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CORROSION CONTROL IN CIVIL WORKS: CATHODIC PROTECTION.(U)
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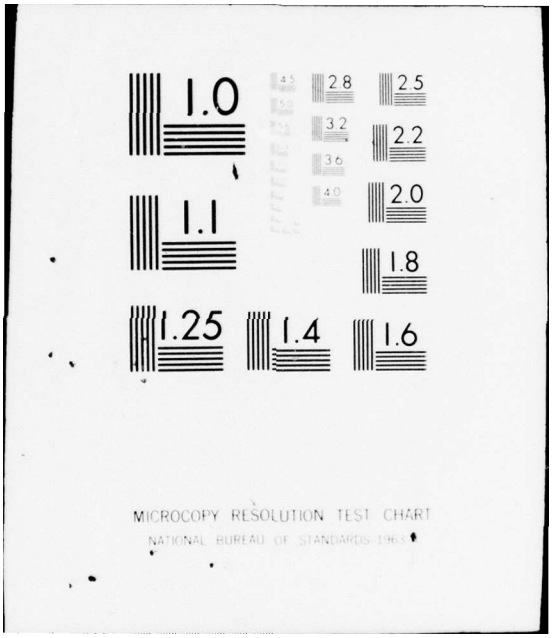
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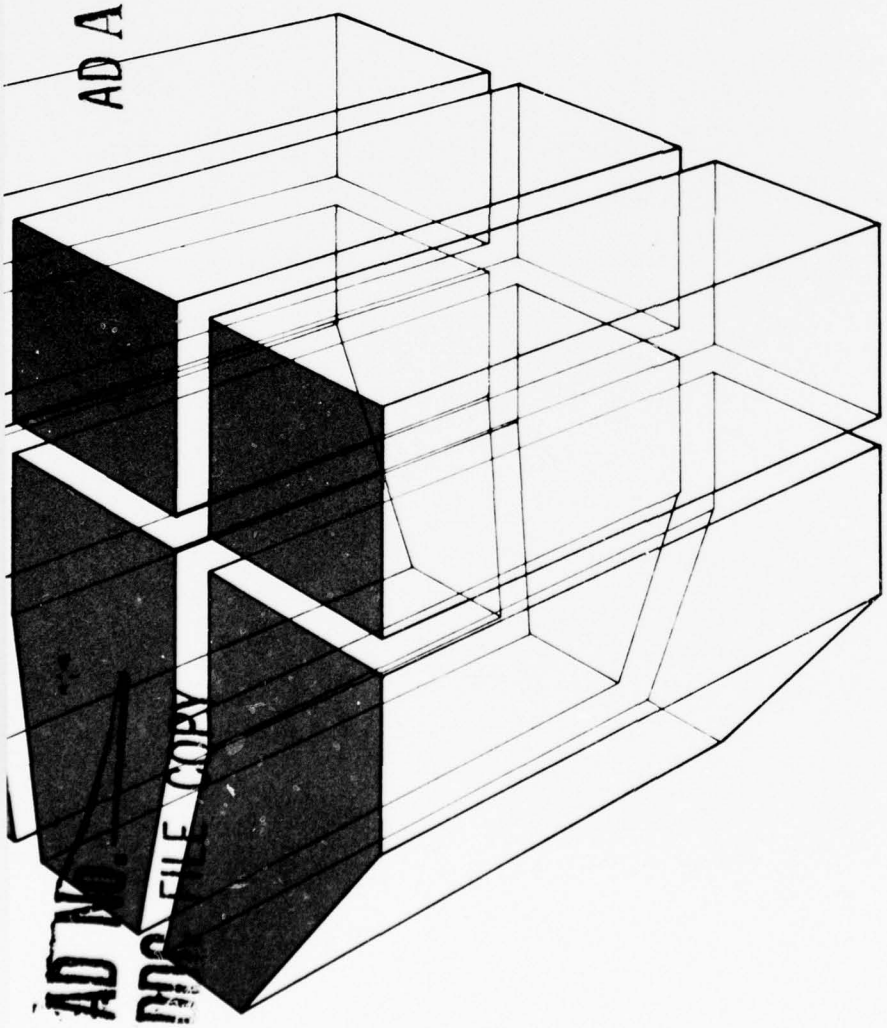

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This report presents the initial results of a study being conducted to mitigate corrosion in Corps of Engineers civil works structures. This phase of the study dealt with specific aspects of cathodic protection.

Basic electrochemical principles and cathodic protection experiments particularly germane to civil works problems are discussed, and an innovative investigation of

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cathodic protection current distribution using the continuum features of electric field analysis is presented. Recently developed automatic controlled rectifiers are analyzed, and their control response measured for applications involving brackish water. Guidelines for application of cathodic protection principles to system design are also presented.

FOREWORD

This study was conducted for the Directorate of Civil Works, Office of the Chief of Engineers (OCE), under CWIS 31204, "Corrosion Mitigation in Civil Works Projects." The OCE Technical Monitor was Mr. J. Robertson.

The research was conducted by the Metallurgy Branch (MSM), Materials and Science Division (MS), U.S. Army Construction Engineering Research Laboratory (CERL). Mr. F. W. Kearney was the Principal Investigator. Other CERL personnel participating in the study were Dr. M. Khobaib, who conducted the laboratory electrochemical experiments, and Mr. W. Mattheessen, who made the electric field plots. Appreciation is also expressed to Dr. P. Hartt of Florida Atlantic University, Boca Raton, FL; Chapters 2 and 3 contain information taken from his notes for the 1976 CERL corrosion course.

Dr. A. Kumar is Chief of MSM and Dr. G. R. Williamson is Chief of MS. COL J. E. Hays is Commander and Director of CERL and Dr. L. R. Shaffer is Technical Director.

CONTENTS

DD FORM 1473 1
FOREWORD 3
LIST OF TABLES AND FIGURES 5

1 INTRODUCTION 9
1.1 Background
1.2 Objective
1.3 Approach
1.4 Mode of Technology Transfer

2 GENERAL ELECTROCHEMICAL PRINCIPLES FOR CATHODIC PROTECTION DESIGN 9
2.1 Principles of Corrosion
2.2 Principles of Cathodic Protection

3 APPLICATION OF CATHODIC PROTECTION PRINCIPLES TO SYSTEM DESIGN 12
3.1 Introduction
3.2 Resistivity
3.3 Structural Configuration and Operation
3.4 Accessibility
3.5 Type and Condition of Protective Coating
3.6 Shielding of Current Interference
3.7 Stray Current Corrosion
3.8 Size and Shape of the Electrolyte Path
3.9 Resistance of Cathodic Protection Circuit
3.10 Summary

4 RECTIFIERS FOR CATHODIC PROTECTION 28
4.1 General
4.2 Automatic Rectifier
4.3 Evaluation of Automatic Rectifiers

5 CONCLUSIONS 34

APPENDIX A: Cathodic Protection Experiments 35
APPENDIX B: Electric Field Analysis 43
APPENDIX C: Polarization by Cathodic Protection 56

REFERENCES 63

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TABLES

Number		Page
1	Classification of Electrolyte Resistivity	12
A1	Mineral Analysis of Tap Water	36
A2	Equivalent Potentials of Reference Electrodes Relative to −0.85 V Reading of Copper-Copper Sulfate Electrode	37
A3	Corrosion Rates of Mild Steel Immersed in Natural Waters	42
B1	Comparative Resistances	55

FIGURES

1	Electrochemical Reactions During Corrosion of Zinc in Air-Free Hydrochloric Acid	10
2	Relationship of Potential to Net Current	13
3	Variation of Potential in a Low-Resistance Electrolyte	14
4	Variation of Potential in a High-Resistance Electrolyte	14
5	Impressed-Current Cathodic Protection	15
6	Sacrificial-Anode Cathodic Protection	15
7	Location of Sausage-Type Graphite Anodes in Miter Gate at Port Allen Lock, LA	16
8	Location of Sausage-Type Graphite Anodes on Skin-Plate Side of Miter-Gate Leaf of Port Allen Lock, LA	17
9	Location of Anodes on Skin Side of Sector Gate of Algiers Lock, LA	17
10	Close-up of Anode Columns of Port Allen Lock, LA	19
11	Damage Caused by Debris or Careless Boat Operation	19
12	Location of Anodes on the Inside of Sector Gate	20
13	Strings of Sausage-Type Anodes	20
14	Use of Button Anodes on Outside of Gates	21
15	Use of Button Anodes in Compartments	22
16	Location of Sacrificial Anodes at Savannah, GA Tide Gate	24

FIGURES (Cont'd)

Number		Page
17	Close-up of a Sacrificial Anode	24
18	Stray-Current Corrosion	26
19	Basic Configuration of Cathodic Protection System	29
20	Basic Elements of Cathodic Protection Rectifier	29
21	Typical Rectifier Assembly	30
22	Basic Configuration of Cathodic Protection System With Automatic Feedback Control	30
23	Block Diagram of Automatic Rectifier Unit	31
24	Switching Action of SCR	32
25	Oscilloscope Traces Showing Switching Periods	32
26	Change of Automatic Rectifier Output Voltage for Change in Conductivity of Electrolyte	33
A1	Test Setup for Cathodic Protection Experiments	36
A2	Decay of Corrosion Potential for Three Environments	37
A3	Diagram of Minipotentiostat	37
A4	Current Decay in Three Environments (potential = −0.850 V)	39
A5	Current Stabilization in Flowing Tap Water at Five Potentials	39
A6	Protection Current Versus Cathode Area	40
A7	Corrosion Rate (Mils per Year) Versus Protection Voltage	40
A8	Variation of Potential With Increasing Distance From Protected Cathode	42
B1	Cross-Sectional View of Electrically Charged, Indefinitely Extended Metal Plates Showing Relationship of Equipotential and Flux Lines Used in Curvilinear-Square Field Mapping	43
B2	Curvilinear-Square Field Plotting: Construction and Subdivision	44
B3	Typical Electrolyte Tank for Model Studies	45
B4	Field Mapping in Electrolyte Tank	45
B5	Electric Field Plot: Single Button Anode Energized	45

FIGURES (Cont'd)

Number		Page
B6	Electric Field Plot: Two Button Anodes Energized	46
B7	Electric Field Plot: Three Anodes Energized	46
B8	Electric Field Plot: Single Anode Energized	46
B9	Small Anode: Shadowing	47
B10	Shadowing: Anode at 45 Degrees	47
B11	Shadowing: Anode at 90 Degrees	48
B12	Comparison of Corrosion Rates	49
B13	Rear Surfaces of Plates Shown in Figure B12	49
B14	Anode Resistance: One Anode	50
B15	Anode Resistance: Two Anodes Far Apart	50
B16	Anode Resistance: Three Anodes	51
B17	Anode Resistance: Two Anodes Close Together	51
B18	Anode Resistance: One Large Anode	52
B19	Anode Resistance Measurements: 3 Percent Salt Water, One Small Anode	52
B20	Anode Resistance Measurements: 3 Percent Salt Water, Two Anodes Far Apart	53
B21	Anode Resistance Measurements: 3 Percent Salt Water, Three Anodes	53
B22	Anode Resistance Measurements: 3 Percent Salt Water, Anodes Close Together	54
B23	Anode Resistance Measurements: 3 Percent Salt Water, One Large Anode	54
C1	Polarization of Iron or Steel Immersed in Water	57
C2	Polarization Curve for Iron or Steel in Water	57
C3	Polarization Curves for a Corrosion Circuit With Insignificant Electrical Resistance	57
C4	Polarization Curves for a Corrosion Circuit With Significant Electrical Resistance	58
C5	Typical Corrosion Cell With Electrolyte Boundary	59

FIGURES (Cont'd)

Number		Page
C6	Degrees of Cathodic Polarization	60
C7	Seawater Corrosion Rate for Steel as a Function of Water Velocity	62
C8	Variation of Cathodic Polarization With Water Velocity	63
C9	Anodic Polarization Curve for a Passive Metal	64
C10	Anodic Polarization Curve in the Passive Region	64
C11	Anodic Polarization Curve for 430 Stainless Steel in Two Environments	65

CORROSION CONTROL IN CIVIL WORKS: CATHODIC PROTECTION

1 INTRODUCTION

1.1 Background

1.1.1 Cathodic protection has been employed in corrosion mitigation for more than a century and a half. Consequently, a large amount of cathodic protection knowledge, such as design data and case histories, is available. Most of this information, however, concerns corrosion mitigation of systems common to the industrial community and has limited application to the somewhat unique corrosion problems encountered in Corps of Engineers civil works systems such as hydraulic structures. In addition, recent developments in solid-state electronics have brought about a new generation of cathodic protection equipment; the small amount of design information available on this equipment is provided by the manufacturers.

1.1.2 This investigation addresses these information needs by combining relevant corrosion principles with current cathodic protection procedures and hardware to provide design guidance specifically for Corps systems and by evaluating some of the new cathodic protection equipment available.

1.2 Objective. The objectives of this study are: (1) to design and conduct basic electrochemical experiments relevant to corrosion mitigation of Corps hydraulic structures in order to provide a rationale for the design, modification, and evaluation of cathodic protection systems for maximum effectiveness, (2) to examine the characteristics and capabilities of existing cathodic protection hardware and determine applicability, and (3) to develop cathodic protection guidelines for systems prevalent in Corps of Engineers civil works operations.

1.3 Approach

1.3.1 The physical and chemical principles of corrosion and corrosion control were reviewed for application to Corps civil works operations (Chapter 2). Experiments were conducted to relate the theoretical cathodic protection criterion to field conditions (Appendix A). These experiments were designed to provide information on several areas for which data are lacking—the effects of environment and time on corrosion potential and current decay, the effects of protection current on weight loss, and the effects of area exposed on current.

1.3.2 Anode requirements were investigated using electric field concepts and electric circuit techniques, when required (Appendix B). This approach provided a more basic comprehension of cathodic protection anode requirements in real situations involving complex structural geometry and avoided the excessive and simplistic empiricism sometimes involved in "lumped-constant" circuit design.

1.3.3 The relevant corrosion principles and results of the above investigations were combined for application to field design problems encountered in Corps civil works operations (Chapter 3).

1.3.4 Rectifiers for impressed-current cathodic protection systems that incorporate feedback control to maintain constant voltage or current have recently become commercially available. The operational characteristics of these rectifiers and factors involved in their use were evaluated (Chapter 4).

1.4 Mode of Technology Transfer. This study will impact Corps of Engineers Guide Specification CE 1508[1] and Technical Manual (TM) 5-811-4.[2]

2 GENERAL ELECTROCHEMICAL PRINCIPLES FOR CATHODIC PROTECTION DESIGN

2.1 Principles of Corrosion

2.1.1 Corrosion, as considered in this study, is the deterioration of a metal or alloy by electrochemical reaction with its environment. Basically, two electrochemical reactions occur:

a. Dissolution of metal: *base metal to metal ions* plus *free electrons*. In chemical notation this is

$$M \rightarrow M + n + ne \qquad \text{[Eq 1]}$$

where M = the base metal
n = an integer determined by the particular metal (valence)
e = an electron.

---

[1] *Cathodic Protection System for Lock Miter Gates*, CE 1508 (Office of the Chief of Engineers, 1967).

[2] *Engineering and Design: Corrosion Control*, TM 5-811-4 (Department of the Army, 1 August 1962).

b. Evolution of hydrogen gas: *hydrogen ions* plus *free electrons* to hydrogen gas. In chemical notation this is

$$2H^+ + 2e \rightarrow H_2 \qquad \text{[Eq 2]}$$

As Eqs 1 and 2 indicate, the negative electrons from the metal combine with positive ions from a conductive (electrolytic) solution at a rate dependent on the *potential* between the metal and the solution.

2.1.2 The reaction between hydrochloric acid and zinc illustrates the electrochemical nature of corrosion. When zinc is immersed in diluted hydrochloric acid, a vigorous reaction occurs; hydrogen gas leaves the zinc surface, and zinc ions enter the solution. Since the hydrochloric acid dissociates in aqueous solution into hydrogen and chloride ions (H^+ and Cl^-) and the chloride ions are not involved in the reaction, the overall reaction is

$$Zn + 2H^+ \rightarrow Zn^{+2} + H_2 \qquad \text{[Eq 3]}$$

2.1.3 When zinc is placed in the acid, some hydrogen ions adjacent to it are adsorbed onto the zinc's surface. The adsorbed hydrogen ions tend to take electrons from the metal and become neutralized hydrogen atoms, while the zinc surface atoms adjacent to the electrolyte tend to release two electrons and go into solution as zinc ions (Zn^{+2}). Two hydrogen atoms combine to form a hydrogen molecule (H_2), which then combines with other hydrogen molecules and evolves from the zinc surface as a hydrogen bubble. The electrons released by the zinc travel through the metal to other surface sites where they are consumed by hydrogen ions, as shown in Figure 1. Eq 3 can be conveniently divided into two partial reactions:

Anodic

$$Zn \rightarrow Zn^{+2} + 2e \qquad \text{[Eq 4]}$$

Cathodic

$$2H^+ + 2e \rightarrow H_2 \qquad \text{[Eq 5]}$$

2.1.4 The zinc dissolution is an anodic or oxidation reaction, as it releases electrons. The neutralization of hydrogen ions is called a cathodic or reduction reaction because it consumes electrons. Neither the anodic nor the cathodic reactions occur at definite locations. The cathodic reaction site may be any distance from the anodic dissolution site.

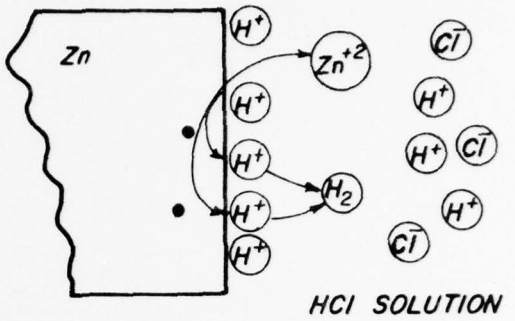


Figure 1. Electrochemical reactions during corrosion of zinc in air-free hydrochloric acid.

2.1.5 All metals, as well as some nonmetals, corrode similarly. Hydrochloric acid corrodes iron and aluminum in addition to zinc. The anodic reactions for these metals are:

$$Fe \rightarrow Fe^{+2} + 2e \qquad \text{[Eq 6]}$$

$$Al \rightarrow Al^{+3} + 3e \qquad \text{[Eq 7]}$$

The cathodic reaction for hydrochloric acid is always that shown in Eq 5.

2.1.6 When metals like zinc, aluminum, and iron corrode in other acids, such as sulfuric, phosphoric, hydrofluoric, formic, and acetic acids, they behave just as they do in hydrochloric acid. In each case, only the hydrogen ion is active. The other anions, such as sulfate and phosphate, usually do not participate in the corrosion reaction, although they may react with the dissolved metallic ions to form solid precipitates (e.g., iron phosphate) on the metal surface.

