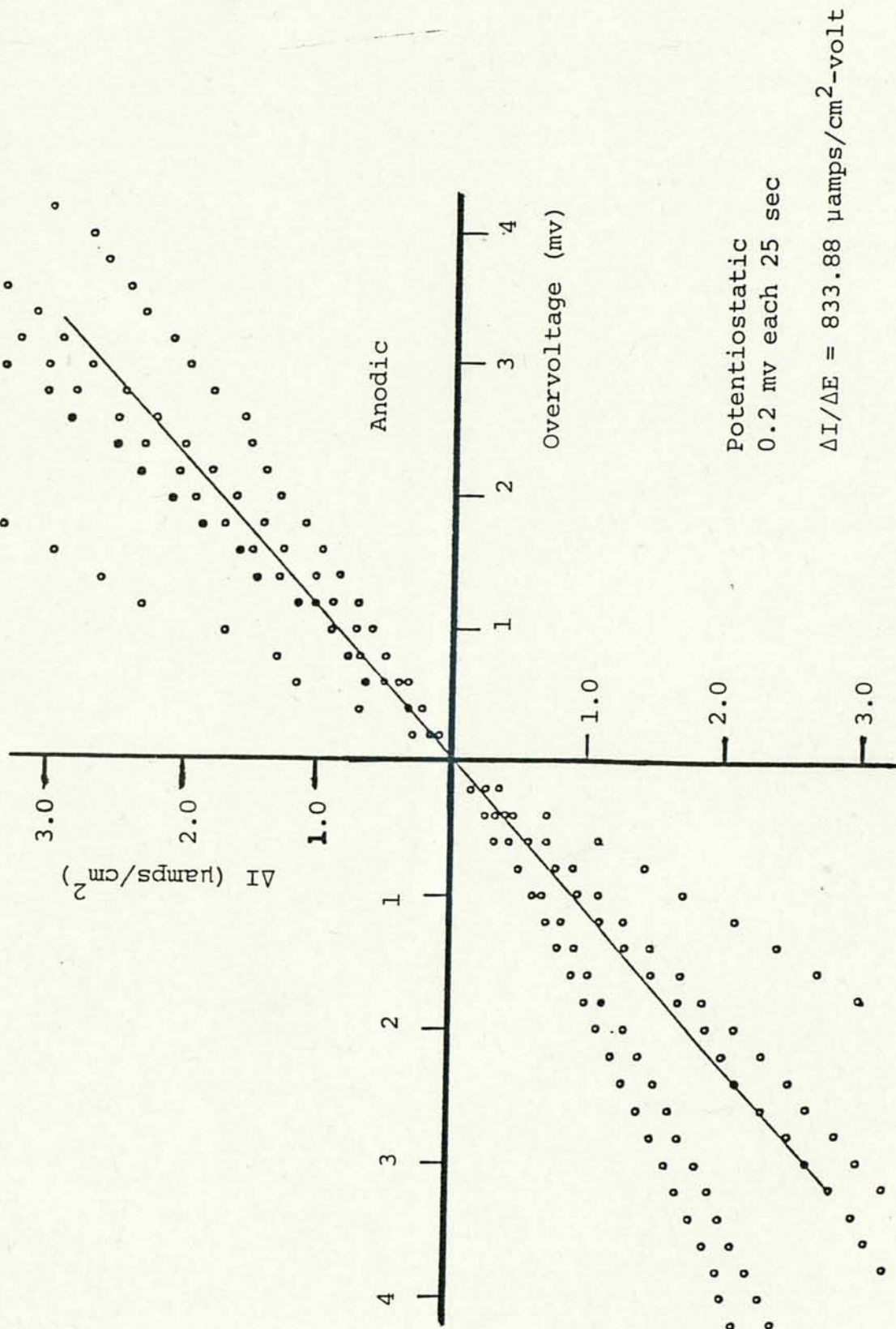


Figure 14 . Linear polarization curve of zinc in calcium hydroxide solution.

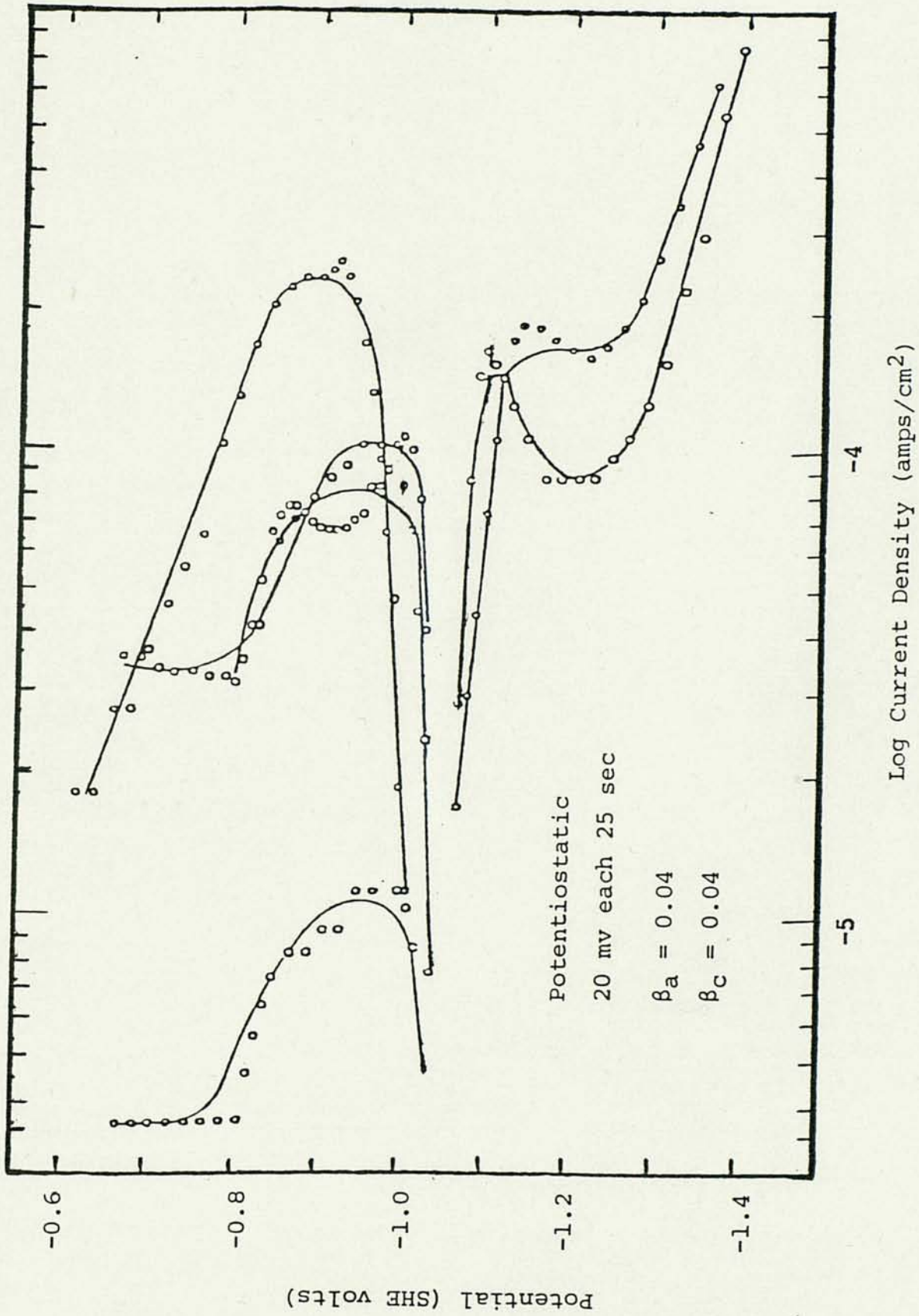


Figure 15 . Tafel plot of zinc in deaerated cement solution.

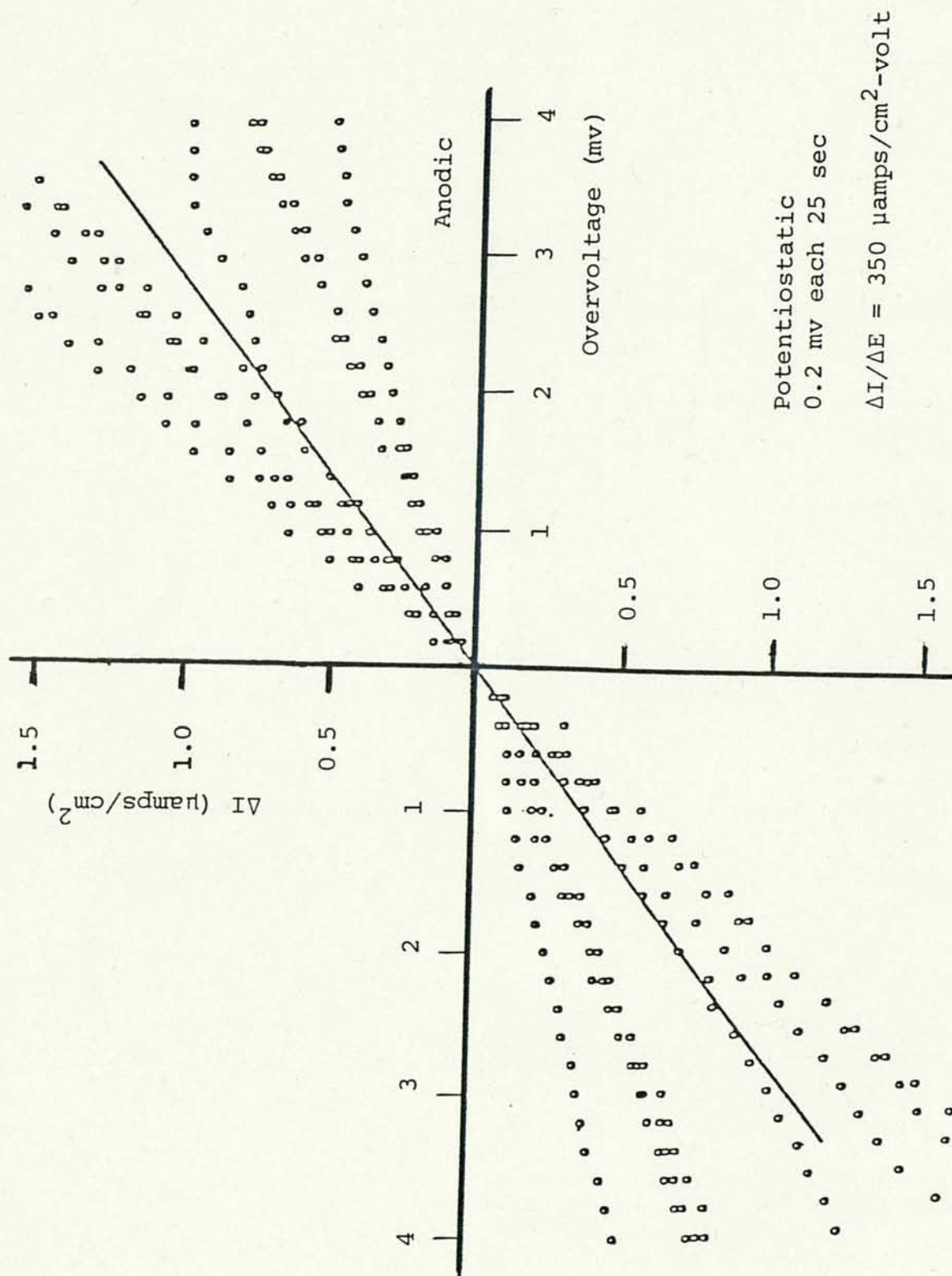


Figure 16 . Linear polarization curve of zinc in deaerated cement solution.

a corrosion potential of -1.02 S.H.E. volts, passivation takes place rapidly in the anodic region. Before passivation an average slope of 0.04 volts/decade was obtained. Passivation in the cathodic region did not take place as rapidly, obtaining an average slope of 0.04 between 2.5×10^{-5} and 9.0×10^{-4} Amps/cm².

The linear polarization curve indicates a slope of $350 \mu\text{A/volt-cm}^2$, corresponding to a corrosion rate of 1.80 mpy.