2.1.7 In addition to the hydrogen ion, several other chemical species in an electrolyte (e.g., oxygen, ferric ion (Fe^{+3}), cupric ion (Cu^{+2})) can participate in electron-consuming cathodic reactions. The common cathodic reactions are:

a. Hydrogen evolution

$$2H^+ + 2e \rightarrow H_2 \qquad \text{[Eq 5]}$$

b. Oxygen reduction (acid solution)

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad \text{[Eq 8]}$$

c. Oxygen reduction (neutral or basic solutions)

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad [Eq\ 9]$$

d. Metal-ion reduction

$$M^{+2} + e \rightarrow M^{+} \qquad [Eq\ 10]$$

(e.g., $Cu^{+2} + e \rightarrow Cu^{+}$

or $Fe^{+3} + e \rightarrow F^{+2}$)

e. Metal deposition

$$M^{+} + e \rightarrow M \qquad [Eq\ 11]$$

2.1.8 Because acids or acidic media are common, hydrogen evolution is a frequent cathodic reaction. Oxygen reduction is also very common, since many aqueous solutions in contact with air contain some dissolved oxygen molecules capable of providing this reaction. Metal-ion reduction and metal deposition are less common reactions that are usually found in chemical process streams. Metal-ion reduction occurs in solutions that are contaminated with metallic ions having two or more possible ionic states (e.g., Cu^{+} or Cu^{+2} and Fe^{+2} or Fe^{+3}). Metal ions in solution tend to take up electrons and deposit on the metal electrode surface.

2.1.9 More than one anodic and one cathodic reaction may occur during corrosion. When an alloy corrodes, its component metals go into solution as ions. If more than one cathodic reaction occurs, the rate of anodic dissolution of the metal equals the sum of all cathodic reactions. Thus, acid solutions containing dissolved oxygen are more corrosive than air-free acids.

2.1.10 The concept of partial reactions can be used to interpret virtually all corrosion problems. When iron, in the form of a steel pier piling or a dam gate, is immersed in freshwater or seawater exposed to the atmosphere, the anodic reaction is:

$$Fe \rightarrow Fe^{+2} + 2e \qquad [Eq\ 6]$$

Oxygen reduction is the main cathodic reaction:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad [Eq\ 9]$$

Since freshwater and seawater are nearly neutral, the sodium and chloride ions (Na^{+} and Cl^{-}) do not participate in the reaction. The overall reaction, obtained by adding Eqs 6 and 9, is

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe^{+2} + 4OH^- = 2Fe(OH)_2\downarrow \qquad [Eq\ 12]$$

The ferrous ion and hydroxide ion may combine to form insoluble ferrous hydroxide ($Fe(OH)_2$) if the ionic concentrations exceed certain limits. Ferrous hydroxide is not stable, however; it reacts with oxygen or water molecules to form ferric hydroxide:

$$2Fe(OH)_2 + H_2O + 1/2\,O_2 \rightarrow 2Fe(OH)_3\downarrow \qquad [Eq\ 13]$$

The final product is thus the familiar brown rust or ferric hydroxide.

2.1.11 If the dissolved oxygen in the water is eliminated, the corrosion rate of iron drops sharply. This result is logical, since oxygen reduction is the main cathodic reaction. Coating the iron or steel surface with paint or some other nonconducting film can reduce the rates of both anodic and cathodic reactions and thus retard corrosion. Similarly, corrosion inhibitors added to the electrolyte form a surface layer which interferes with either or both of the anodic and cathodic reactions. In cathodic protection, external electrical devices "pump" the electrons required for the cathodic reaction to the metal surface. Consequently, iron dissolution, which also releases electrons to the metal surface, is greatly reduced by the counterflow of electrons that this external voltage supplies.

2.2 Principles of Cathodic Protection

2.2.1 The discussion of electrochemical reactions and corrosion cells has thus far dealt primarily with isolated corrosion cells and the nature of electrochemical reactions. The fundamental principle of cathodic protection is the application of a *counter potential* to prevent the electrochemical interchange which occurs in corrosion. In cathodic protection practice, the metal to be protected is made negative (cathodic) with respect to a "protecting" electrode (anode). This externally applied electric current can be supplied in two ways: by an external power source (impressed current) or by a metal that is more electrochemically positive than the protected metal (sacrificial anode). Although the examples below consider only a single cell, the surface of a submerged piece of steel (or any other metal) consists of many such cells, which may be microscopic in size.

2.2.2 Because the current flow between anode and cathode causes polarization, the potential difference (driving force) between the two electrodes is invariably less than the open-circuit potential with no net current flowing across the electrode-electrolyte interface. Figure 2 shows how potential varies with current density. As a net current flows, the potential of the anode becomes more noble (positive), and the potential of the cathode becomes more active (negative). The potential difference between the two effectively decreases as greater amounts of current flow through the cell. The magnitude of polarization (difference in potential for an electrode passing a net current compared to that for a state of no net current) principally depends on current density or current per unit electrode area. If the corrosion cell circuit contains metallic electrodes and an electrolyte of high conductivity, and if no high resistance reaction produces films on the metal surfaces, then electrical resistance is minimal, and anode and cathode potentials achieve very nearly the same value. This situation often occurs with iron or steel in seawater, which has high conductivity. In a high-resistance electrolyte, such as a freshwater low in chlorides, a potential difference between anode and cathode is maintained. Figures 3 and 4 illustrate potential variation in low- and high-resistance electrolytes.

2.2.3 Cathodic protection essentially introduces a direct current from an outside source that alters polarization and reduces or halts current flow from the metal into the electrolyte at the anodic sites. Introducing this current requires a modification of the circuitry of the electrochemical or corrosion cell. One type of modification, which is called impressed-current cathodic protection (Figure 5), involves electrically coupling a submerged, corroding metal structure or component, which consists of many microelectrodes or "local action cells," to the negative terminal of a dc power supply or rectifier and bonding the positive terminal to an auxiliary piece of submerged metal. This auxiliary metal is commonly termed an impressed-current anode.

2.2.4 Although any conducting solid can illustrate basic cathodic-protection theory, in practice the chemical makeup of the anode material determines the efficiency of the protection system. An anode material naturally positive to the structure that requires protection will produce the same result as a dc power source and anode system; i.e., it will supply current through the electrolyte to the metal structure. Use of a naturally positive anode material (Figure 6) is called sacrificial-anode cathodic protection.

2.2.5 In both impressed-current and sacrificial-anode protection systems, positive current flows through the electrolyte to the structure to be protected. This metal structure thus becomes the cathode in a galvanic couple; it is polarized cathodically (negatively), and its corrosion rate is reduced.

2.2.6 Appendix C provides additional details on polarization by cathodic protection.

3 APPLICATION OF CATHODIC PROTECTION PRINCIPLES TO SYSTEM DESIGN

3.1 Introduction. This chapter presents guidelines for applying the principles of cathodic protection described in Chapter 2 and the results of the studies presented in Appendices A and B to field design problems encountered in Corps civil works operations.

3.2 Resistivity

3.2.1 The electrolyte's resistivity largely determines which anodes to use. Anode-alloy chemistry and installation procedures are important in both high- and low-resistivity electrolytes. Table 1 indicates what levels of resistivity are classified as low, moderate, and high.

Table 1

Classification of Electrolyte Resistivity

Resistivity (ohm-cm)	Classification
Below 2,500	Very low
2,500 to 7,500	Low
7,500 to 10,000	Moderate
Above 10,000	Progressively higher

3.2.2 High-resistivity electrolytes generally require an impressed-current system employing anode materials like duriron, graphite, or a nobler metal. If anode selection is properly based on the environment, such impressed-current anodes will have a longer life than galvanic anodes. In low-resistivity electrolytes, galvanic anodes such as aluminum, zinc, and magnesium are often more economical.

3.2.3 The limited driving voltage of galvanic anodes can produce only a small amount of current in high-

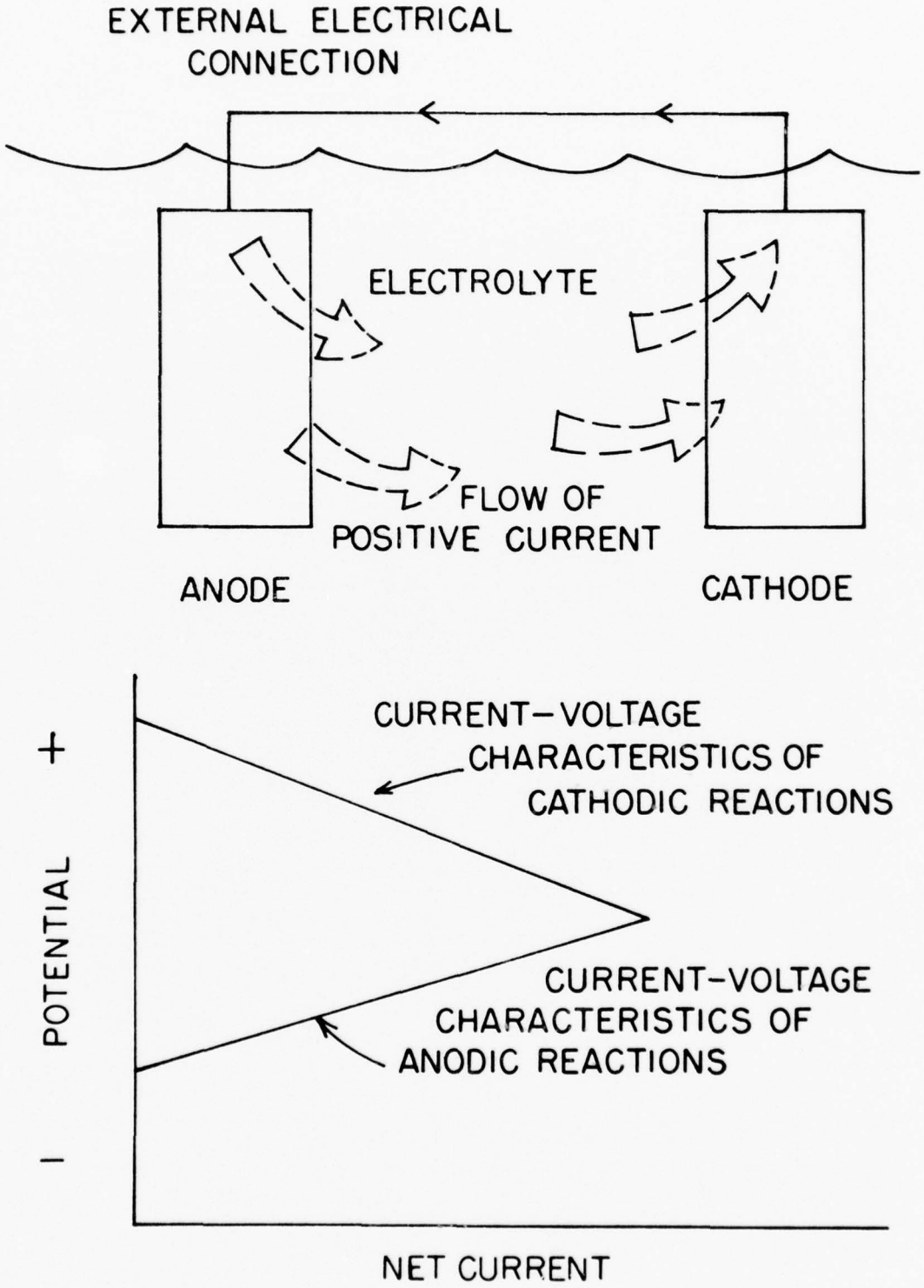


Figure 2. Relationship of potential to net current.

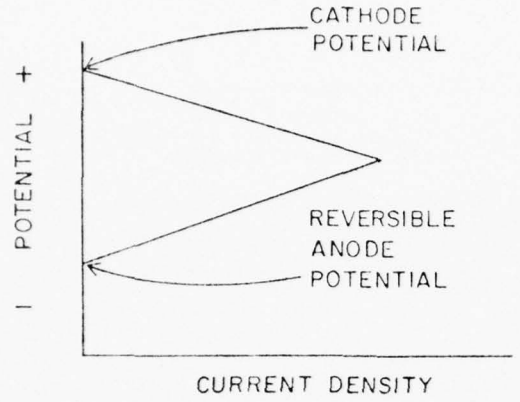


Figure 3. Variation of potential in a low-resistance electrolyte.

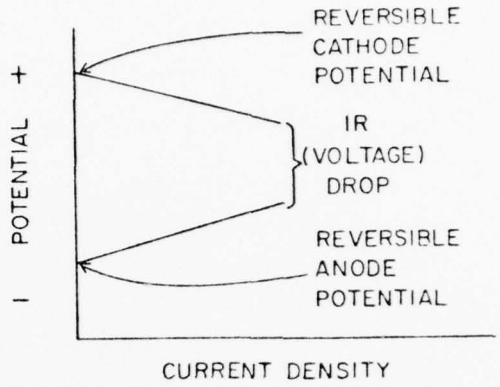


Figure 4. Variation of potential in a high-resistance electrolyte.

resistivity electrolytes, so these anodes are generally used only in salty and brackish water. Magnesium anodes, which have more negative corrosion potential than aluminum or zinc, have been used in freshwater, but the large number of anodes needed to produce the required current in this situation may cause high installation costs.

3.2.4 An advantage of using galvanic anodes in high-resistivity electrolytes is that they present little danger of overprotection (creation of a structure potential which is too negative). Potential changes of steel structures in freshwaters, as effected by galvanic anodes, rarely exceed −0.90 V with respect to a copper-copper sulfate reference electrode. A practical example is the use of magnesium on intake gates in the Columbia and Missouri Rivers. These gates are set in slots in concrete and have stainless steel rollers on each end. Excessive current on the rollers from overprotection might cause hydrogen embrittlement, and stray current might damage the concrete.

3.2.5 Galvanic anodes are more practical than impressed-current anodes for high-resistivity electrolytes when a rectifier system will not be properly maintained, either because of inaccessibility or environmental exigencies. Where power is not available for a rectifier system, galvanic anodes may be the only alternative.

3.2.6 On the other hand, although galvanic anodes are quite efficient for low-resistivity electrolytes and are generally easy to install and maintain, a rectifier system may sometimes be more economical.

3.3 Structural Configuration and Operation. The following examples illustrate the influence of a structure's configuration and operation on the design of a cathodic protection system.

3.3.1 *Vertically Framed Miter Gate*

3.3.1.1 A vertically framed miter gate with buckle plates located between vertical girders (Figure 7) protects anodes from mechanical damage. Using local anodes in compartments rather than remote anodes avoids damage from floating debris and ice. A disadvantage of local anodes is that the girders shield the current, necessitating placing an anode in each compartment; this shielding effect almost never occurs on the skin plate side of the gate. If such a structure is adequately painted, some current will travel from the anode in one compartment to a neighboring structure surface. Excessive voltage must generally be applied to the anode to sufficiently polarize the structure surface that the anode cannot "see." Because the structure immediately adjacent to the external anode may then be significantly overprotected, hydrogen gas may evolve there, thus "blistering" the coating.

3.3.1.2 The usual practical maximum voltage measured with a copper-copper sulfate half-cell is taken as 2 V.

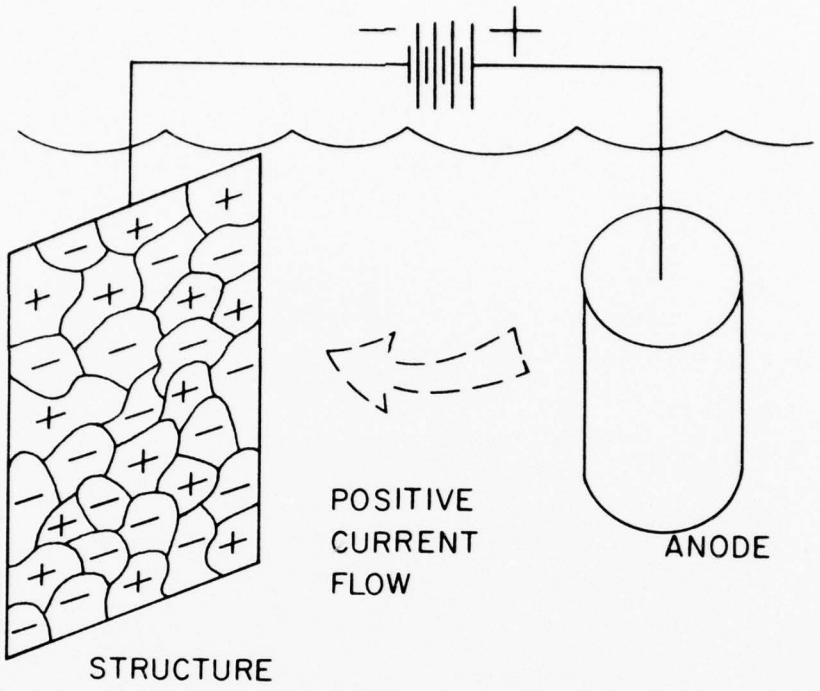


Figure 5. Impressed-current cathodic protection.

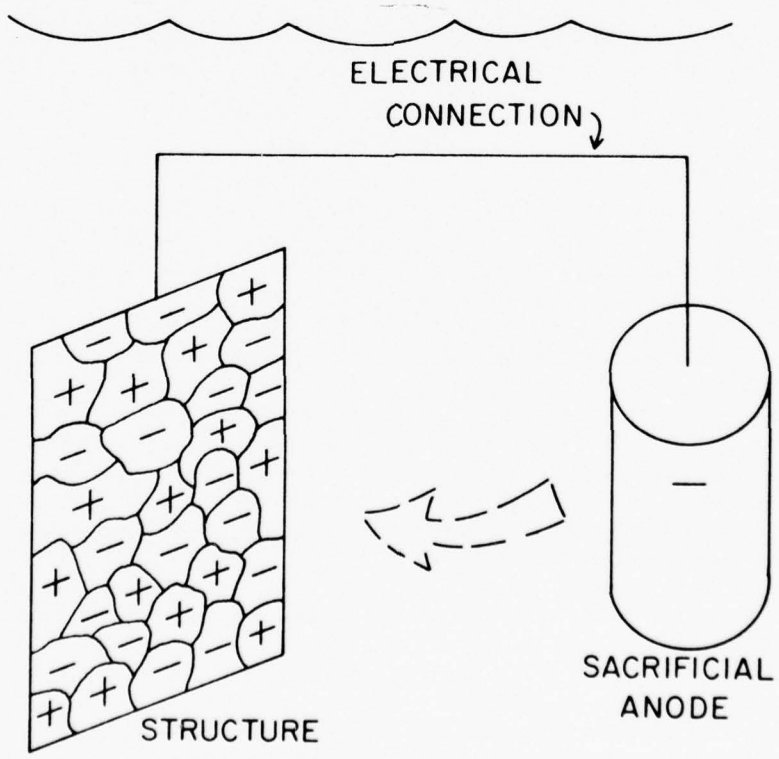


Figure 6. Sacrificial-anode cathodic protection.