Zinc in Aereated Cement Solution

A corrosion potential of -0.650 S.H.E. volts was observed for zinc in nonstirred aereated cement solution. Anodic linearity in the Tafel region was noticed over 1.50 decades of current density with a slope of 0.06 volts/decade. A range of curvature was observed in the cathodic region. A slope of 0.270 volts/decade was obtained between 1.0×10^{-6} and 2.0×10^{-6} Amps/cm². Passivation in the anodic region began at -0.40 S.H.E. volts while no passivation was noticed in the cathodic region.

The effects of the linear polarization technique are shown in Fig. 18. A slope of $5.0 \mu\text{A/volt-cm}^2$ was obtained corresponding to a corrosion rate of 0.063 mpy.

Zinc in Aerated Cl⁻ Cement Solution

The effects of the addition of 0.325 wt.% Cl⁻ on zinc in nonstirred aerated cement solution can be seen in Fig. 19 and 20. With a corrosion potential of -0.710 S.H.E. volts, an anodic slope of 0.60 volts/decade was obtained between 5.50×10^{-4} and 8.0×10^{-4} Amps/cm².

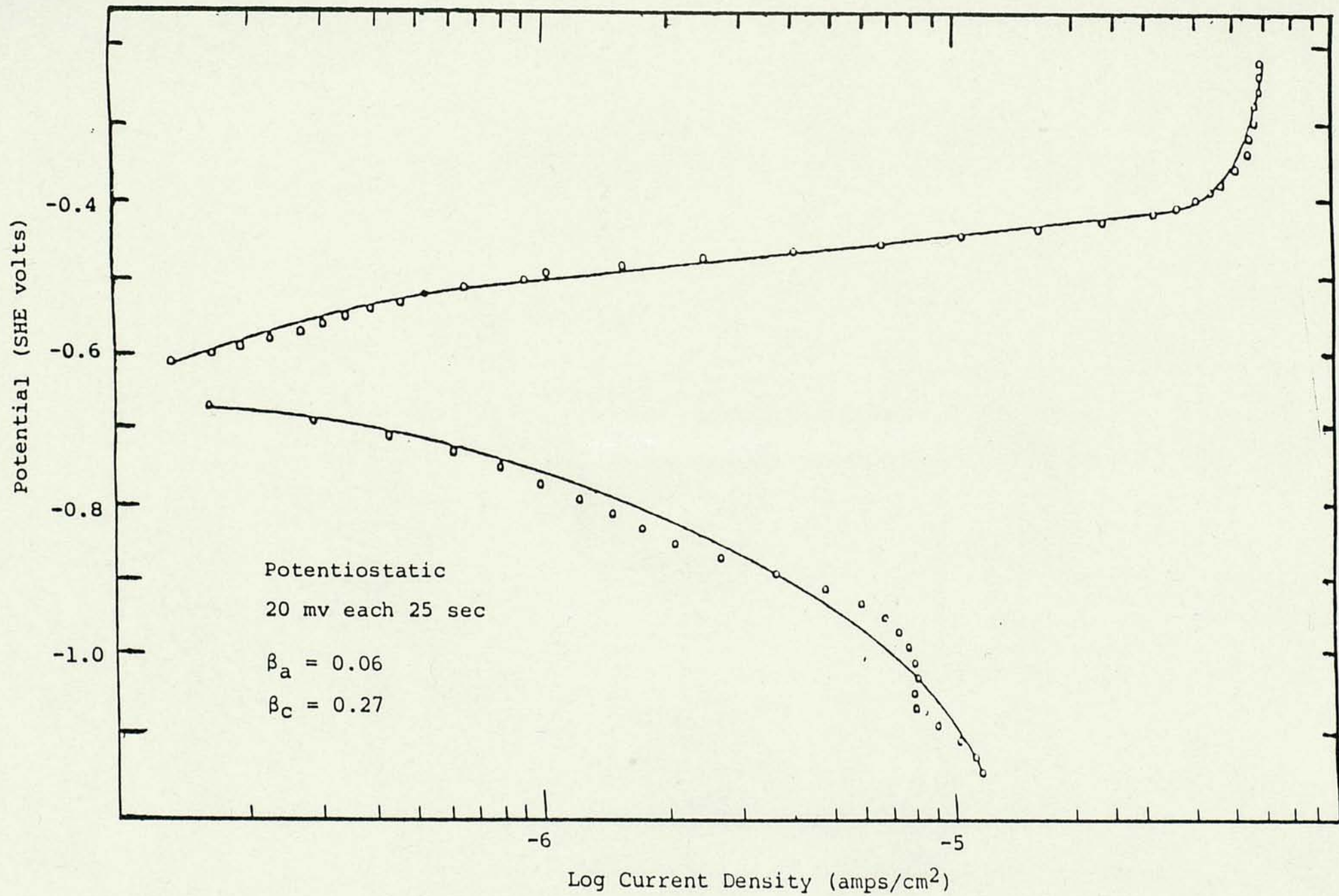


Figure 17. Tafel plot of zinc in aerated cement solution.

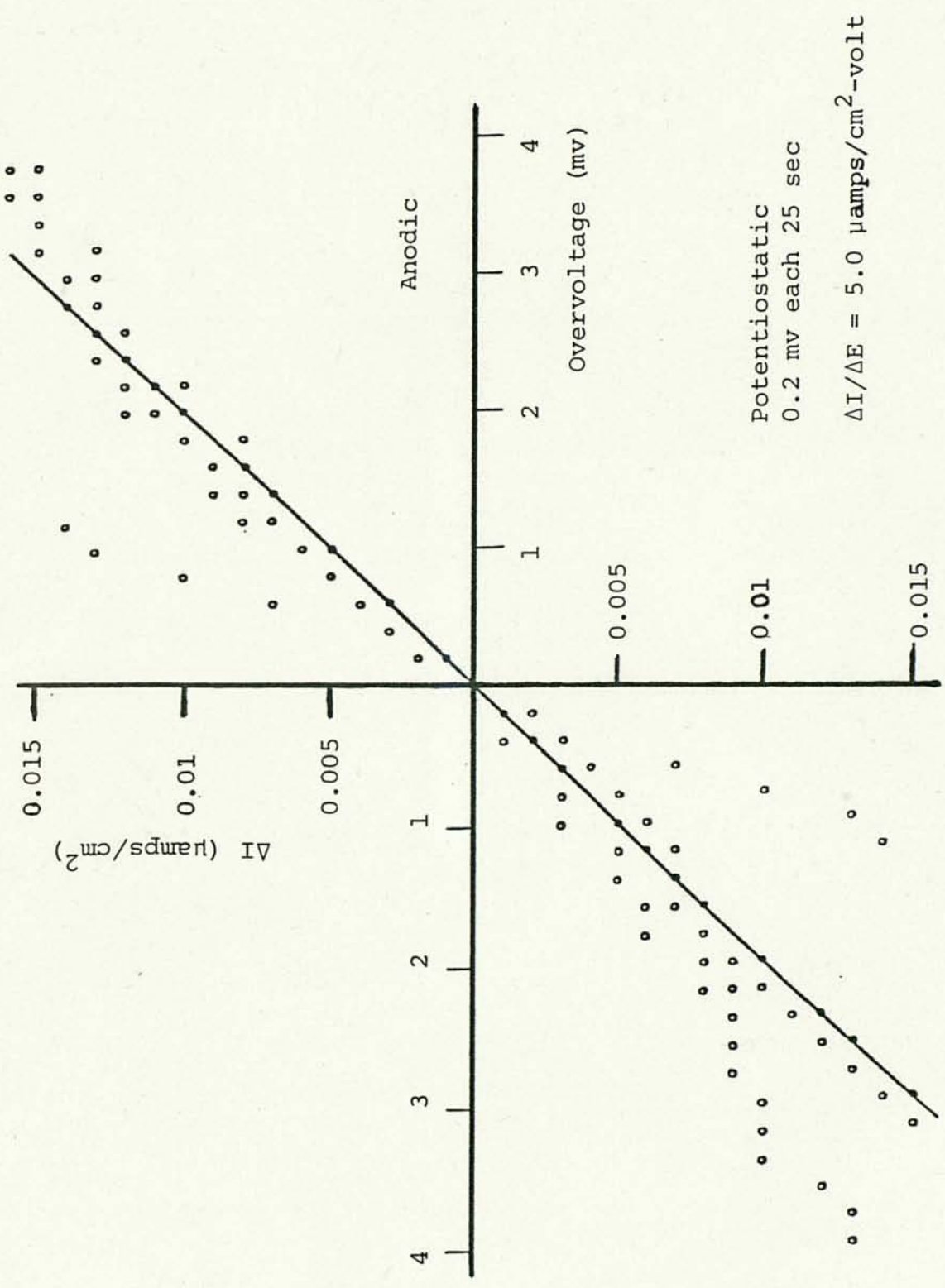


Figure 18 . Linear polarization of zinc in aerated cement solution.

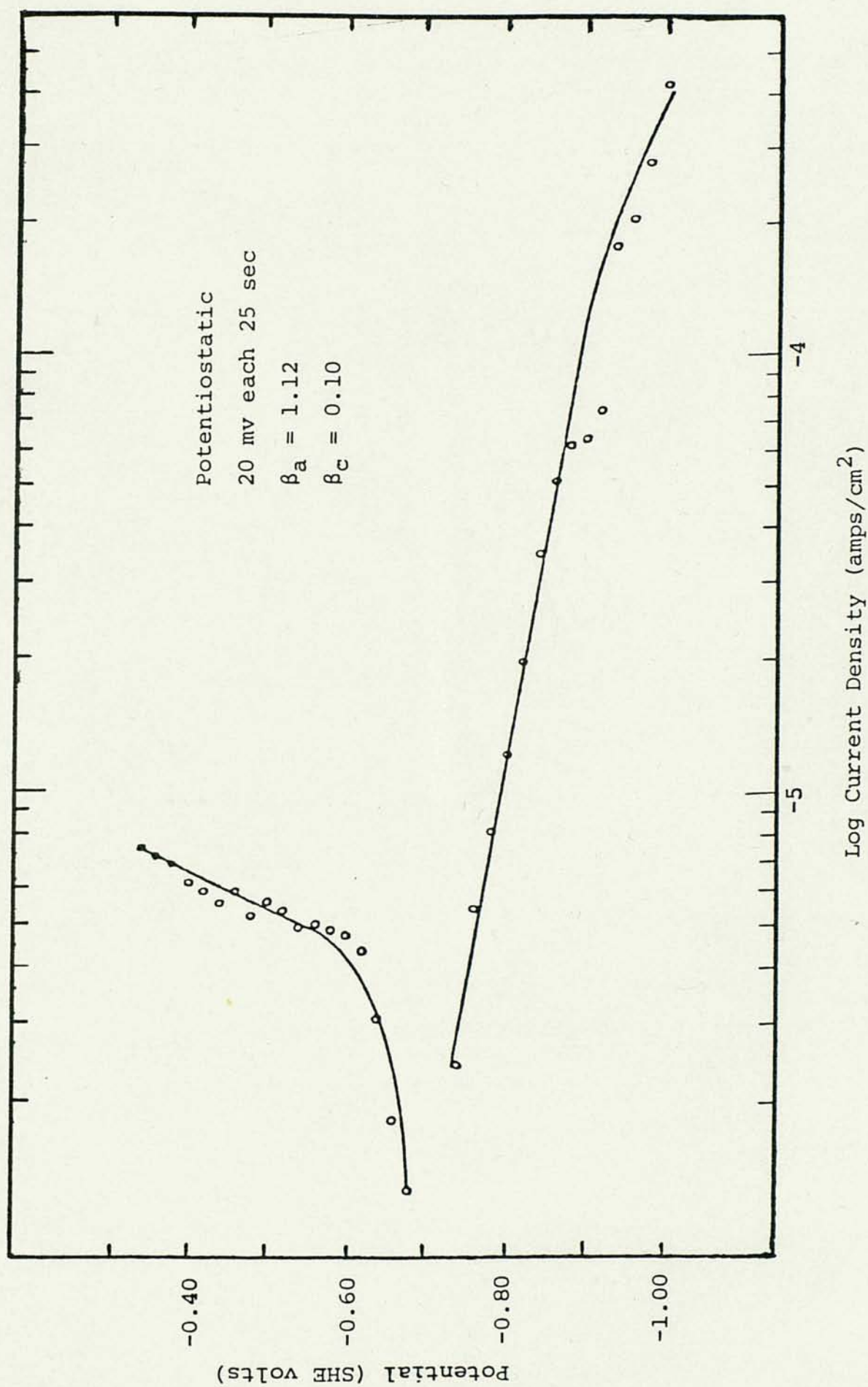


Figure 19 . Tafel plot of zinc in aerated Cl⁻ cement solution.