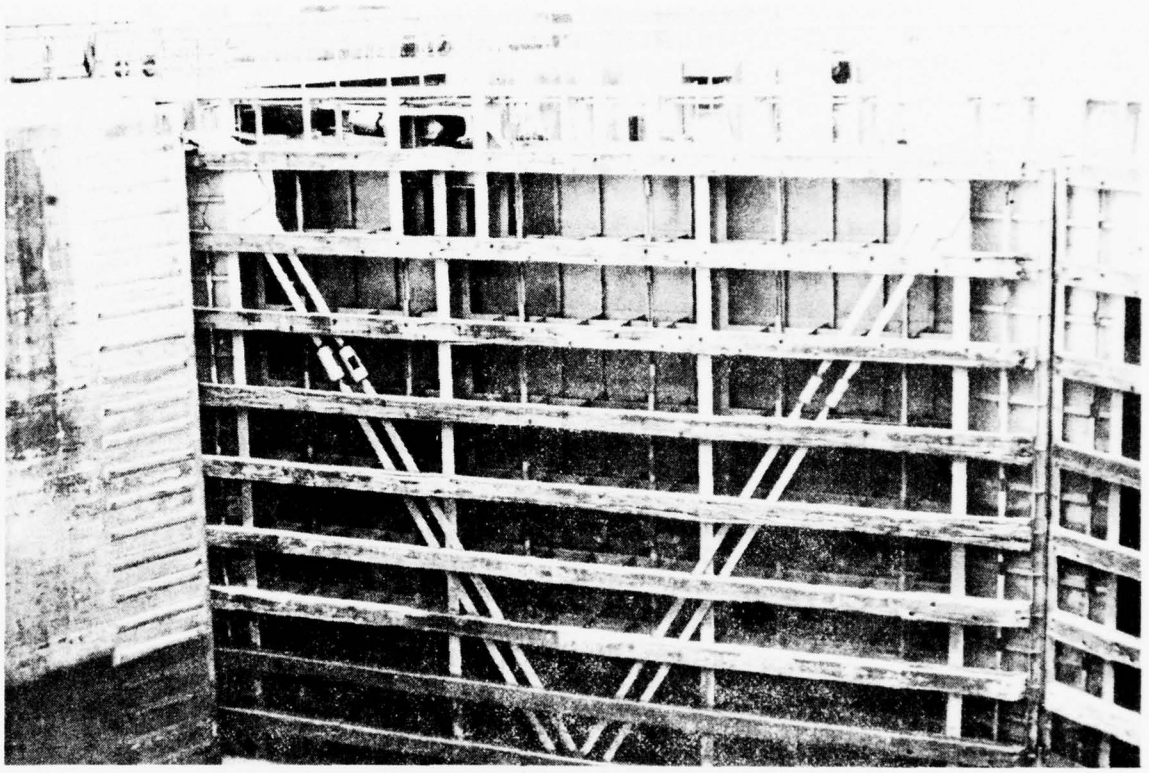


Figure 7. Location of sausage-type graphite anodes in miter gate at Port Allen Lock, LA. Eight vertical columns of anode strings are required to distribute the current in compartments.

3.3.1.3 Cathodic-protection design must also consider the water level in the lock chamber. Once a protective calcareous deposit forms, a properly designed system performs well regardless of water height; this film protects the wet surface that extends above the air-water interface as the water level decreases. That portion of the structure's surface still submerged is not overprotected because of the increased resistance in the cathodic-protection circuit. This increased resistance can arise from a reduced water cross section; more importantly, however, the number of anodes in the system is reduced, because the anodes at the top of the gate no longer contact the electrolyte.

3.3.2 *Horizontally Framed Miter Gate*

3.3.2.1 Anodes can be attached to the skin plate of horizontally framed miter gates and sector gates on either the upstream or downstream sides, as shown in Figures 8 and 9. Such anodes are vulnerable to mechanical damage; grooved, wood timbers are therefore used to support and protect the anodes on a structure; the timber should, of course, be suitable for submersion. Z-shaped clip angles about 4 in. (101.6 mm) long, which are welded at intervals along each side, can be used to fasten the timber to the skin plate. Nails, bolts, screws, or other metallic fasteners not bonded to the structure cannot be used because they will collect current at one end and discharge it from the other, thereby causing rapid stray current corrosion. Positioning the clip angles only at the seabs partly shields them from the current. Blast cleaning and subsequent coating of angles with 6 mils (0.15 mm) of vinyl paint (V-108 in Corps of Engineers Guide Specification 1409) prevents excess current from draining from the anode at the angles. If such current drain were to occur, rapid pitting would result.

3.3.2.2 There are six anodes on the skin side of each leaf of the miter gate, as shown in Figure 8. This number uniformly distributes current on the gate surface. Using fewer anodes, e.g., four on each

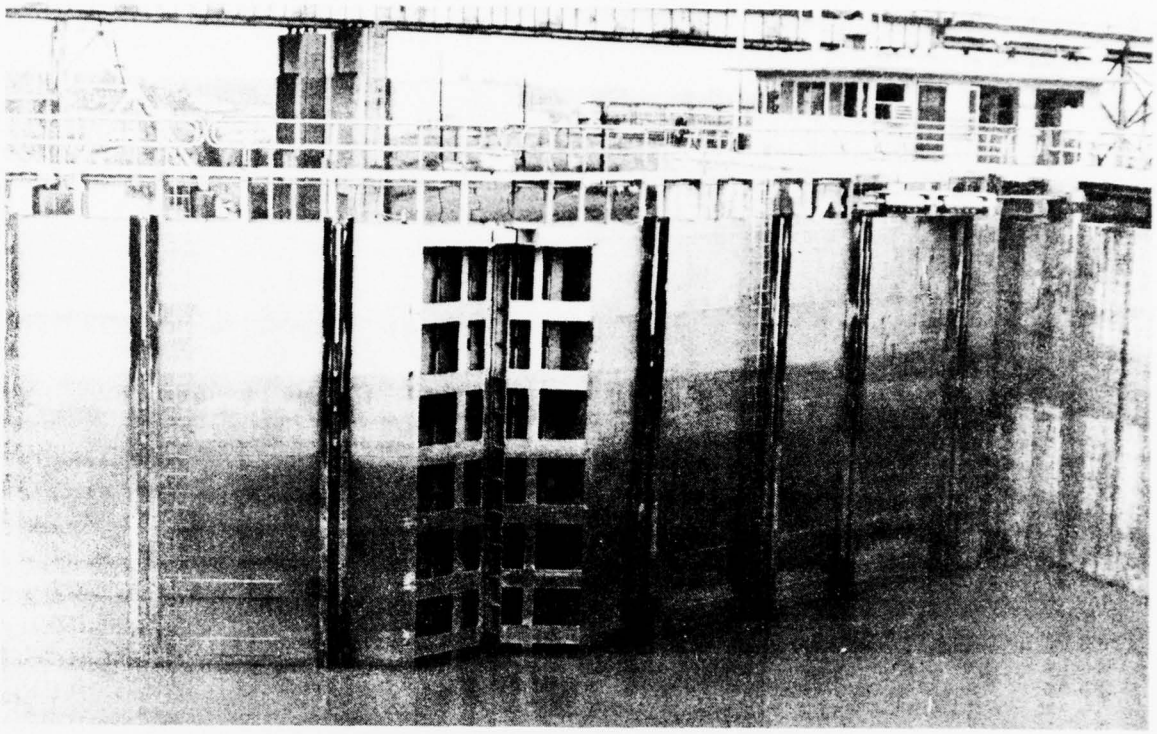


Figure 8. Location of sausage-type graphite anodes on skin-plate side of miter-gate leaf of Port Allen Lock, LA. Six columns of string anodes are required to distribute the current.

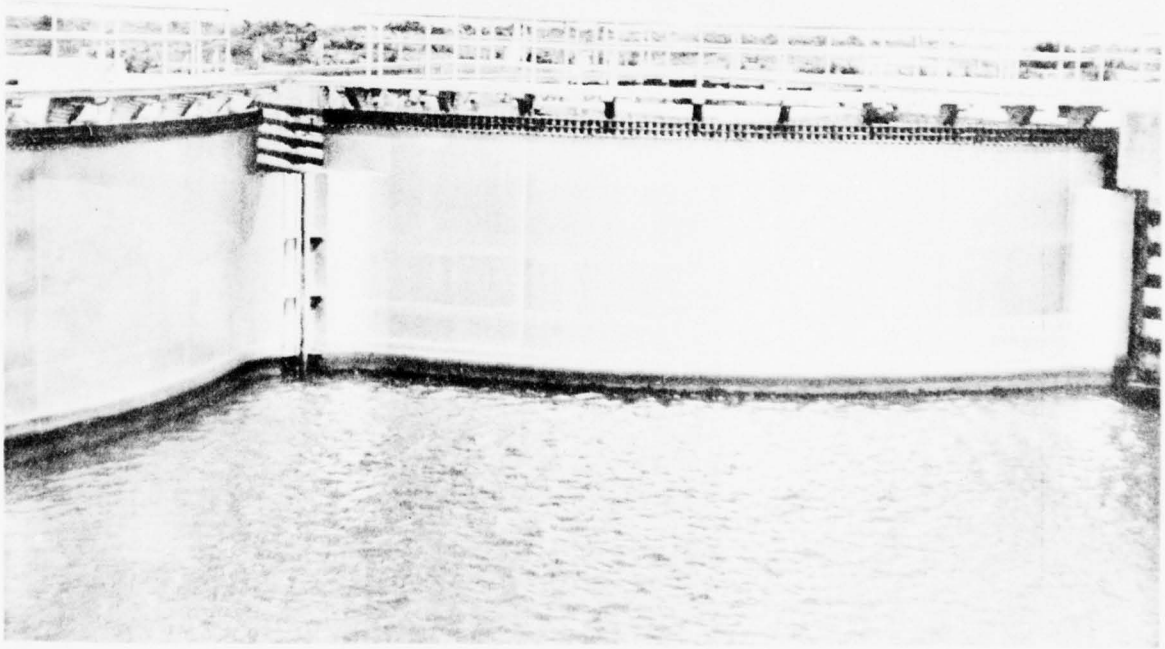


Figure 9. Location of anodes on skin side of sector gate of Algiers Lock, LA. Two columns of sausage anodes are provided.

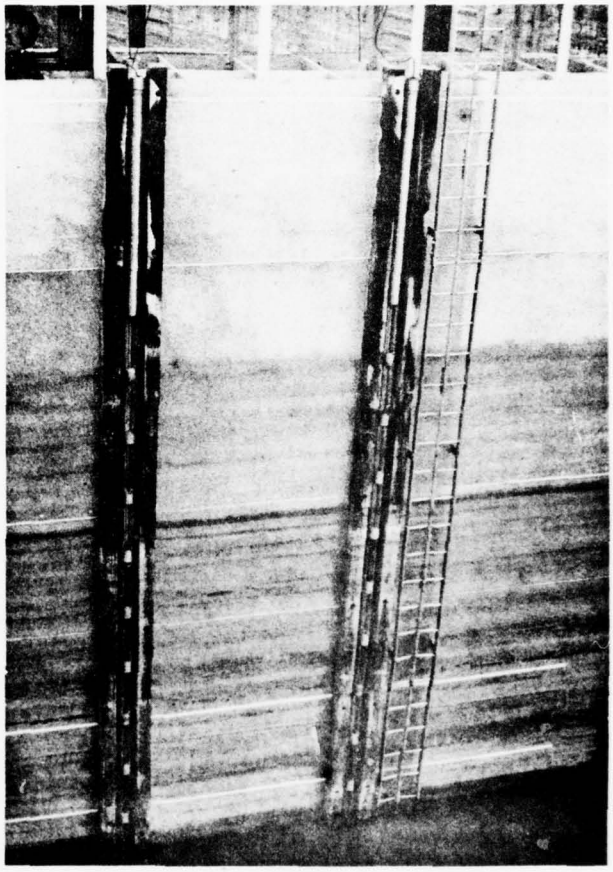


Figure 10. Close-up of anode columns of Port Allen Lock, LA. Two sausage-type graphite anodes can be seen in each column.

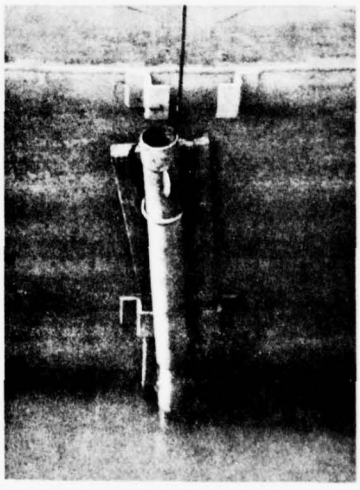


Figure 11. Damage caused by debris or careless boat operation.

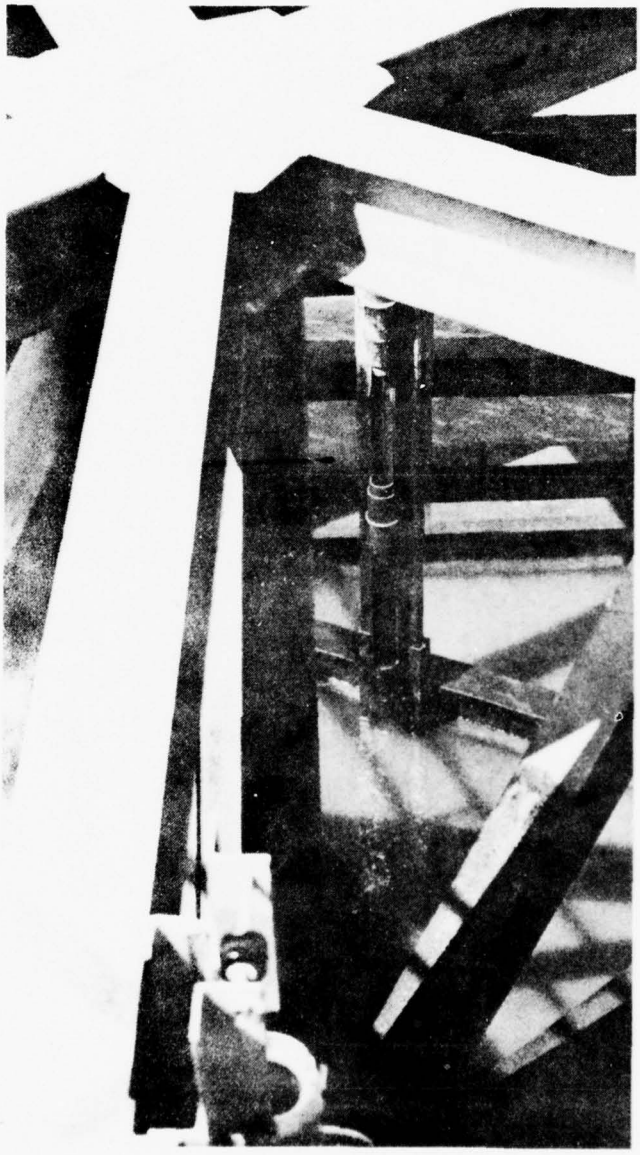


Figure 12. Location of anodes on the inside of sector gate.

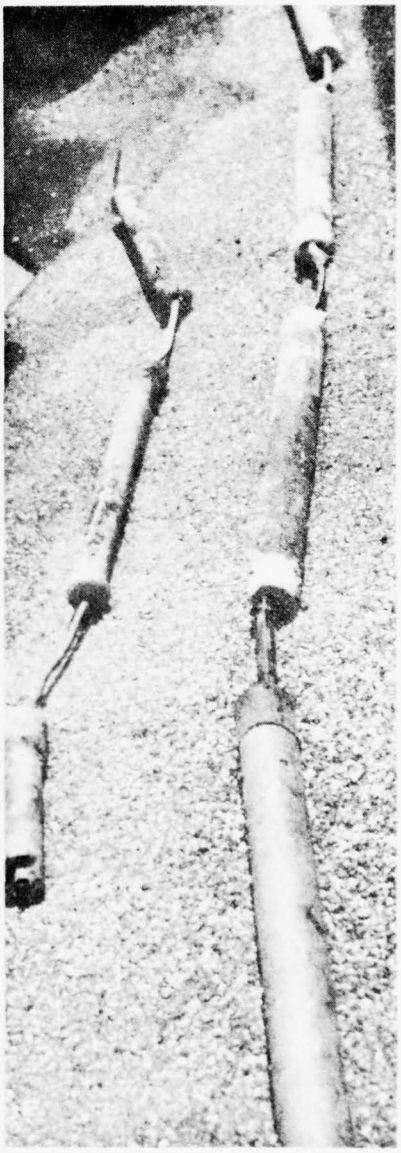
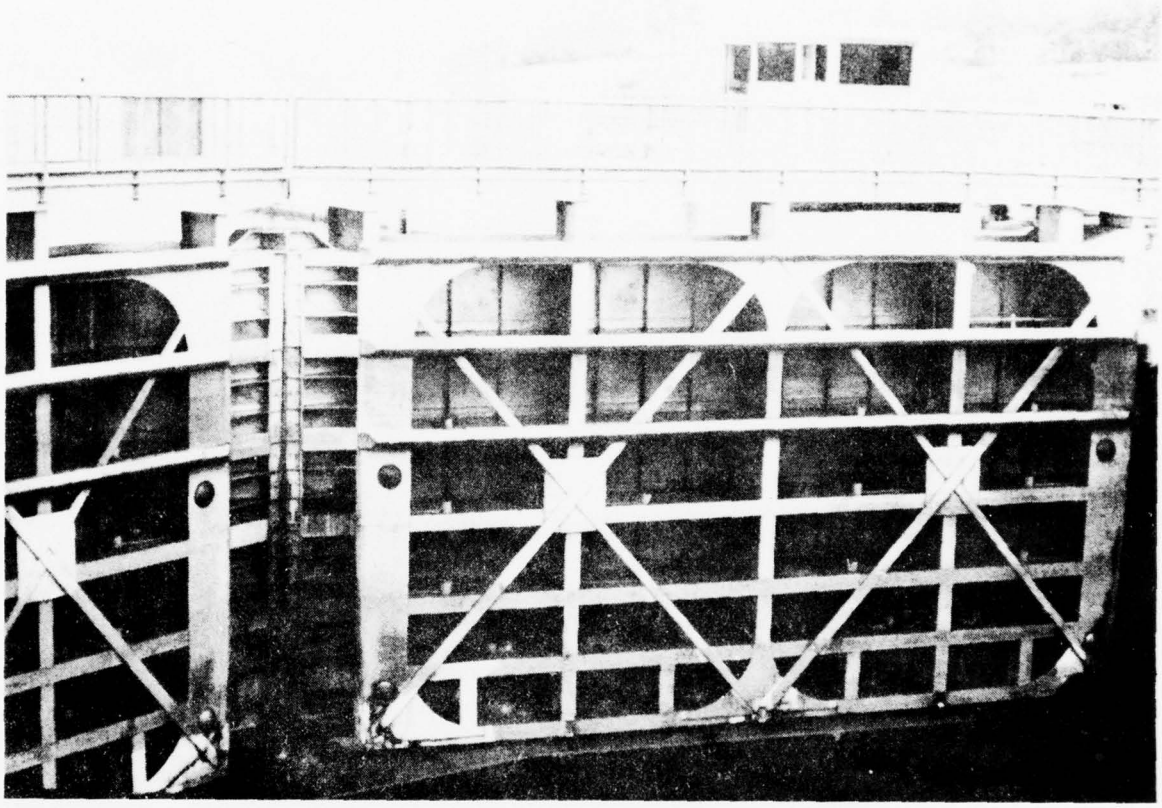
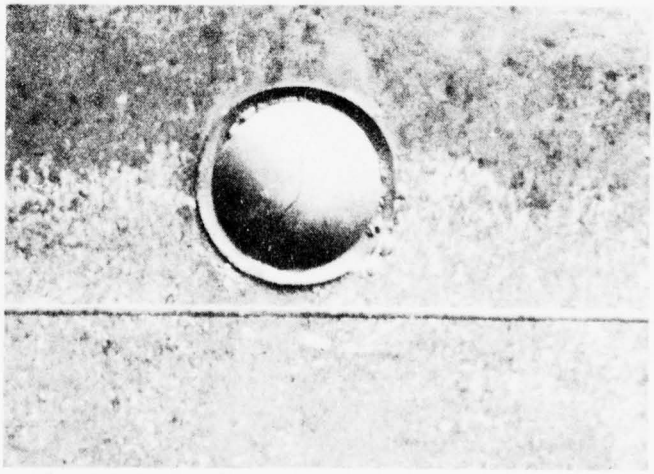


Figure 13. Strings of sausage-type anodes. Anodes can be lifted out and replaced if they are destroyed.