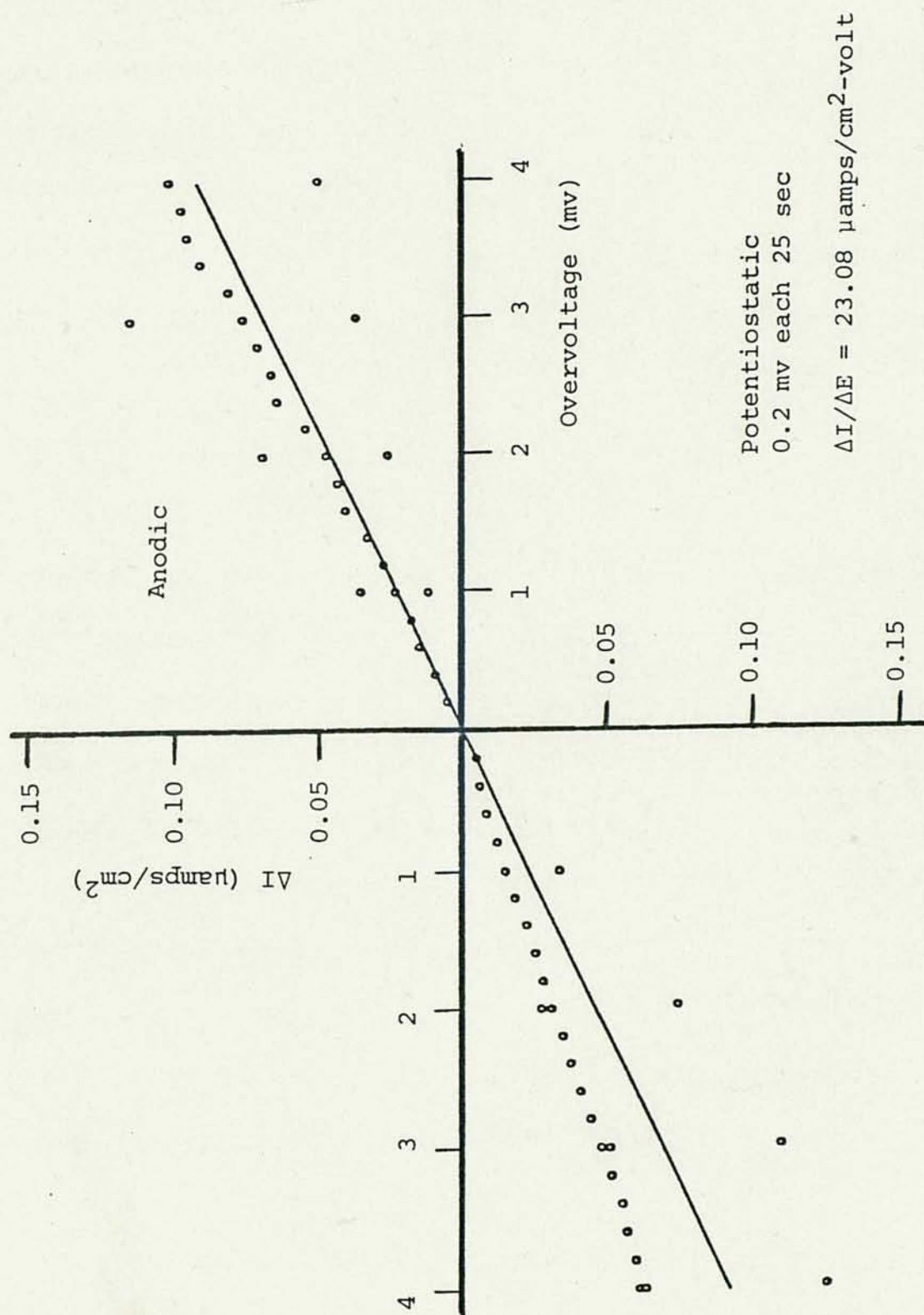


Figure 20 . Linear polarization curve of zinc in aerated Cl^- cement solution.

The cathodic curve showed linearity for over 1.50 decades of current density. A slope of 0.10 was obtained through this linear region. There was no indication of passivation in either region for ± 300 mV from the corrosion potential.

The linear polarization plot reveals an average slope of 23.077 $\mu\text{A}/\text{volt}\cdot\text{cm}^2$. The corrosion was calculated to be 0.54 mpy.

Cadmium in Aerated Cement Solution

The results of the Tafel plot of cadmium immersed in nonstirred aerated cement solution are shown in Fig. 21. The equilibrium corrosion potential was -0.560 S.H.E. volts. About $+100$ mV from E_{corr} the anodic curve exhibited a one decade of measurement linearity in accordance with the Tafel equation. The cathodic curve was linear for 1.5 decades of measurement but did not exhibit Tafel behavior. Tafel slopes were found to be $\beta_a = 0.770$ and $\beta_c = 0.080$. There was no indication of passivation in the anodic region for over $+600$ mV from E_{corr} and in the cathodic region for over -100 mV.

The linear polarization results produce an average slope of 17.86 $\mu\text{A}/\text{volt}\cdot\text{cm}^2$ with a corrosion rate of 0.472 mpy.