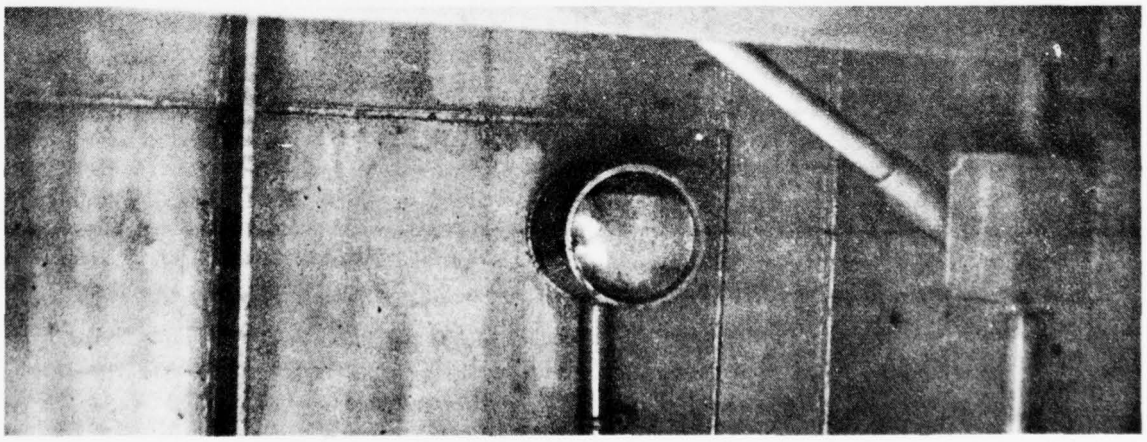
a. Location of button anodes on the leaf of Cordell Hull Lock, TN.



b. Close-up of button anodes. Slight blistering caused by overprotection can be seen.

Figure 14. Use of button anodes on outside of gates.

a. Location of button anodes and sealed junctions in the compartments of Cordell Hull Lock, TN.



b. Close-up of junction sealed watertight.

Figure 15. Use of button anodes in compartments.

leaf, would require more concentrated current around each of the anodes. This distribution, in turn, would increase the necessary driving voltage. Also, the higher current density from four anodes might blister the paint on the adjacent steel. If the coating were a thick, hot-applied coal tar, reducing the number of anodes to four per leaf would probably produce minimal adverse effects.

3.3.2.3 Sausage-type graphite anodes have provided adequate service in the New Orleans District on lock gates such as those shown in Figures 7 and 8. These figures show the location of the anodes on the compartment side as well as on the skin side of the miter gate; in cold climates, consideration must be given to ice build-up. Figure 10 shows a close-up of the anode column. Figure 11 shows the skin side of a sector gate whose anode has been damaged by floating timber or careless boat operation. The inside of the sector gate can also be protected by the same type of anodes or galvanic anodes, as shown in Figure 12. These anodes can be conveniently replaced, for they can be fished out even if they fall into the water. New anodes can be spliced, as Figure 13 shows.

3.3.2.4 Button-type anodes can also be used to distribute the current uniformly outside (Figure 14) or in the compartments (Figure 15). All connections and joints must be properly sealed by a compound.

3.3.2.5 Lock miter gates, such as those shown in the figures, are an excellent example of appropriate use of cathodic protection because the submerged surfaces are accessible only by costly dewatering.

3.3.3 *Tainter Gates*

3.3.3.1 Tainter gates with skin plate on both the upstream and downstream sides are another example of how a structure's configuration affects design. Because these surfaces curve vertically, attaching anodes horizontally on the gate is necessary. The electrical connection to the center of each anode can be made by passing cable through a hole drilled in the skin plate of the gate and through the timber support.

3.3.3.2 Because drift, ice, and extreme water turbulence on the downstream side would damage the anodes fastened there, cathodic protection is impracticable for this face. Moreover, the amount of current required to polarize steel in this turbulent water would be excessive.

3.3.3.3 The interior surfaces of the compartmented gate (Figure 12) are below water, and are easily protected cathodically because the current cannot stray and the anodes are protected. Placing one horizontal anode in the center of each of the two lower compartments can provide sufficient protection for well-painted surfaces. Neoprene hose can be used to insulate the anode from the steel cross bracing.

3.3.3.4 The electrical cables attached to the anodes pass through manholes inside the gate, proceed to the top compartment (which is always dry), go out one end along the pivot arm of the gate to the hinge point, and return along the concrete pier to the rectifier. Protecting the inside of tainter gates by impressed-current cathodic protection is unrealistic, because the numerous sharp edges and corners of structural members may damage the electrical leads during operation. About one-third of these interior surfaces or 20 percent of the entire surface is submerged. The unsubmerged upper two-thirds cannot be cathodically protected, and painting is the only applicable technique here.

3.3.3.5 The submerged surfaces are, however, difficult to repaint because removing mud and debris is costly and little space is available for workmen. If the lower compartments' coating lasted as long as the upper compartments', access would be necessary only every 30 years. The underwater coating will last 15 years by itself and 30 years if supplemented by cathodic protection. A 2-in. (50.8 mm) diameter magnesium rod, supported on the cross bracing that runs the length of each underwater compartment and fastened with U-bolts, will last about 15 years and supply enough current to protect the surface. In lower resistivity waters, larger anodes are required to obtain this same 15-year life. Poorly painted surfaces, which require greater current, demand two rods or slab anodes.* There are no cable problems with magnesium anodes, which are easy to install and maintain.

3.4 Accessibility

3.4.1 The sector gates in brackish water on the Brazos River in the North Pacific Division illustrate

*Refer to section 3.5 for typical current density requirements; the type of anode needed to obtain the required current densities is based on the manufacturer's data.

how accessibility of anodes affects cathodic protection design. These lock gates, which prevent salt water from intruding, have a differential of only about 1 ft (0.3 m). The gate surfaces are inaccessible except by construction of cofferdams and a temporary canal around the lock, which is a very costly undertaking. The waters here are highly corrosive, and the best coatings last only about 7 years. In this type of situation, cathodic protection is necessary. A galvanic system with large cast-magnesium anodes was chosen for this situation. Attaching impressed-current anodes and insulating them from the structure would be costly, but galvanic anodes can be suspended in the water from the top of the gate. Another example of galvanic protection is the protection of tide gates in the Savannah District (Figures 16 and 17).

3.4.2 Accessibility is seldom if ever a problem on new construction, but the designer must remember that anodes generally will require replacement. Indeed, the choice of a cathodic-protection system must consider not only initial cost, but subsequent maintenance costs.

3.5 Type and Condition of Protective Coating

3.5.1 Proper amounts of cathodic protection current will not damage underwater coatings such as vinyl, coal tar, and phenolic. Polarization of painted surfaces should not exceed about -1.2 V with respect to a copper-copper sulfate reference electrode, although high quality coatings can hold up at somewhat more negative voltages.

3.5.2 The best deterrent to corrosion in open waters is a protective coating in conjunction with cathodic protection. All coatings tend to corrode at holidays, and cathodic protection currents are intended to prevent gradual development of rust under the paint and consequent enlargement of the holidays. While bare steel in freshwater requires about 2 mA/sq ft (21.5 mA/m^2), newly painted surfaces may require much less current. The amount of current needed depends on the number of holidays in the coating and on whether sharp edges are well-coated. For example, on tainter gates newly painted with vinyl, 0.5 mA/sq ft (5.4 mA/m^2) has been required for polarization, although some of this current may have strayed and thus not contributed to cathodic protection. For installations where current could not stray, newly painted gates have been polarized with 0.1 mA/sq ft (1.1 mA/m^2). Because a paint film gradually suffers mechanical damage (vinyl and coal-tar coatings underwater do not deteriorate chemically as they age), enough capacity should be incorporated in the cathodic-protection design to supply the added current needed as the coating deteriorates after damage. Because the cost differential in rectifiers is small relative to the overall cathodic protection cost, it is advisable to size the rectifier unit three to four times greater than the minimum required to provide reserve capacity and possible expansion of the cathodic protection system.

3.5.3 Even a relatively poor paint coating can greatly improve current distribution. The exterior surface of one roller gate, for example, was cathodically protected 18 years after a phenolic coating was applied. The coating was estimated to be effective on only about 50 percent of the upstream gate's surface. Bare surface regions were rusted, so the entire gate appeared urgently in need of recoating. After polarization and deposition of the carbonate coating, however, from 50 ft (15.2 m), the surface appeared to be completely coated with paint. Even though the old coating was worn, it did help distribute current from the three anodes on the upstream face more uniformly. On the other hand, turbulence on the downstream side prevented the anode on that side from polarizing the surface of the gate.

3.5.4 The condition of the structure's surface thus affects the total current and the anode spacing required of a proposed cathodic-protection system. If the anodes are spaced farther apart, the current required of each anode to effect polarization may be greater as the coating deteriorates than if the anodes had been closer together. Current from each anode should never be so great that it causes the paint near the anode to blister. The designer of cathodic protection systems should know both the type and condition of any coating on the steel and be able to estimate what its condition will be 10 or 15 years later.

3.6 Shielding of Current Interference

3.6.1 Achieving uniform cathodic-current density, and hence, uniformly and adequately protecting an irregularly shaped structure, such as a miter gate, can be a formidable problem. The current tends to concentrate on that portion of the structure closest to the anode. Because the resistivity of natural waters is generally at least a million times greater than that of structural steel, the current flows along the shortest anode-to-structure distance. On some

Figure 16. Location of sacrificial anodes at Savannah, GA tide gate.

Figure 17. Close-up of a sacrificial anode.

experimental gates whose coating had badly deteriorated, current distribution was poor, even several months after the current was applied, although the distribution gradually improved and became adequate. Deposition of a carbonate film, which increases the resistance of structure surfaces on which it forms, causes this improvement and makes greater current density available for surfaces farther from the anode.

3.6.2 A paint coating in reasonably good condition largely eliminates shielding problems. In fact, a paint coating is generally necessary for cathodic-protection systems on hydraulic structures.

3.7 Stray Current Corrosion

3.7.1 When metallic components or members are in the electrolyte path, stray-current corrosion may occur (Figure 18). Since current from the anode seeks the path of least resistance, most of it passes through the intermediate piece of steel. The end of the steel nearest the anode is cathodically protected because the current is flowing from electrolyte to metal at this point. At the opposite end, however, current leaves the metal, and corrosion occurs.

3.7.2 Bonding the intermediate member to the structure, as shown in Figure 18, can eliminate this problem. A significant percentage of the cathodic-protection current probably flows from the anode to the intermediate member, however, and returns to the rectifier without re-entering the electrolyte. Thus, bonding eliminates corrosion of the intermediate metal, but the desired current still does not reach the structure.

3.7.3 On hydraulic structures, excessive straying of current generally occurs when the anodes are remote from the cathode. For example, a 1200-ft (365.8 m) wire-rope anode is located 500 ft (152.4 m) upstream of a dam consisting of nineteen 100-ft (30.5 m) long roller gates supported by steel-reinforced concrete piers founded on rock. When 100 A of current are forced from the anode into the river, only 5 A collect at the gates. The remaining 95 A take an alternate path through the reinforcing steel in the concrete, the lock walls, and the armored noses of the piers back to the rectifier. The negative side of the rectifier is bonded to the service bridge of the dam, which is metallically connected to all the gates.

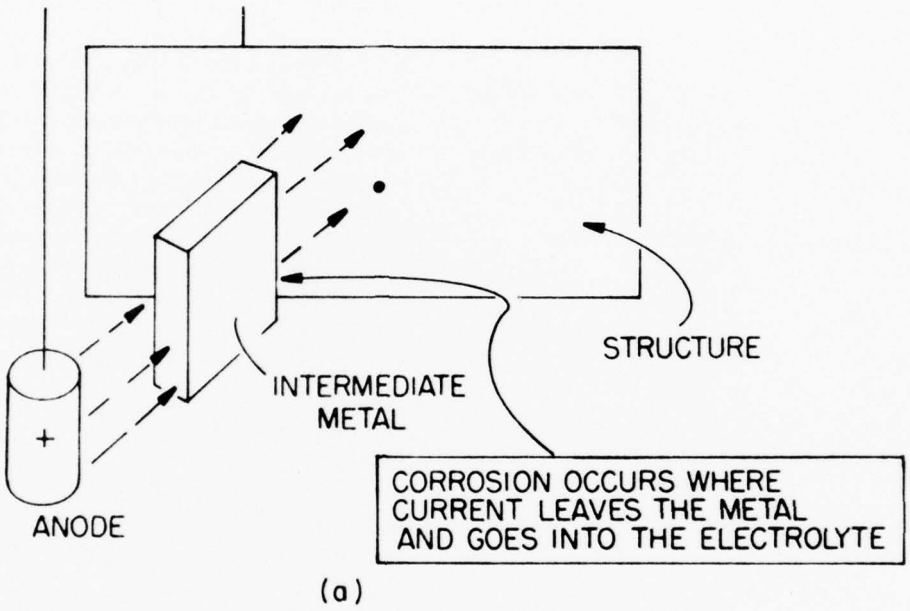
3.7.4 Another example is the set of nine steel anodes suspended from the bottom of the service bridge of Lock and Dam No. 15 on the Mississippi River. These anodes are approximately in line with the pier noses and about 30 ft (9.1 m) from the gate. Tests showed that 50 percent of the anodes' current reached the gate by way of the water path, 30 percent was collected by the piers, and 20 percent was unaccounted for; this is too much stray current.

3.7.5 Stray current through reinforcing bars in concrete is a particular problem. First, cathodic current that takes this path may be unavailable to protect the structure. Second, corrosion of reinforcing bars can result in cracking and spalling of concrete, and replacement or repair can be extremely expensive. This second problem arises when corrosion products accumulate at the rebar-concrete interface where current passes from metal to environment. As the reaction products build up, the volume increases, resulting in tensile stresses that cause cracking.

3.7.6 Concrete appears to be solid, but 30 to 40 percent of its structure actually consists of voids ranging in size from macroscopic air holes to holes as small as several atoms in diameter. In submerged applications, these voids fill with water, so that the concrete then serves as an electrolyte. The string of duriron anodes laid on the rock floor across a lock chamber at Lock and Dam No. 15 illustrates stray-current flow through concrete. After the current discharged from the anode has traveled a few feet, it has a water path 100 ft (30.5 m) wide and about 27 ft (8.2 m) deep (approximately 3,000 sq ft [250 m^2]). Since the concrete's resistance to the flow of current is about eight times greater than that of the water itself, only a small proportion of the current might be expected to stray to the concrete lock walls. Current may only travel 1 or 2 in. (25.4 or 50.8 mm) through this high-resistance path before it enters and travels along a rebar. Since the rebar's resistivity is considerably less than the water's, a significant percentage of the current takes this stray-current path.

3.7.7 Another poor location for anodes is the concrete cross-over for cables located just upstream of the string of anodes. Because this concrete is in the area of maximum potential gradient, it would be exposed to high-current density.

3.7.8 At Lock and Dam No. 15, there are 60 duriron anodes (2 in. × 9 in. [50.8 mm × 228.6 mm] each) connected with 12 in. (304.8 mm) of No. 6 neoprene-covered, seven-strand cable. At each end of



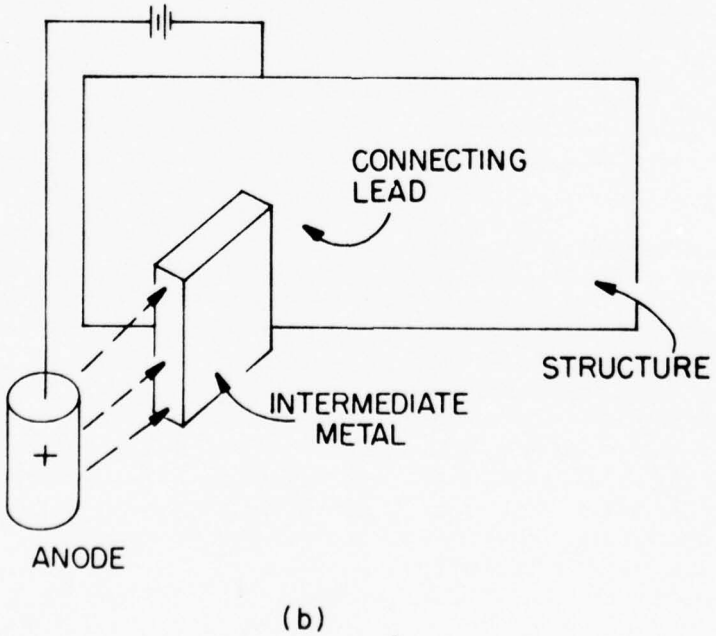


Figure 18. Stray-current corrosion.

the string, the cable is placed inside garden hose, which, in turn, is placed inside a conduit fastened within the ladder recess on each lock wall. Ice cannot damage this installation. Since the anodes are in the auxiliary lock used primarily for small boat traffic, determining whether the anodes might be vulnerable to the propeller backwash of larger ships is impossible. Each anode has a current density of 0.28 mA/sq ft (3.0 mA/m²), which is insufficient to cause anode deterioration. The current distribution on the gate is reasonable, even though the bottom one-third of the gate collects more than the top one-third.

3.7.9 If the lock walls rested on steel piling connected to the gates, locating the anodes in the piling would be improper, because the piling would then receive most, if not all, of the current. Stray current might accelerate corrosion for pilings not connected metallically to the gate.

3.8 Size and Shape of the Electrolyte Path. The electrolyte path is important when the current must travel a path that is long compared to its cross section. An example of this situation is the customary recess position of the emergency miter gates in the Chittendon Locks, Seattle District. These gates are recessed for at least 11 months of the year. There is about 6 in. (152.4 mm) clearance between the gate and wall. Because the water surrounding the gates is very corrosive and because coating life in this exposure is short, the design engineers have considered cathodic protection. The path for current in this case is a rectangle 6 in. (152.4 mm) wide, 40 ft (12.2 m) long, and 25 ft (7.6 m) deep. If anodes within the crevice are far apart, this narrow width requires that the current be "crowded" in the electrolyte. Because the circuit by which current could leave the anode, travel through the narrow-path electrolyte, and eventually enter the gate has a high resistance, relatively little cathodic current goes this way, and only the area near the anode is protected. Thus, closely spaced anodes—for example, 1-in. (25.4 mm) diameter magnesium anodes suspended vertically in the lot and spaced about 4 ft (1.2 m) apart—should be considered by the design engineer.

3.9 Resistance of Cathodic Protection Circuit

3.9.1 The resistance of the electrical circuit significantly affects the power costs of the installation. Thick cable is recommended for cathodic protection because of the low voltages that protection generally involves. Cable resistance to flow of current from a rod anode can be expressed as

$$R = \frac{0.012\rho \log \frac{D}{a}}{L} \qquad \text{[Eq 14]}$$

where ρ = the specific resistance of the electrolyte in ohms/cm³
D = the distance between anode and structure
a = anode radius
L = anode length in feet.

3.9.2 This equation can seldom be used in designing cathodic systems for hydraulic structures because anodes are generally not entirely surrounded with electrolyte. Most such anodes rest in a grooved timber or against a plastic holder of some kind. The equation does, however, illustrate the following important points:

a. Resistance varies inversely with the length of the anode.

b. Resistance is directly proportional to the resistivity of the electrolyte.

c. The effect of D and a is less than the other factors, especially when D/a is greater than 50.

3.10 Summary. The following points are particularly important to cathodic protection system design.

3.10.1 *Current Density.* About 2 mA/sq ft (21.5 mA/m²) is required to protect bare steel in freshwater; about 3 to 10 mA/sq ft (32.3 to 107.6 mA/m²) is required in quiet seawater.

3.10.2 *Current Density on the Anode.* Current density should not exceed 1000 mA/sq ft (10 763.9 mA/m²) on duriron. Manufacturer's recommendations should be followed for graphite.

3.10.3 *Impressed-Current Anodes.* Graphite anodes corrode rapidly at the ends and are vulnerable to mechanical damage. Duriron is brittle, so anode shapes of duriron anodes such as the type G, 2 in. × 9 in. (50.4 mm × 228.6 mm) with a cable running through the center and button type are satisfactory. Duriron's electrolytical resistance is very good. Various schemes for holding the segmented anodes on gates are available, but they are costly to construct

and provide significant resistance to the flow of current. Duriron anodes 2 in. × 80 in. (50.4 mm × 2.0 m) and 3 in. × 80 in. (76.2 mm × 2.0 m) are very good for soils in which their brittleness is not such a disadvantage. Aluminum anodes are commonly used in potable water tanks.

3.10.4 *Anode Location.* Positioning anodes directly upon a hydraulic structure generally works best. Remote anodes create stray-current corrosion and are susceptible to damage.

3.10.5 *Anode Supports.* Mechanical damage to anodes and supports has been a troublesome problem for cathodic protection installations on hydraulic structures. Of course, the mechanical features of a cathodic-protection design may be rugged enough to withstand the exposure, but the costs of making the features this rugged may be unjustifiable.

3.10.6 *Galvanic Anodes.* Magnesium is generally best for freshwater. Zinc and aluminum alloys are widely employed in seawater.

3.10.7 *Protection Criteria.* A structure is considered protected when a potential of −.85 V with respect to a copper-copper sulfate reference electrode is achieved. An alternative criterion states that protection is realized by a −.3 V shift in potential relative to its initial corrosion potential. In most natural waters, a calcareous deposit forms on the structure during polarization, giving a good visual indication that the cathodic-protection system is working.

3.10.8 *Permanence of Polarization.* A steel structure in freshwater that has been polarized for some time will require at least several days to depolarize if the cathodic-protection current is shut off.

3.10.9 *Current Distribution.* When the electrolyte's path is long in comparison to its cross section, current distribution will be a problem. When current density is not uniform, proper placement of anodes will provide satisfactory distribution on a structure.

3.10.10 *Stray Current.* Damage due to stray current must be considered whenever conducting materials other than the structure to be protected are present. Reinforcing bars in concrete especially warrant consideration.

4 RECTIFIERS FOR CATHODIC PROTECTION

4.1 General

4.1.1 The purpose of the rectifier unit in cathodic protection is to convert the ac power available at the site into direct current of the proper voltage and current values for the particular cathodic protection system. Figure 19 shows the interrelationship of the rectifier unit with the rest of the cathodic protection system and the ac line.

4.1.2 Figure 19 is a generalized block diagram of a cathodic protection rectifier unit. The first basic element is the line transformer, which changes the site ac voltage to the required rectifier voltage levels —the primary and secondary voltages. Typical values would be 120 to 480 V on the transformer primary and 10 to 50 V on the secondary. The transformer usually has provision for varying the output voltage; the two most commonly used methods are *winding taps*, in which the secondary winding has connections for selecting portions of the winding to provide different voltage levels, and *variable transformers*, in which the windings of the line transformer are fixed but an auxiliary variable transformer changes the voltage supplied to the transformer.

4.1.3 The key element for changing the alternating current into the required direct current for cathodic protection use is the solid-state rectifier, which operates in much the same manner as a check valve in a hydraulic system; that is, it permits current flow in one direction but blocks the flow in the reverse direction. Figure 20 shows the sequence of voltage transformation and rectification in the rectifier unit. Figure 21 shows a typical arrangement of the components of a rectifier unit.

4.1.4 Most rectifier systems used in cathodic protection have manually adjustable systems using either the transformer taps or a variable autotransformer to set the cathodic protection voltage level. After installation of the cathodic protection system, the protection level is initially adjusted using a half-cell reference voltage and then secured. Because the various phenomena associated with corrosion are long-term in action and slowly varying, the protection achieved by this initial setup is often satisfactory

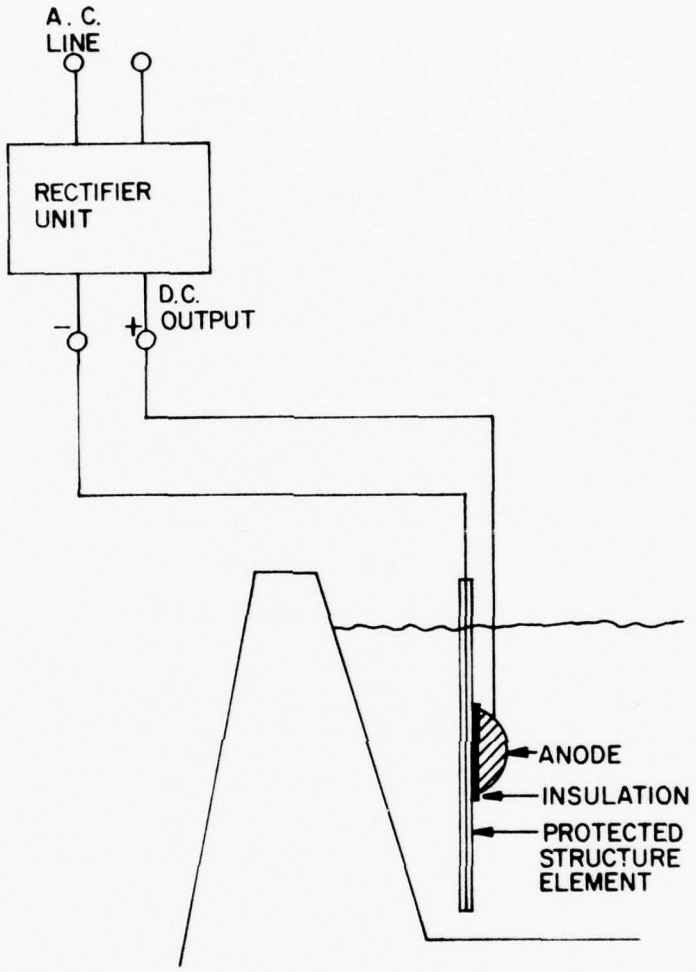


Figure 19. Basic configuration of cathodic protection system.

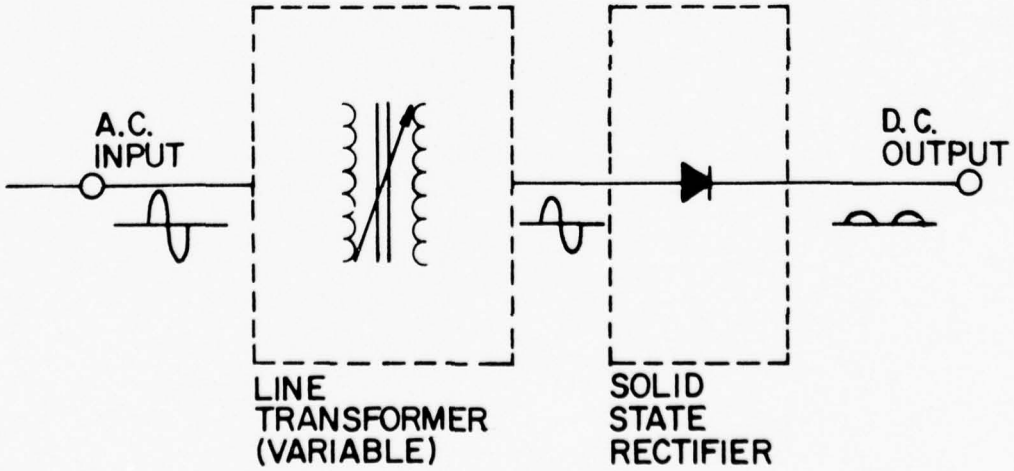
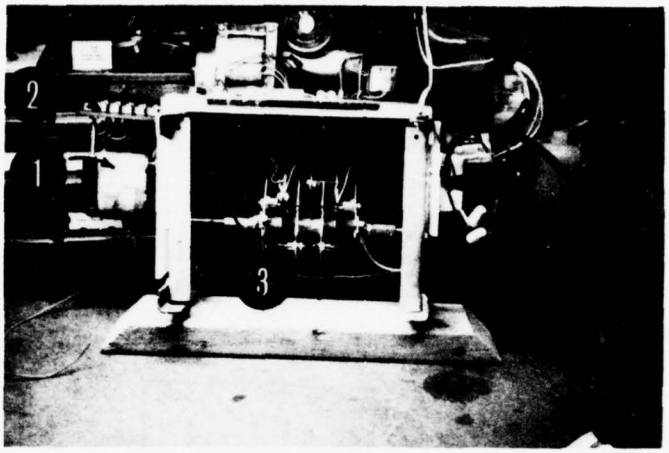


Figure 20. Basic elements of cathodic protection rectifier.



1 Transformer
2 Taps
3 Rectifier "stack"

Figure 21. Typical rectifier assembly.

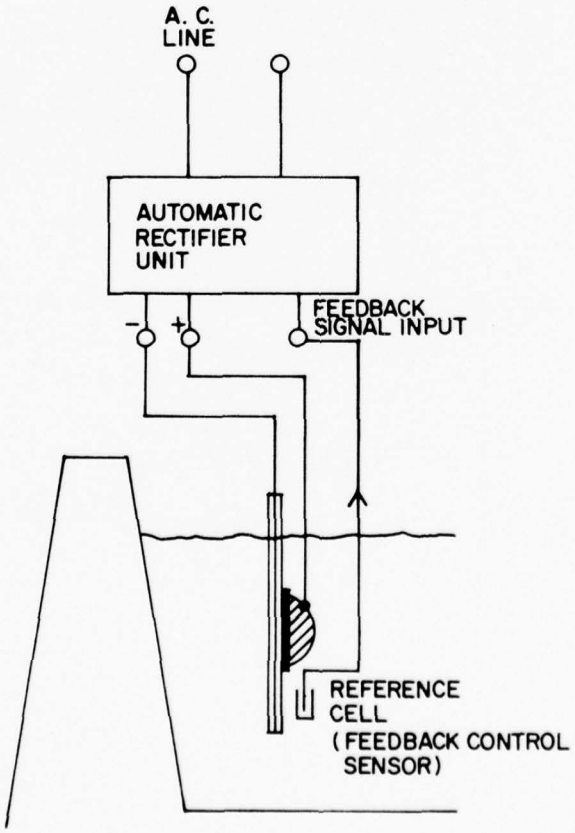


Figure 22. Basic configuration of cathodic protection system with automatic feedback control.

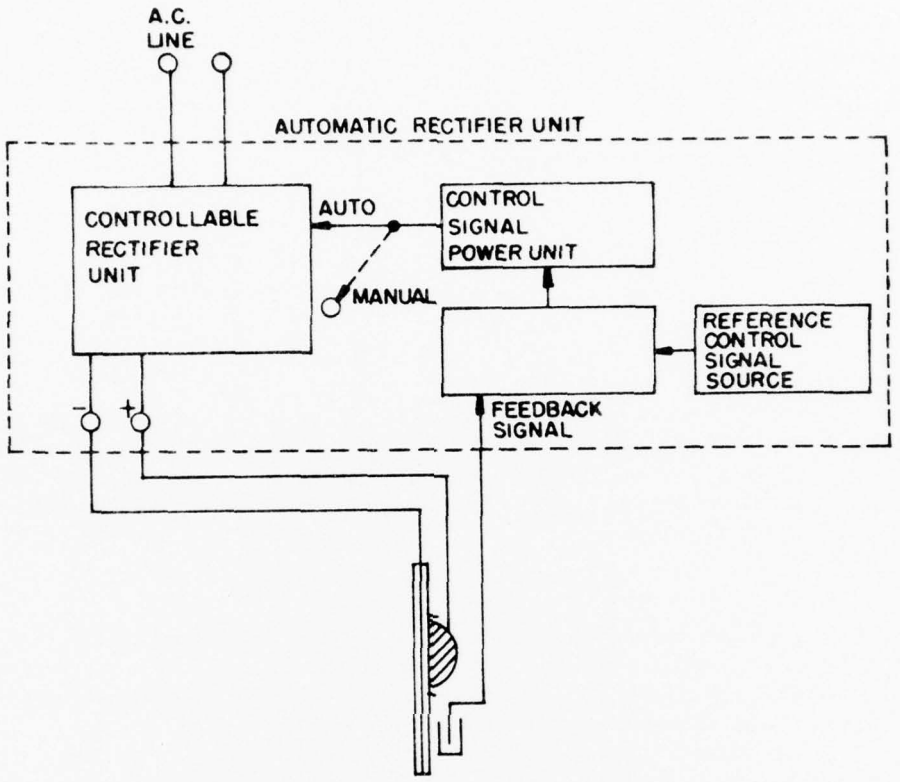


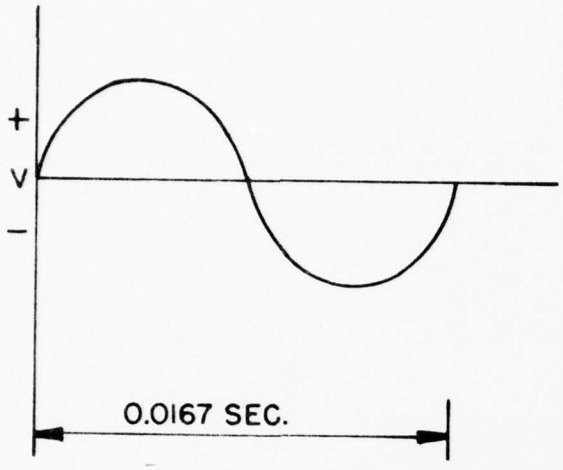
Figure 23. Block diagram of automatic rectifier unit.

for quite some time. However, manually adjusted systems are sometimes inadequate, particularly when changes in electrolyte conductivity occur due to some variation in composition. A typical example of this is the conductivity of water in channels with varying proportions of salt water and freshwater. Automatic rectifiers should be employed to accommodate these variations in the electrolyte.

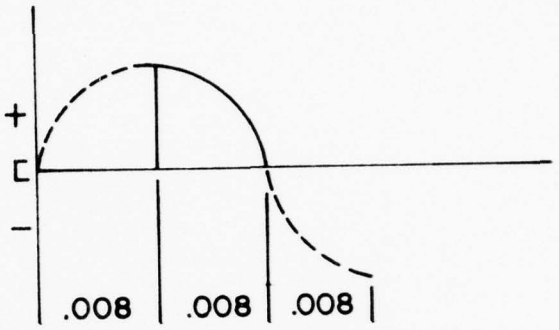
4.2 Automatic Rectifier

4.2.1 A rectifier unit for automatic control has the same basic elements as the manual system, but incorporates additional circuits to automatically change the output voltage or current to maintain a constant protection level as measured by a feedback control sensor. Figure 22 shows the interrelationship involved with an automatic control system.

4.2.2 Here the basic system is as shown in Figure 19, but is augmented by the addition of a reference cell in the vicinity of the structure to be protected. The output of this cell is fed back to the automatic rectifier unit, which changes the dc output level to maintain the protection voltage at a constant preset value. Figure 23 shows a block diagram of the electronic system that performs this control action. In operation, the protection voltage level desired is set by the reference or control signal source, which is fed into an electronic comparator circuit simultaneously with an electrical signal from the reference half-cell. If the two signals are of the same value (that is, the protection voltage level for the structure coincides with the preset control level), no error voltage is developed by the comparator and no correction signal is applied to the controllable rectifier unit. If, for any reason, the protection voltage level differs from the value set by the "demand" control signal, the comparator develops a difference, or error voltage, which actuates the control power unit. This changes the voltage applied to the protected structure so that the protection level again coincides with the preset value. Thus, the change in protection voltage engendered by the electrolyte conductivity change is nullified by an automatic modification of the applied voltage.



a. Time duration period of one cycle of 60 Hz ac line voltage; complete cycle supplied to rectifier stack produces full power output.



b. One cycle "clipped" (switched off) for half of positive phase, resulting in half power supplied to rectifier.

Figure 24. Switching action of SCR.

4.2.3 The device most commonly used in controllable rectifier systems is the silicon-controlled rectifier (SCR). SCRs, also called thyristors, are semi-conductors resembling silicon diodes but having a third terminal called a "gate" added for control purposes. A silicon diode will conduct in its forward direction and block the flow of current in its reverse direction, whereas an SCR will block in both directions until a firing signal is impressed on the gate-cathode circuit. When this occurs, the SCR will conduct in the forward direction.

4.2.4 SCRs may be substituted for regular diodes in any of the common rectifier circuits to produce controlled rectification, and the dc output can be varied from 0 to 100 percent by varying the timing of the firing signals.

4.2.5 Figure 24a shows an ac voltage for one complete cycle while Figure 24b shows the switching action of the SCR.

4.3 Evaluation of Automatic Rectifiers

4.3.1 Figure 25 shows oscilloscope traces made during the evaluation study of commercial automatic rectifiers.

4.3.2 Figure 26 is a chart recording the output voltage of two commercial automatic rectifiers which change in conductivity. This trace was made during a laboratory test of these rectifiers for use in the brackish water conditions of the intracoastal waterway system. Point (1) on the chart represents freshwater, with salinity progressively increasing to 3 percent at point (10).

4.3.3 During the study of automatic rectifiers, it was observed that the commercially available units possessed adequate operational capability for typical Corps problems in regard to speed of response to

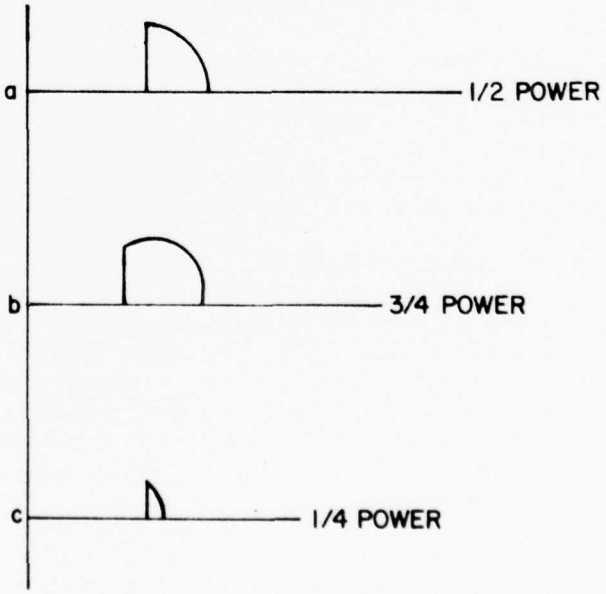


Figure 25. Oscilloscope traces showing switching periods.