Cadmium in Aerated Cl^- Cement Solution

The effects of the addition of 0.325 wt.% Cl^- on cadmium in nonstirred aerated cement solution are shown in Fig. 23 and 24. The corrosion potential was observed at -0.260 S.H.E. volts. The anodic slope of 0.64 volt/decade was linear from 9.0×10^{-7} to 1.40×10^{-6} Amps/cm^2 . The cathodic slope of 0.40 volt/decade was linear between

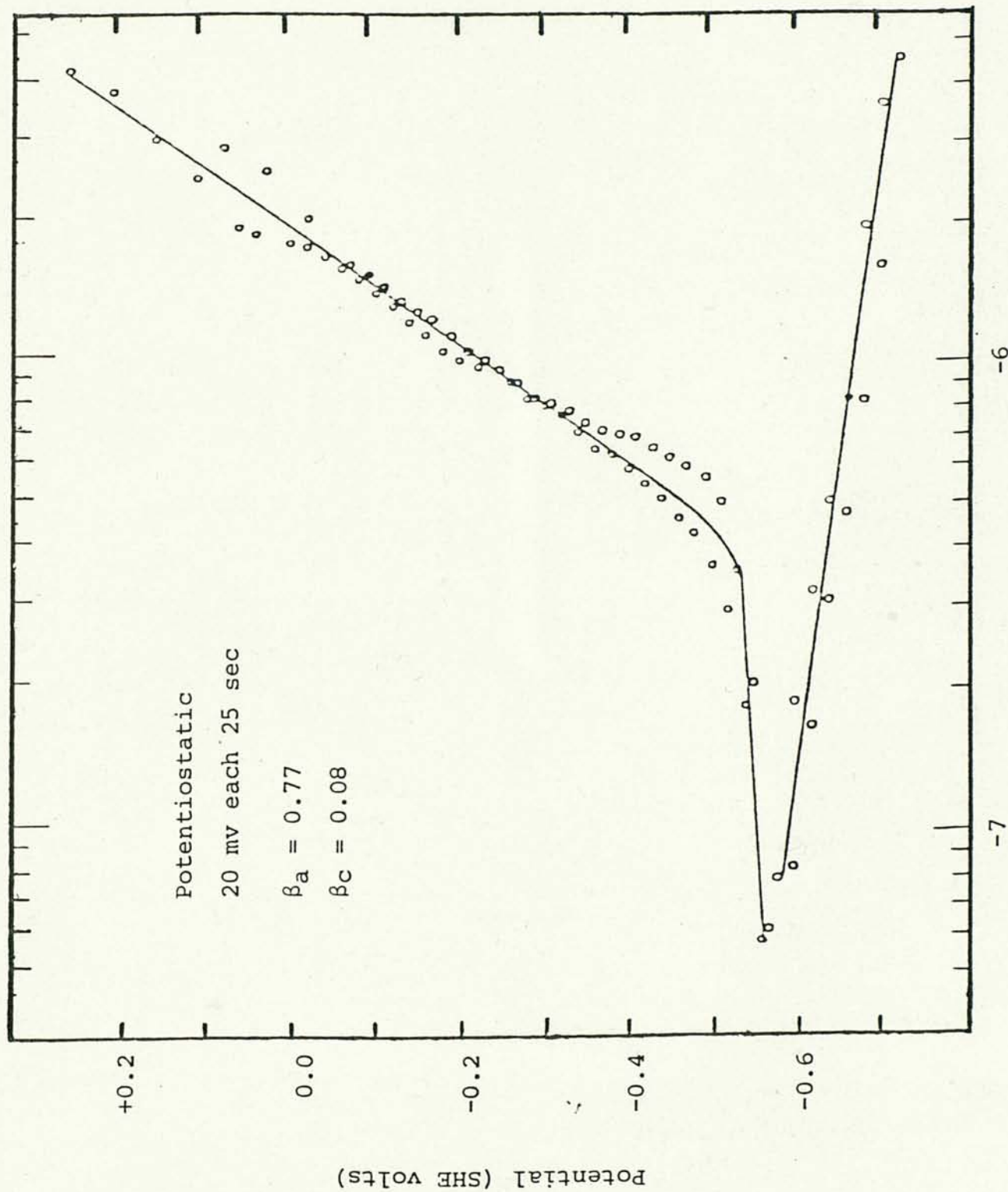


Figure 21. Tafel plot of cadmium in aerated cement solution.