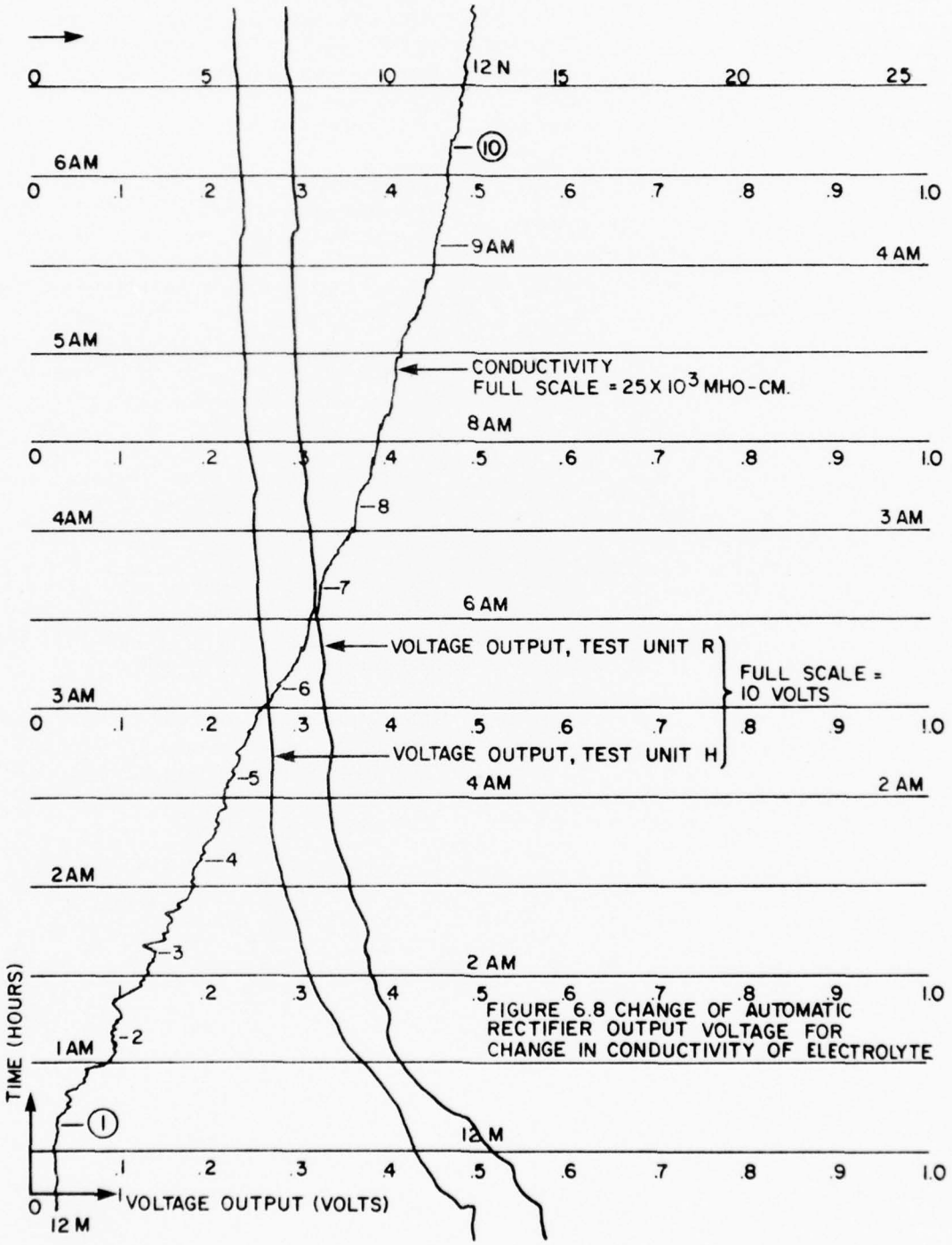


FIGURE 6.8 CHANGE OF AUTOMATIC RECTIFIER OUTPUT VOLTAGE FOR CHANGE IN CONDUCTIVITY OF ELECTROLYTE

Figure 26. Change of automatic rectifier output voltage for change in conductivity of electrolyte.

conductivity changes and voltage compensation range. Two potential problem areas became evident, however, in application of the units in the field.

4.3.4 First, overvoltage protection was completely lacking or ineffective. Although most units incorporate current-limiting or short circuit protection, the circuitry does not preclude excessive voltage malfunctions. Overvoltage on painted structures, of course, could cause severe paint blisters.

4.3.5 Second, only one half-cell is used in the feedback circuit; thus, there is no provision for a redundant, back-up sensor in the event of "fouling" or malfunction of the reference cell.

5 CONCLUSIONS

5.1 This study developed cathodic protection guidelines for systems prevalent in Corps of Engineers civil works operations based on (1) the principles of corrosion and cathodic protection, (2) electrochemical experiments relevant to corrosion mitigation of Corps hydraulic structures, and (3) investigation of anode requirements using electric field concepts.

5.2 The electrochemical experiments relating to corrosion situations encountered in Corps of Engineers civil works operations indicated that a minimum cathodic protection voltage of −0.850 V relative to a copper-copper sulfate electrode is mandatory. With less than this value, the corrosion rate increases significantly. The experiments also indicated that the location and voltage reading of the reference electrode are very important. Since a reference electrode more than ¼ in. (6.4 mm) from the structure in the anode direction will give a higher voltage reading, accidentally placing the reference electrode within the high potential gradient of an anode could result in a large and erroneous reading. A third conclusion from the experiments is that the size of area exposed has a significant effect on the corrosion rate.

5.3 Because the required cathodic protection level must be maintained over the entire surface susceptible to corrosion, the continuum aspects of electric field design were explored. This method was found to offer two salient advantages for cathodic protection system design:

a. It alerts the designer to areas of underprotection caused by shadowing (conversely, it reveals possible overvoltage areas that could cause paint failure). Results indicated that cathodic protection is affected drastically by the placement of an extraneous conductor whose area is only 5 to 10 percent of that of the area to be protected.

b. It provides guidance in anode placement for cathodic protection designs involving structures of irregular shape. For example, paralleling anodes was found to decrease corrosion resistance.

5.4 An additional part of this study was a survey of commercially available automatic rectifiers. This survey revealed two major shortcomings: inadequate feedback sensor input design and unsatisfactory overvoltage protection.

APPENDIX A:

CATHODIC PROTECTION EXPERIMENTS

A.1 Criterion for Protection

A.1.1 The accepted criterion for cathodic protection of submerged iron and steel structures has been a negative voltage of at least 0.850 V measured between the structure surface and a saturated copper-copper sulfate reference electrode. For large bare structures, a potential change of 300 mV has been used as an alternate criterion.* Increasing use of iron and steel in submerged structural applications necessitates development of detailed design criteria for cathodic protection; this development demands preliminary basic data on some fundamental aspects of corrosion behavior. Knowledge of current requirement, the nature of the structure (painted, partly painted, bare), the area affected, the conductivity of the electrolyte, and the effect of velocity is needed to deal with the problem of providing adequate protection.

A.1.2 A metal immersed in an aqueous environment develops an electrical potential. This potential, known as electrode potential or corrosion potential, characterizes the metal's behavior in a specific corrosive environment. A metal's potential in natural environments seldom agrees with the standard electrode potential. Variations result from polarization phenomenon and other secondary processes which occur when the metal is immersed in the electrolyte. Quite frequently, the corrosion potentials vary with time as well. Occasionally, the steady-state value of potential is achieved in several hours, if the corrosive conditions are maintained constant. In contrast, when an impressed current is applied for cathodic protection, attaining the steady-state current value may take several weeks.

A.1.3 This appendix describes the method and results of experiments designed to provide information on several of the problem areas discussed above —effects of environment and time on corrosion potential and current decay, effects of protection current on weight loss, and effects of area exposed on current.

*The National Association of Corrosion Engineers lists two additional criteria in Recommended Procedure 01-69:

1. A minimum negative (cathodic) polarization voltage shift of 100 mV measured between the structure surface and a saturated copper-copper sulfate reference electrode contacting the electrolyte.

2. A structure to electrolyte voltage at least as negative (cathodic) as that originally established at the beginning of the Tafel segment of the E-Log-I curve.

A.2 Specimen Preparation

A.2.1 Test specimens of a representative structural steel, ASTM A 36, were cut from a large steel plate. The specimen dimensions—6 in. × 3 in. × 0.045 in. (152.4 mm × 76.2 mm × 1.1 mm)—were limited by the capability of the analytical balance used in the weight loss tests. The specimens were sanded with grade 120 abrasive paper and then cleaned by dipping in a 30 percent hydrochloric acid solution for 30 minutes. The specimens were then washed under running distilled water, followed by alcohol and acetone. They were then dried at 150°F (66°C) in an oven for 30 minutes.

A.2.2 A small insulated plastic tank was used as a container for the electrolyte. Tests were conducted in tap water (both flowing and still), and a 3.5 percent sodium chloride solution. Table A1 lists the composition of the tap water. The flowing water condition was obtained by providing three outlet holes of ¼ in. (6.4 mm) diameter in the tank. The water was drawn directly from the tap and the velocity was controlled by the inlet valve. Figure A1 shows the complete test setup.

A.3 Corrosion Potential Measurements (Open Circuit). Corrosion potential of the steel plate was determined for three conditions: still tap water, flowing tap water, and still 3.5 percent salt solution. A calomel half-cell was used as the reference electrode. Table A2 shows the conversions of different half-cell potentials, as measured with an electrometer, to that for the copper-copper sulfate half-cell. Electrical contact between the steel plate and calomel electrode was maintained through a salt bridge. Potential readings were recorded for 30 days from the time the steel plate was immersed in the electrolyte. Corrosion potential versus time was recorded for all three test conditions (Figure A2).

A.4 Current Decay Measurement. Figure A3 shows the electrical circuit arrangement for measuring the current. The constant voltage minipotentiostat shown in Figure A3 was used to supply a constant voltage of −0.778 V with reference to the calomel half-cell (equivalent to −0.85 V with respect to a copper-copper sulfate half-cell). The minipotentiostats were designed, hard-wired and then checked

Table A1

Mineral Analysis of Tap Water*

		mg/ℓ	me/ℓ			mg/ℓ	me/ℓ
Iron (total)	Fe	.00		Phosphate			
Manganese	Mn	.00		(unfiltered)	PO_4	0.0	.00
Calcium	Ca	13.6	.68	Silica	SiO_2	6.8	
Magnesium	Mg	11.7	.96	Fluoride	F	1.1	
Strontium	Sr	.13		Boron	B	0.3	
Sodium	Na	32.9	1.43	Nitrate	NO_3	0.0	.00
Potassium	K	2.6	.07	Chloride	Cl	5	.14
Ammonium	NH_4	0.9	.05	Sulfate	SO_4	34.1	.71
Barium	Ba	<0.1					
Cadmium	Cd	.00		P Alkalinity	($CaCO_3$)	12	.24
Chromium	Cr	.00					
Copper	Cu	.00		M Alkalinity	($CaCO_3$)	117	2.34
Lead	Pb	< .05					
Lithium	Li	.00		Hardness	($CaCO_3$)	82	1.64
Nickel	Ni	< .05					
Zinc	Zn	.00		Total Dissolved Minerals		179	
mg/ℓ = milligrams per liter				Turbidity		0	
Me/ℓ = milliequivalents per liter				Color		0	
Mg/ℓ × .0583 = grains per gallon				Odor		0	
				Temp. (at tap)		53.2°F	
				pH (in lab)		9.0	

*Analysis conducted by the laboratory of the Illinois State Water Survey, Champaign, IL.

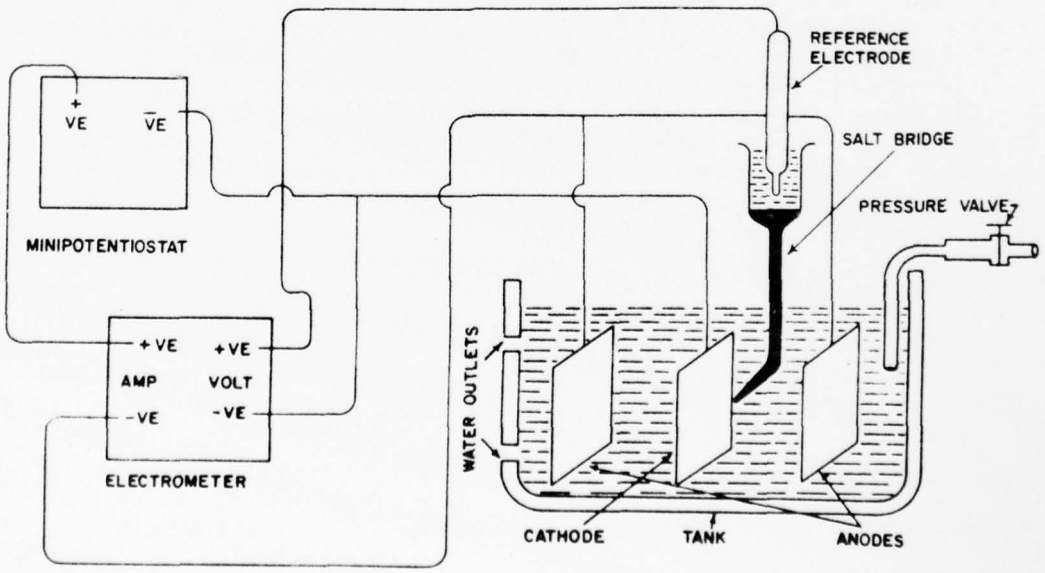


Figure A1. Test setup for cathodic protection experiments.

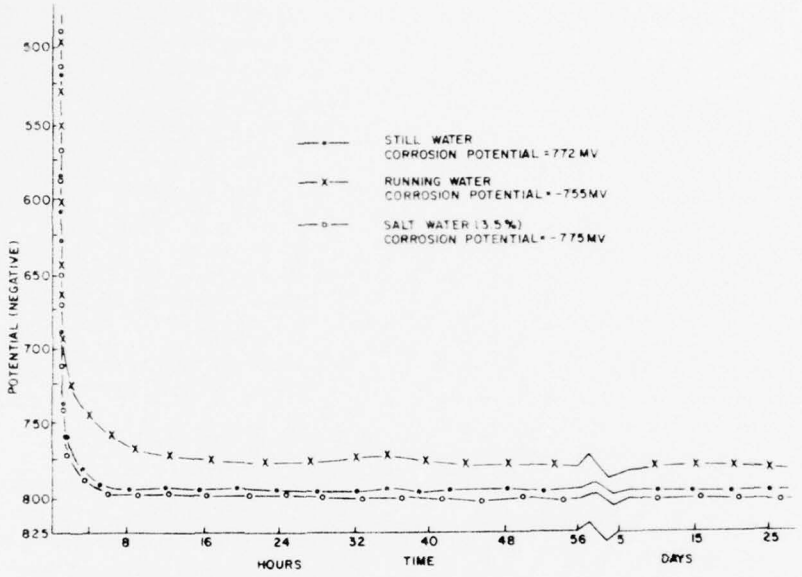


Figure A2. Decay of corrosion potential for three environments. The figure shows the time required to reach steady-state potential with respect to a copper-copper sulfate reference electrode when bare steel is immersed in still tap water, running tap water, and still saltwater.

Table A2

Equivalent Potentials of Reference Electrodes Relative to −0.85 V Reading of Copper-Copper Sulfate Electrode

Type of Comparative Reference Electrode	Comparative Reference Electrode Reading Equivalent to −0.85 V on the Copper-Copper Sulfate Electrode
Calomel (saturated)	−0.778 V
Silver/Silver Chloride (0.1 N silver chloride solution)	−0.840 V
Silver/Silver Chloride (silver screen with deposited silver)	−0.780 V
Pure Zinc (special high grade)	+0.250 V

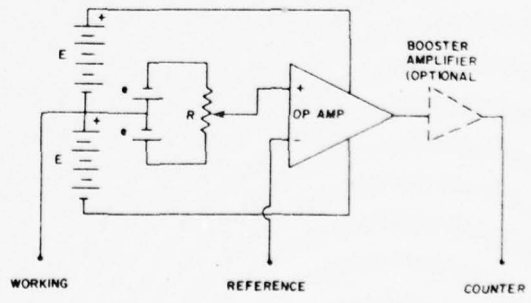


Figure A3. Diagram of minipotentiostat.

for at least a week before use in the testing. Two 304 stainless steel plates were used as the counter electrodes. Current readings were taken for 10 to 15 days. Tests were conducted in still tap water, flowing tap water, and still 3.5 percent salt solution. Figure A4 shows the current decay with respect to time. In the case of flowing tap water, the current decay was noted for constant potentials of −0.850, −0.825, −.800, −0.750, and −0.700 V. Figure A5 shows the variation of current with time at different potentials.

A.5 Area Exposure Tests. Six plate specimens with different areas exposed were prepared. One side of each specimen was completely coated with vinyl paint; the other sides were partially painted, leaving 0.025, 1.5, 3, 9, and 18 sq in. (0.16, 9.7, 19.4, 58.1, and 116.1 cm^2) exposed. A constant protective voltage of −0.850 V with respect to the copper-copper sulfate half-cell was maintained by the minipotentiostat for 1 week. Current readings were taken at different intervals. Figure A6 shows the variation of the steady-state current with the area exposed.

A.6 Weight Loss Measurements

A.6.1 The weight loss specimens were prepared as for the other tests. They were then weighed to an accuracy of 0.1 mg on an analytical balance. Precautions against humidity and contamination were taken. After weighing, each specimen was quickly and carefully placed as a cathode in the running water tank as shown in Figure A1 (or stored in a desiccator).

A.6.2 Two 6 in. × 3 in. × .89 in. (152.4 mm × 76.2 mm × 22.6 mm) 304 stainless steel plates were used as counter electrodes and were placed at equal distances from each face of the specimen; the specimen was completely immersed in water.

A.6.3 All the electrical connections were checked and special care was taken to totally insulate the specimen from any other foreign metallic piece. A similar plate was cleaned, weighed, and placed in the same tank but without any protection. Constant voltages of −0.850 V, −0.825 V, −0.800 V, −0.775 V, −0.750 V, and −0.700 V with respect to a copper-copper sulfate half-cell were applied as the protection voltages by a Princeton Applied Research Potentiostat. Intermittent current readings were taken during the 10-day tests. A saturated calomel electrode with a salt bridge was used as the reference electrode. The top of the salt bridge was maintained at a distance of 1 to 3 mm from the steel plate.

A.6.4 After 10 days, the specimens were taken out of the tank, visually inspected, and then washed in running water with careful wire brushing. The specimens were then washed with alcohol and dried in an oven at 150°F (66°C) for 30 minutes. The final weight, measured on the same analytical balance as the initial weight, was recorded. Figure A7 is a plot of protection voltage versus the loss in terms of mils per year, calculated from the equation

$$\text{mpy} = \frac{534W}{DAT} \qquad \text{[Eq A1]}$$

where W = weight loss, mg
D = density of specimen, g/cm^3 (−7.56 for steel)
A = area of specimen, sq in.
T = exposure time, hr.

A.7 Results and Discussion

A.7.1 *Corrosion Potential.* Although most common metals tend to dissolve in corrosive environments, their rates of corrosion vary substantially. The corrosion potential is a reasonable indicator of the dissolution of the metal. In the case of steel immersed in freshwater (containing dissolved oxygen), the corrosion potential results from the anodic dissolution of iron (Fe) to iron ions (Fe^{+2}) and the cathodic reduction of oxygen (O_2). A metal (Fe) in equilibrium with its own ion (Fe^{+2}) builds up an electrical potential, termed reversible potential, at the metal-electrolyte interface. However, the potentials of some metals in solutions of their own ions do not seem to be reversible; iron falls into this group. In the field, the corrosion potential measured by a copper-copper sulfate reference cell does not represent the equilibrium state (reversible electrode potential) but a steady-state condition. Quite frequently, the irreversible electrode potentials vary with time. Occasionally, the change of potential takes place during many hours. In this study, a steady-state value was attained within 24 hours for all three test conditions (i.e., still tap water, flowing tap water, and still salt water).

A.7.2 *Current Decay*

A.7.2.1 Immersing steel in an electrolyte perturbs the uniform properties of the electrolyte in the interface region. The iron ions and water molecules tend to assume a certain time-average-arrangement. In the ideal case, the metal and solution continuously interchange ions. Ions pass from the surface of the

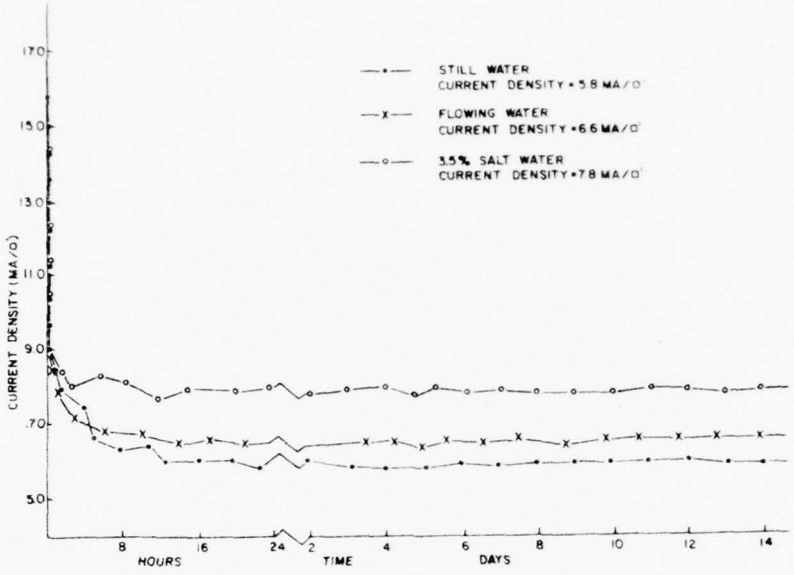


Figure A4. Current decay in three environments (potential = −0.850 V). This figure shows the time required to reach steady-state current when a plate of steel is maintained at −0.85 V with respect to a copper-copper sulfate reference electrode by an impressed current. The steady-state current density is shown in the graph.

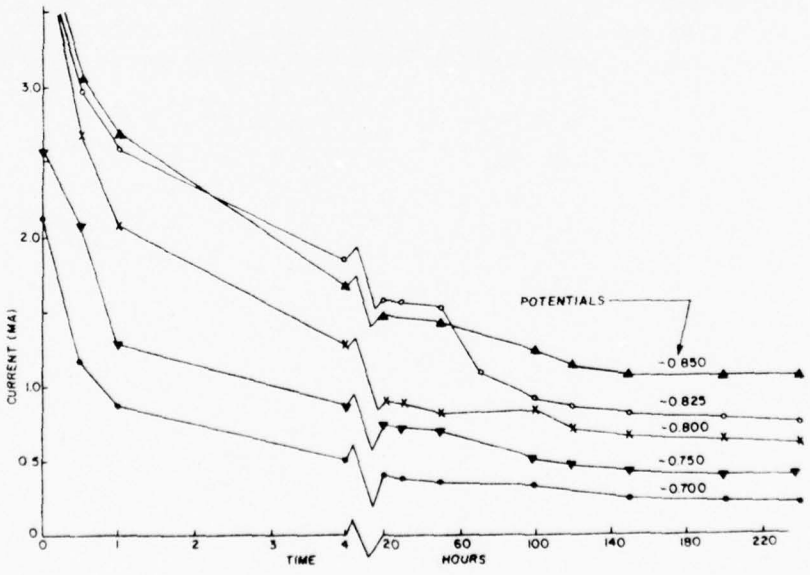


Figure A5. Current stabilization in flowing tap water at five potentials. This figure shows the time required to reach steady-state impressed current which is required to maintain a bare steel plate at five different potentials ranging from −0.700 to −0.850 V with respect to a copper-copper sulfate reference electrode.

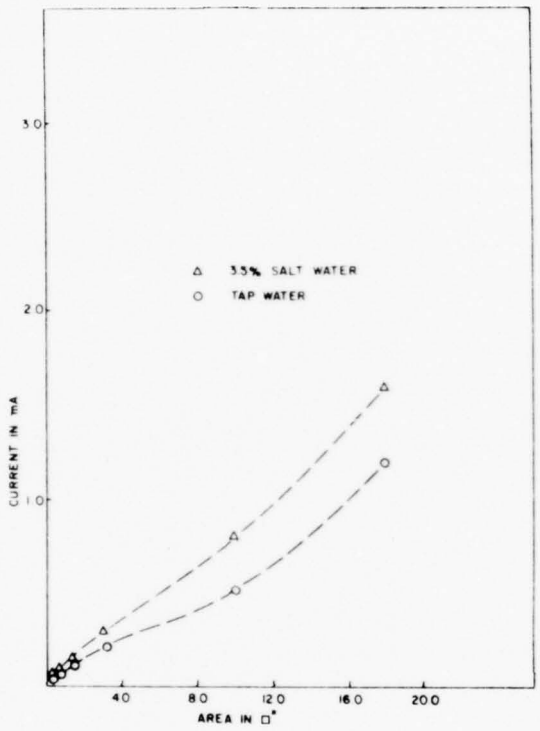


Figure A6. Protection current versus cathode area. This figure shows the steady-state cathodic protection current required to shift the potential to −0.850 V with respect to a copper-copper sulfate reference electrode for bare steel exposed to tap water as well as salt water. SI conversion factor: 1 sq in. = 6.4516cm².

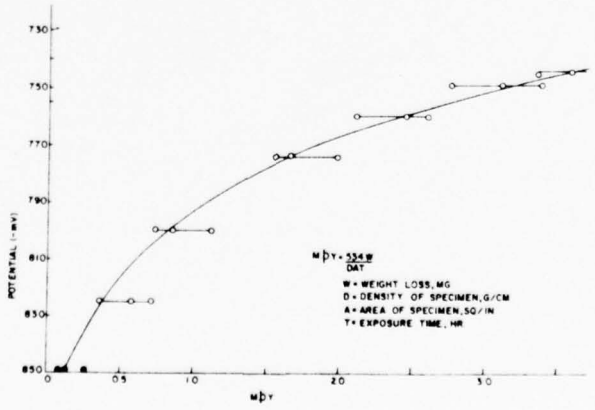


Figure A7. Corrosion rate (mils per year) versus protection voltage. This figure shows the corrosion rate in mils per year (mpy) as a function of the cathodic protection voltage with respect to a copper-copper sulfate reference electrode. SI conversion factor: 1 mil = .0254 mm.

metal into solution, while ions from the solution are simultaneously transferred to the metal. A kinetic equilibrium between the electrode and the solution can exist only when the rate of ion migration from the metal into solution ($M_s^+ \rightarrow M_l^+$) is equal to the velocity of the opposing process ($M_l^+ \rightarrow M_s^+$). In practice, however, the situation is complicated, and an equilibrium state is never attained; the nature of metal itself, the physiochemical state and structure, the condition of the surface, the presence of protective films on the metal, the molecules absorbed on the surface, and the mechanical deformation and stresses in the metal each have an effect. The nature of the electrolyte (i.e., the concentration of ions in the solution, nature and concentration of dissolved gases, etc.) also has a marked effect. On the other hand, the oxide film formed on the surface may break and reform depending on the dynamics and condition of the electrolyte. The mobility of interfacial products in running water is quite high compared to that in still water, and a steady state will be attained more readily.

A.7.2.2 In the current decay experiments, the current was initially high and gradually reached a steady-state value in several hours. Because the test piece was maintained at constant potential with respect to the reference cell, the difference in current reading with time was the result of interfacial reaction near the test piece. Since the conductivity of salt water is very high compared to that of tap water, a higher initial current value was obtained. In both cases, the current decay was due to the interfacial reaction at the test piece, i.e., formation of double layer and oxide film. These factors may appear simple, but pinpointing the kinetics of each factor is very complex. It must be noted here that for all the tests the current recorded is that required to maintain −0.850 V with respect to a copper-copper sulfate reference electrode—complete protection criterion. With less voltage, continuous slow formation of oxide film on an unprotected plate will occur, resulting in a different rate of current decay.

A.7.2.3 In short, once the test piece reaches a steady state with the electrolyte, a steady value of current is achieved. However, the time to breakdown and rebuilding of the complex layers around the test piece as well as the external disturbance in power supply will result in minor current changes. If all the other conditions are maintained constant, as in this experiment, the steady-state current value is achieved in several hours.

A.7.3 *Area Exposure*

A.7.3.1 The steady-state current also depends on the area exposed. In most cases, paint is the primary corrosion mitigation technique, and additional corrosion prevention is achieved through cathodic protection. It is expected that the current will be linearly proportional to the cathodic area in a cathodic control process when the field is uniform and the electrolyte has very low resistivity. Figure A6, a plot of current versus area, however, shows a deviation from linearity due to (1) high electrolyte resistivity and (2) a nonuniform field in the cathodic area caused by different areas of the cathode being exposed. As Figure A6 shows, the deviation from linearity is less in an electrolyte of 3.5 percent salt water than in freshwater. This nonuniformity of the electric field due to fringe effects is discussed in Appendix B.

A.7.3.2 The average cathodic protection current requirement, as shown in Figure A6, is 12 mA/sq ft (129.2 mA/m^2) for bare steel. Designers have frequently used 2 mA/sq ft (21.5 mA/m^2) as the criterion for coated steel. It appears that size effects play a major role; experiments are being conducted to determine this effect.

A.7.4 *Weight Loss*

A.7.4.1 The weight loss tests indicated that polarization to a potential of −0.85 V with respect to a copper-copper sulfate reference electrode provides adequate protection (Figure A7). Table A3 shows mils per year loss at various field installations for comparison. Figure A6 indicates that an error of only 50 mV will result in an increased corrosion rate.

A.7.4.2 The tests also indicate that the position of the reference electrode on miter gates and related structures where impressed-current anodes are attached is important. It is apparent from the field distribution curve (Figure A8) that if a reference electrode ¼ in. (6.4 mm) from the structure reads −0.85, the structure is being underprotected. For a protection corresponding to −0.85 V with respect to a copper-copper sulfate reference electrode, the external power supply should be adjusted so that the potential reading is larger (−0.877 for this example).

A.7.4.3 These results very clearly emphasize that structures must be maintained at least at −0.850 V with respect to a copper-copper sulfate reference electrode and that the location and voltage reading of the reference electrode are very important.

Table A3

Corrosion Rates of Mild Steel Immersed in Natural Waters

Type of Water	Test Site	Test Duration, years	Average General Penetration mil/yr (μm/yr)
Freshwater	Plymouth freshwater reservoir	15	1.7 (43.2)
River Water	La Cadene Granite bed, very pure water	5	2.7 (68.9)
	Dole high calcareous water	5	0.4 (1.0)
Seawater	Halifax, Nova Scotia	15	4.3 (109.2)
	Plymouth	15	2.6 (66.0)
	New York Harbor	0.68	2.37 (60.2)
	Miami, Florida	0.39	6.30 (160.0)
	Haifa, Israel	0.25	6.78 (172.2)

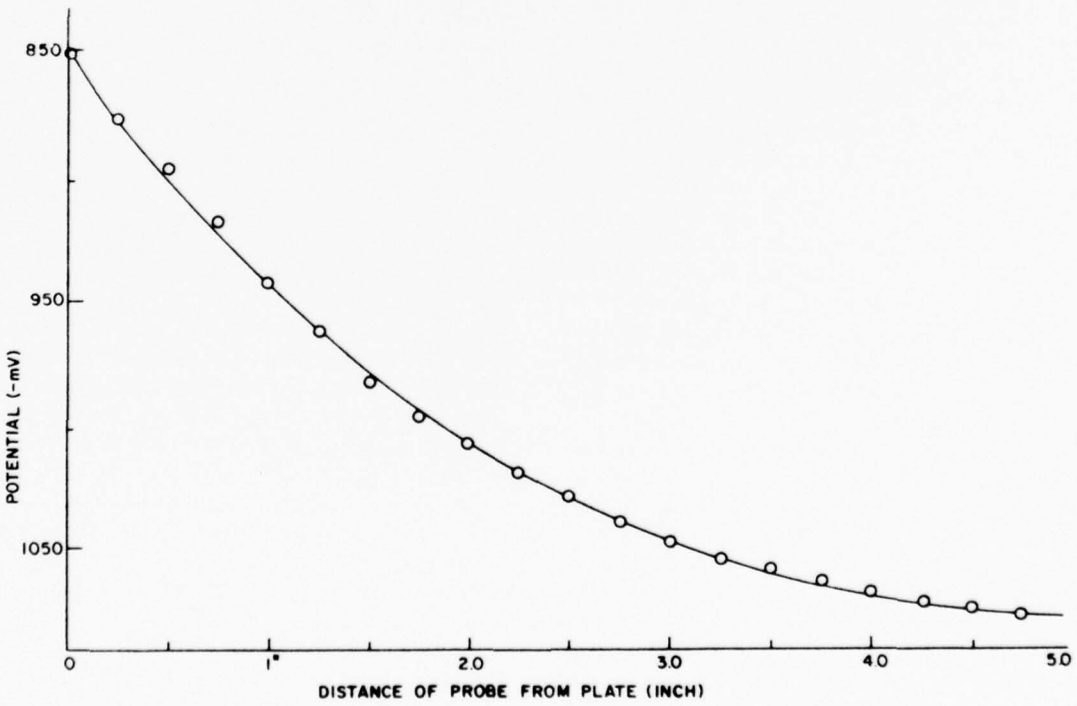


Figure A8. Variation of potential with increasing distance from protected cathode. This figure shows the voltage drop in an impressed-current system. SI conversion factor: 1 in. = 25.4 mm.

APPENDIX B:

ELECTRIC FIELD ANALYSIS

B.1 Principles of Field Mapping

B.1.1 The essential element of cathodic protection is the external current source which opposes the corrosion potential of the metal to be protected *at every point* of the exposed surface. This potential must be maintained over changes in structural geometry. To implement this, a design approach based on the continuum aspects of electric field analysis was investigated. This approach provides a practical overview which uses some versatile techniques such as curvilinear-square field mapping and superposition synthesis.

B.1.2 A field is defined as a region of space which possesses at each point some definite physical quantity that is a continuous function of the space coordinates. For example, the region in the vicinity of two surfaces which are maintained at a constant temperature difference may be thought of as a temperature field, since each point possesses a scalar quantity—temperature—and a vector quantity—temperature gradient. A map of this field would indicate various isotherms and heat flow lines. Similarly, maps of electric fields consist of lines of equal potential called equipotential lines, and flux lines connecting points on a current source, such as an anode, to a "sink," which would be the protected metal surface. Figure B1 shows the interrelationships of the various field lines and associated geometry.

B.1.3 In practical structures using cathodic protection, the electric potential fields encountered have a three-dimensional variation; that is, space variations occur along the x, y, and z coordinate axes, and a strictly accurate quantitative analysis involves evaluation of the gradients in all three directions. Except for very simple geometrical configurations, these evaluations cannot be carried out analytically. Fortunately, many of the fields encountered in practice can be reduced to two-dimensional fields, at least as a first approximation; it is in analyzing these fields that the curvilinear-square method of field mapping is most useful. Although this method is approximate, it will prevent gross errors in many areas of practical importance in cathodic protection design. The curvilinear-square method may be used to advantage, for instance, in accounting for the effect of electric field fringing due to interference of surrounding metallic elements.

B.1.4 In mapping a two-dimensional field, the essential problem is that of filling the region surrounding two specified boundary geometries with curvilinear squares so that the connecting volume between these boundaries may be envisioned as being completely filled with "unit squares."

B.1.5 The first requirement in laying out curvilinear squares is that the mean or average 'a' dimension of a square equal the mean or average 'l' dimension (Figures B1 and B2).

B.1.6 The second requirement is that the intensity of flux lines be drawn normal to the equipotential lines. The latter are, by definition, cross sections of

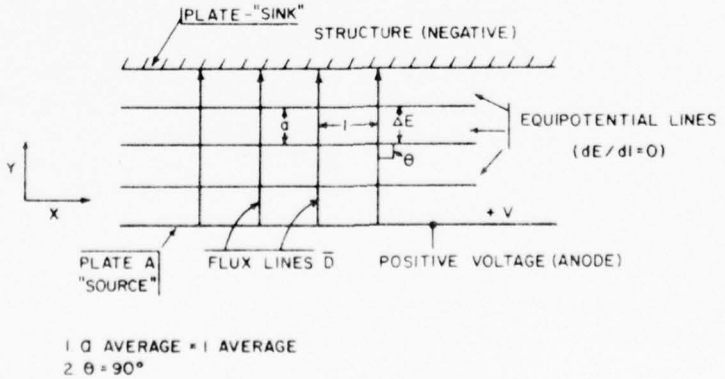


Figure B1. Cross-sectional view of electrically charged, indefinitely extended metal plates showing relationship of equipotential and flux lines used in curvilinear-square field mapping.

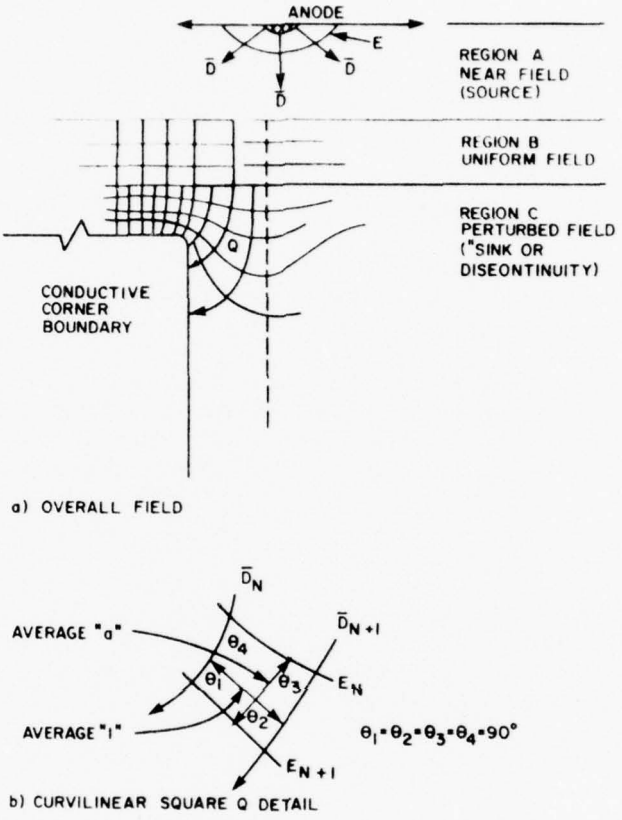


Figure B2. Curvilinear-square field plotting: construction and subdivision.

surfaces which possess zero space rate of change of potential; i.e., the voltage change directed along an equipotential line must be equal to zero ($dE/dl = 0$). Third, all conducting surfaces are equipotential surfaces; it is a fundamental principle of electricity that free charges cannot exist on a conductor; hence, no potential difference can exist over a conductive surface, which is the essential criterion for an equipotential surface or line. This conveniently establishes an equipotential geometry from which a map can be constructed—for example, the conductive corner boundary of Figure B2.

B.1.7 Figure B2 summarizes these principles graphically. Figure B2 shows:

a. Region A, the field emanating from the source. The initial field shape conforms to the surface of the source—in this case a button anode.

b. Region B, the area at some distance from the source and remote from conductive surfaces where the field becomes uniform and planar; Figure B1 illustrates a field of this type.

c. Region C, the area in the vicinity of conductors or other sources where the field is distorted and becomes nonuniform. At a conductor, the field assumes the shape of the boundary, while in the proximity of other sources, the field lines result from the superposition of the individual source fields.