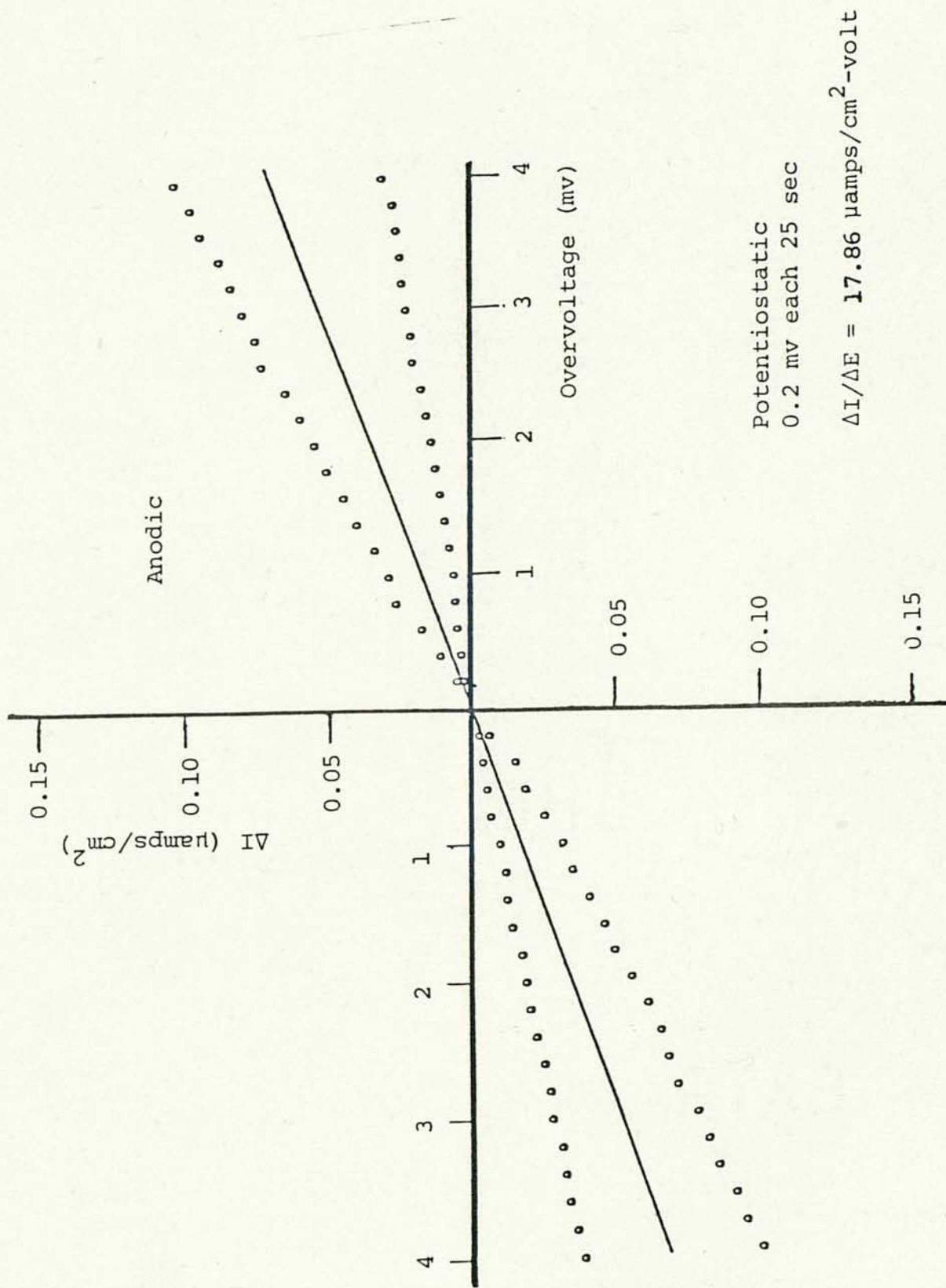


Figure 22. Linear polarization curve of cadmium in aerated cement solution.

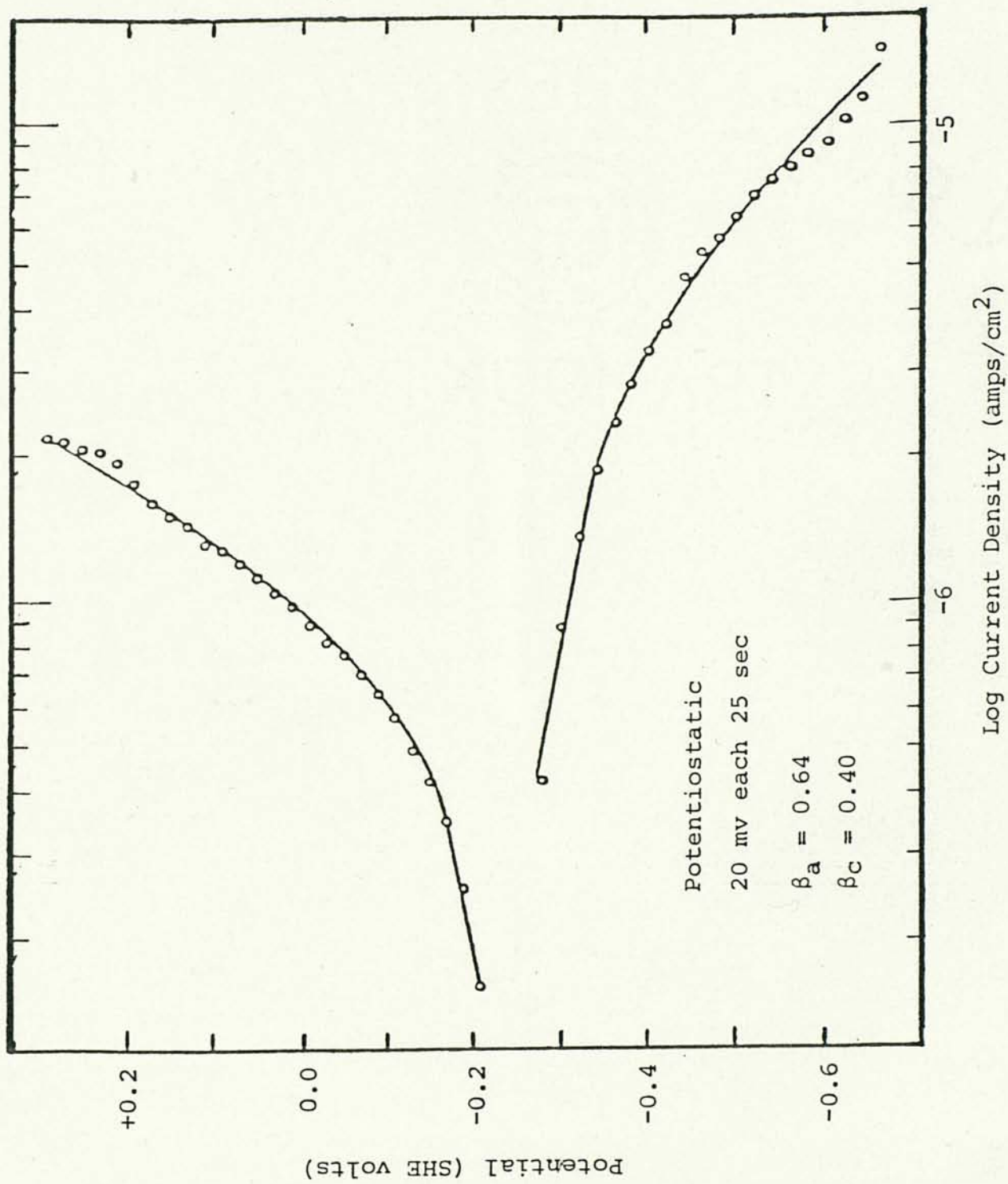


Figure 23. Tafel plot of cadmium in aerated Cl⁻ cement solution.

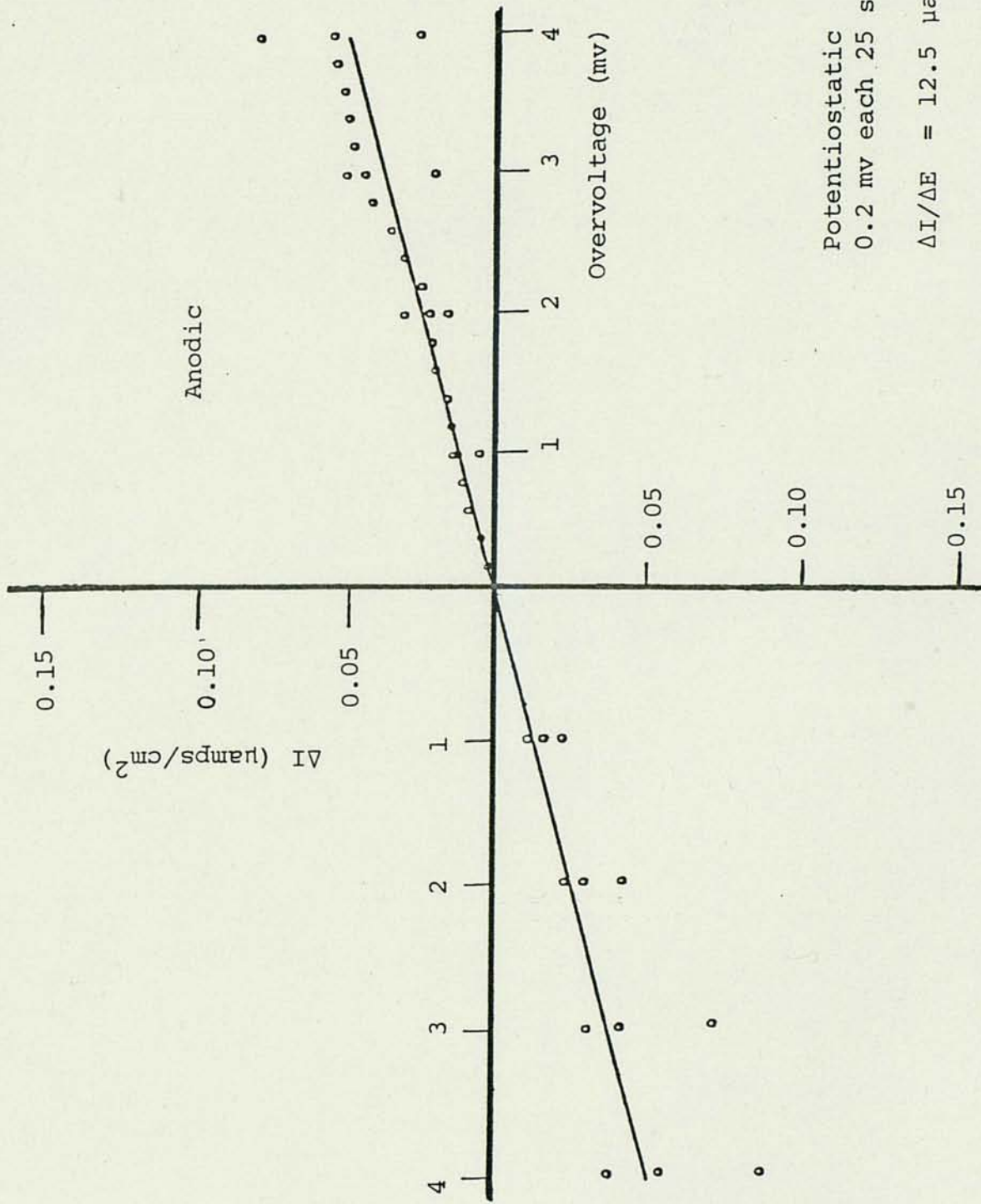


Figure 24. Linear polarization curve of cadmium in aerated Cl^- cement solution.

4.50×10^{-6} and 7.20×10^{-6} Amps/cm². There was no indication of passivation with a \pm 200 mV polarization from E_{corr} .

The linear polarization plot reveals an average slope of 12.50 $\mu\text{A/volt-cm}^2$ with a corrosion rate of 1.12 mpy was obtained.

Table 2

Summary of Experimental Data

ZINC in :	E_{corr} (SHE volts)	I/E (Amps/volt-cm ²)	NPY		Assumed $\beta_a = \beta_c = .12$	Average Area (cm ²)
			Average	Maximum		
CaOH Soln.	- 1.17	833.33	2.36	5.02	12.80	8.42 ± 1.84
Deaerated cement soln.	- 1.02	350.00	1.80	3.01	5.58	9.99 ± 0.68
Aerated Cl ⁻ cement soln.	- 0.71	23.08	0.55	0.84	0.35	6.59 ± 0.93
Aerated cement soln.	- 0.65	5.00	0.063	1.47	0.77	7.88 ± 1.16
CADMIUM in :						
Aerated Cl ⁻ cement soln.	- 0.26	12.50	1.12	1.62	0.27	7.67 ± 0.70
Aerated cement soln.	- 0.56	17.86	0.47	0.78	0.39	7.51 ± 0.76

CHAPTER VIII

CONCLUSIONS

1. The experimental data reveals that the corrosion potential, E_{corr} , and the corrosion rate are higher in the homogeneous calcium hydroxide solution than in the heterogeneous cement solution. This is probably due to the presence of silicates in the cement (phosphates are known inhibitors and silicates likewise form insoluble compounds).
2. A variation in the velocity of the electrolyte was studied only on zinc immersed in deaerated cement solution. The differences noted were that E_{corr} in the stirred solution was lower than that in the unstirred solution and that the stirred solution was more unstable than the unstirred solution.
3. The Tafel curves of the corrosion systems under study did not exhibit "pure" Tafel equation behavior and it was not possible to calculate the corrosion rates solely on the basis of these curves.
4. The majority of the laboratory corrosion rates are in agreement within a factor of three with assumed corrosion rates" ($\beta_a = \beta_c = 0.12$ volt/decade).
5. There was no indication that the sample electrode area or the age of the saturated cement had any effect on the corrosion rates.
6. The addition of Cl^- in aerated cement had the effect of increasing E_{corr} and the corrosion rate in zinc while lowering E_{corr} and increasing the corrosion rate in cadmium.

CHAPTER IX

RECOMMENDATIONS FOR FURTHER STUDY

The stability of the unstirred cement systems indicate that more research should be undertaken as to its effect upon corrosion rate.

The linear polarization technique might be applied directly to steel reinforcement rods encased in curing concrete. With automation of this technique, the corrosion rate could be recorded as a function of time.

The effect of the addition of inhibitors on cement should be undertaken.

FOOTNOTES

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