B.2 Laboratory Electric Field Mapping

B.2.1 Large electrolyte tanks were constructed for performing laboratory electric field mapping of structural models. Three button anodes and a plane cathode sheet were placed in the 5 ft long × 10 ft wide × 4 ft deep (1.5 m × 3.0 m × 1.2 m) electro-

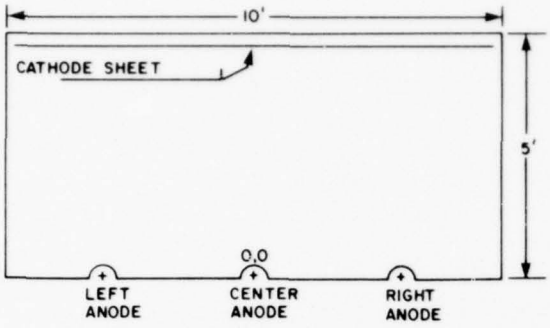


Figure B3. Typical electrolyte tank for model studies. The center anode is the coordinate system origin point for field plots made in this tank. SI conversion factor: 1 ft. = 0.3048 m.

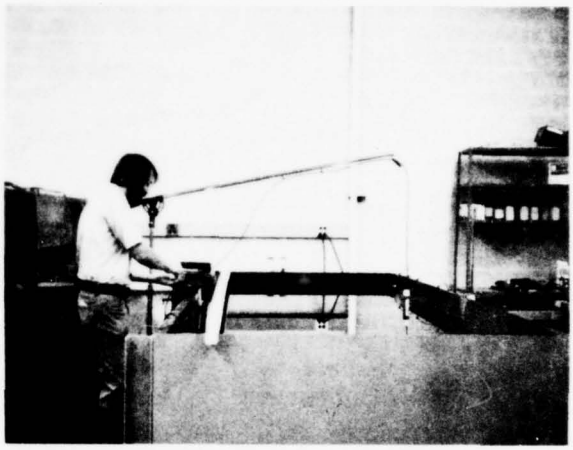


Figure B4. Field mapping in electrolyte tank.

lyte tanks, as shown in Figure B3. A suitable half-cell (copper-copper sulfate or silver-silver chloride) was mounted on a microphone boom and moved to follow a particular equipotential line; sufficient coordinate points were noted to construct the field plots. The anodes were energized and the electric field plots were made. Figure B4 shows a field plot being made in one of the electrolyte tanks.

B.2.2 Figures B5 through B8 show the electric field plots of fields resulting from energizing one or more of the anodes. In each case, the anode to cathode potential was adjusted to give a protective value of −0.850 V (with respect to a copper-copper sulfate reference electrode) at the cathode sheet. Figure B5 is a plot of the center electrode energized. This plot shows the constant voltage contours as indicated. Figure B6 shows the field resulting from energizing the left and right anodes, and Figure B7 shows the field for all three anodes energized. For comparison, Figure B8 shows a field plot of an anode having approximately twice the surface area of that used in obtaining the plot in Figure B5.

B.2.3 These plots were made with no conducting materials in the electrolyte. The only interfering conductors were the metal walls of the electrolyte tank; this effect is observed by the deviation of the contour of the 1-V equipotential line. Figures B9 through B11 are field plots of a single anode energized in the electrolyte tank with a 1.5 sq ft (0.14 m^2) metal specimen intervening between the anode and cathode sheet.

B.2.4 Figure B9 shows the effect of fringing or shadowing associated with a plate of this size at right angles to the electric flux lines from the anode to the cathode sheet. Figure B10 shows the distortion of the field when the interfering specimen is oriented 45

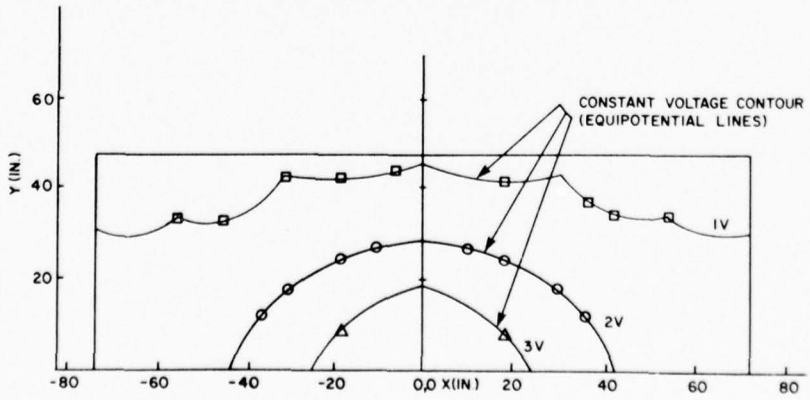


Figure B5. Electric field plot: single button anode energized. SI conversion factor: 1 in. = 25.4 mm.

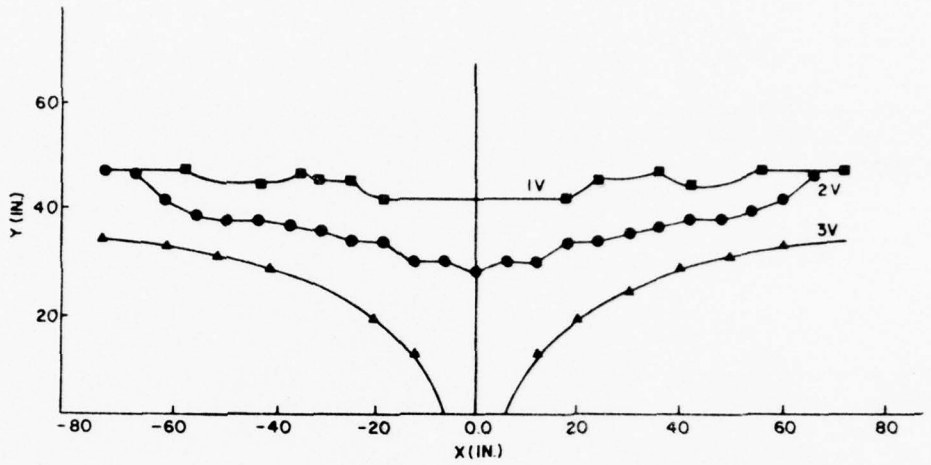


Figure B6. Electric field plot: two bottom anodes energized. SI conversion factor: 1 in. = 25.4 mm.

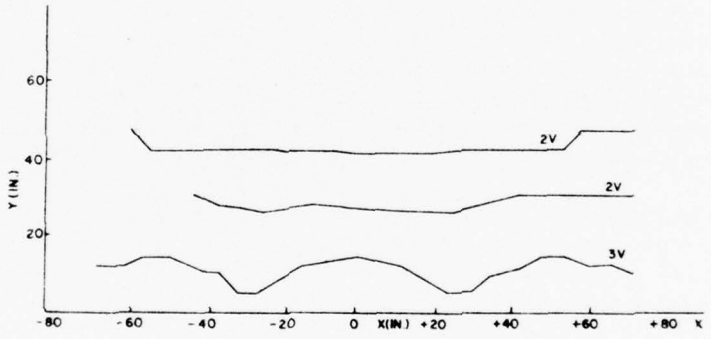


Figure B7. Electric field plot: three anodes energized. SI conversion factor: 1 in. = 25.4 mm.

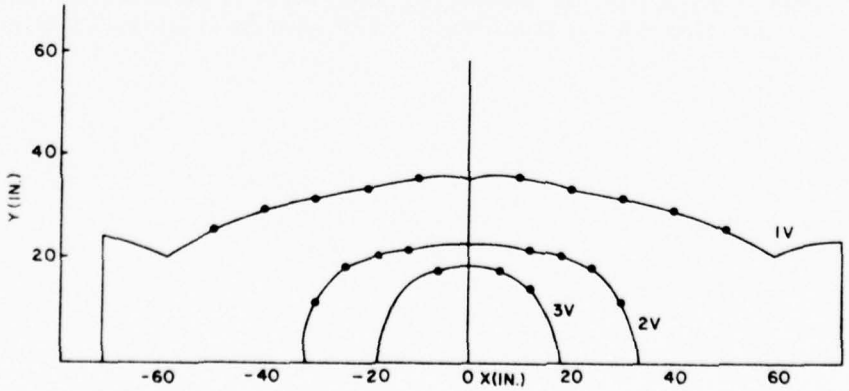


Figure B8. Electric field plot: single anode energized. Surface area of anode twice the area of that used in plot in Figure B5.

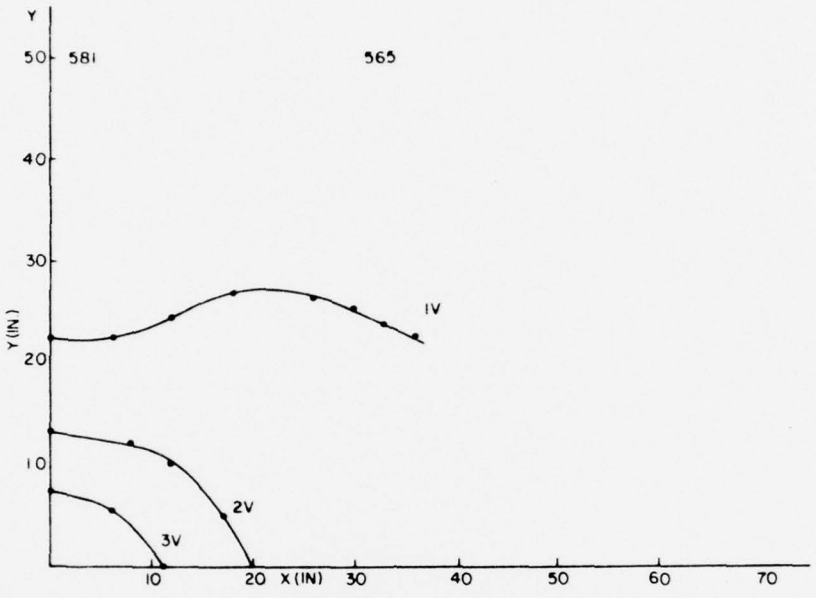


Figure B9. Small anode: shadowing.

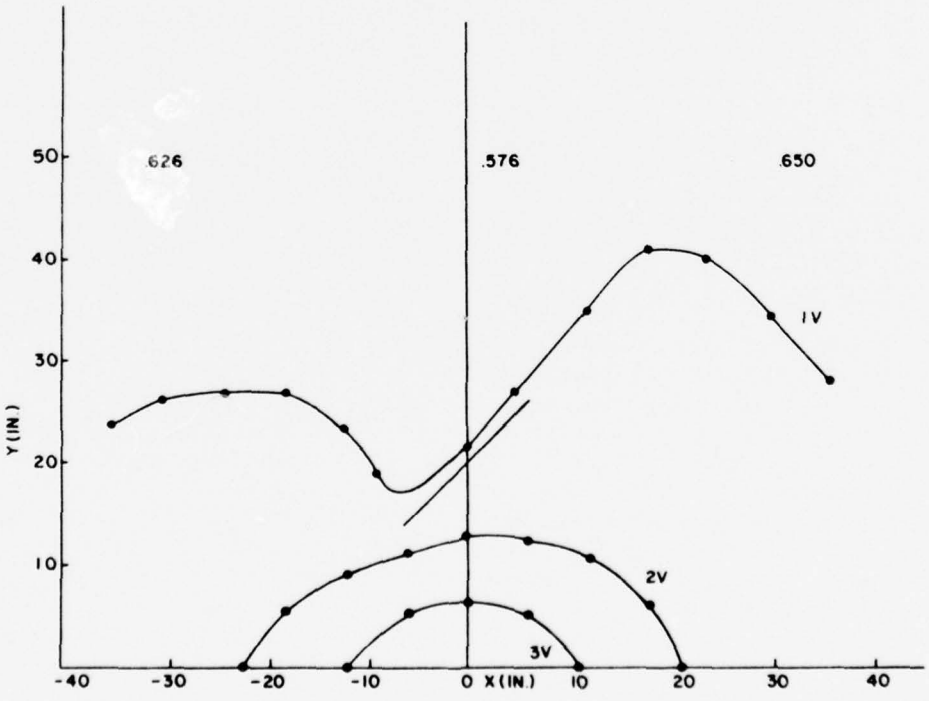


Figure B10. Shadowing: anode at 45 degrees.

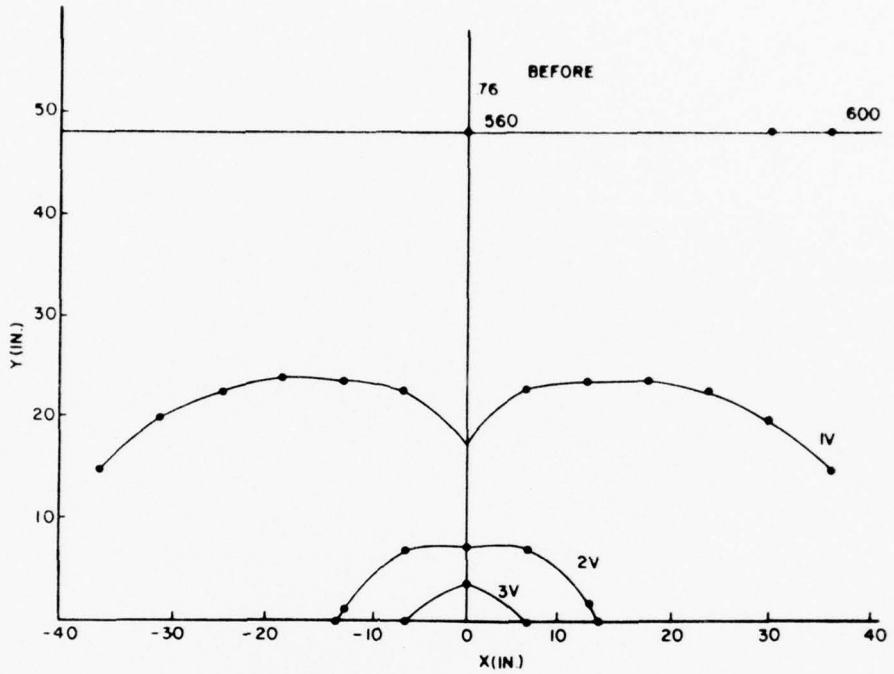


Figure B11. Shadowing: anode at 90 degrees.

degrees to the flux lines. Figure B11 is the field obtained when the interfering element is oriented parallel to the electric flux lines.

B.2.5 These field plots show that the relatively small interfering conductive object caused severe distortion of the field; thus, even with a large surface area, such as the skin side of a miter gate, cathodic protection is affected drastically by the placement of an extraneous conductor whose area is only 5 to 10 percent of the gate area.

B.2.6 The effect of this "shadowing" can be readily seen in Figures B12 and B13. Figure B12 shows two plates in an electrolyte tank that had been exposed to a mildly corrosive electrolyte for a period of 2 weeks. The plate on the left had cathodic protection at the recommended level of −0.850 V with respect to a copper-copper sulfate reference electrode, while the plate on the right was maintained at −0.750 V with respect to a copper-copper sulfate reference electrode; the severe corrosion resulting from underprotection of the right plate is obvious. Figure B13 shows the back of these two plates. In this case, the plate whose surface was at the correct or recommended potential appears to the right while the corroded plate is on the left. This photo shows an equal amount of corrosion on both plates due to the decreased protection level caused by the field "shadow."

B.2.7 Figures B14 through B18 are plots of current resulting from various voltages impressed between one or more anodes and the cathode sheet in freshwater for the geometry shown in Figure B1. These tests gave the effective anode resistance for the particular configuration. The resistance was determined by the voltage-current relation in Ohm's law:

$$R = \frac{\triangle E}{\triangle I} \qquad \text{[Eq B1]}$$

where $\triangle E$ = voltage change
$\triangle I$ = change in current flow resulting from the voltage change.

Figure B14 shows the resulting resistance for the center anode alone, which is 92.6 ohms. Figure B15 shows the resistance obtained from the left and right anodes connected together—44.2 ohms. Figure B16 shows the resistance for all three anodes connected together, which results in a resistance of 27.6 ohms. These tests show the effect of paralleling anodes and the resultant decrease in resistance. To further illustrate this effect, Figure B17 shows the resultant cur-

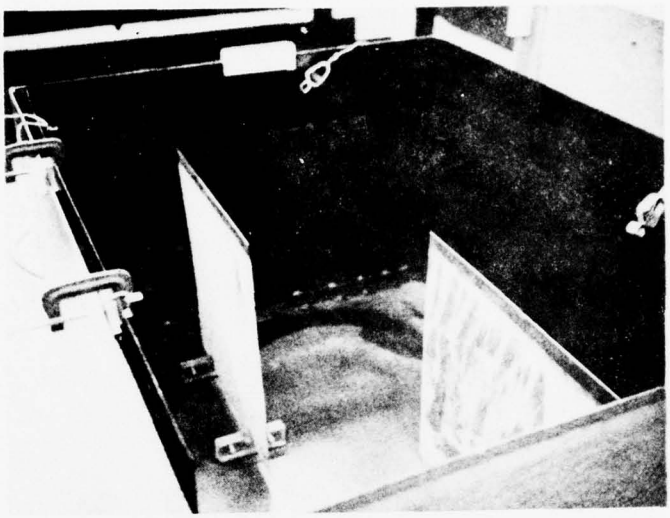


Figure B12. Comparison of corrosion rates.

Figure B13. Rear surfaces of plates shown in Figure B12.

rent versus voltage curve for the right and center anodes connected together; this is similar to the condition given by Figure B3, except that the two anodes in Figure B3 were separated by 3 ft (0.9 m), while the anodes used to obtain Figure B17 were separated by 6 ft (1.8 m). Although it would seem that the resistance should be lower for the two anodes in closer proximity, the opposite effect was measured, as the resistance increased to 56 ohms. This paradox is resolved by using curvilinear square mapping for the two situations. If one large anode is energized, the resulting field is shown in Figure B18.

B.2.8 Figures B19 through B23 show the resistance of the anode configurations used in Figures B14 through B18 in simulated brackish water (3 percent salinity). The comparative resistances are summarized in Table B1.

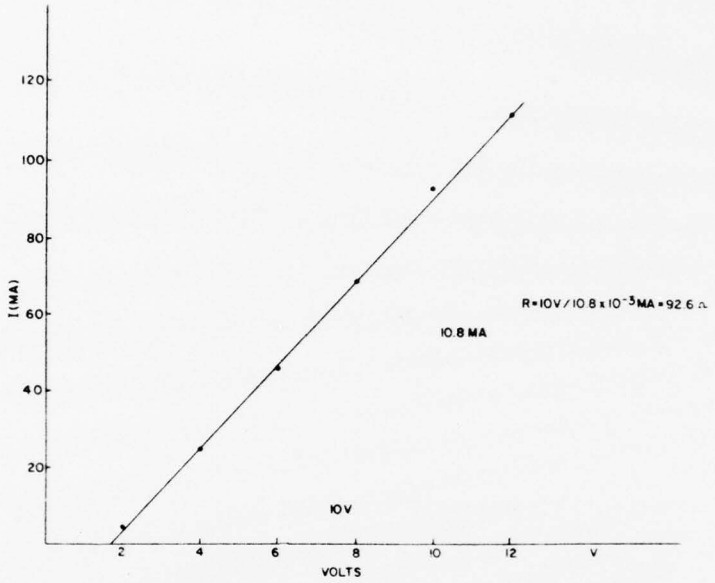


Figure B14. Anode resistance: one anode.

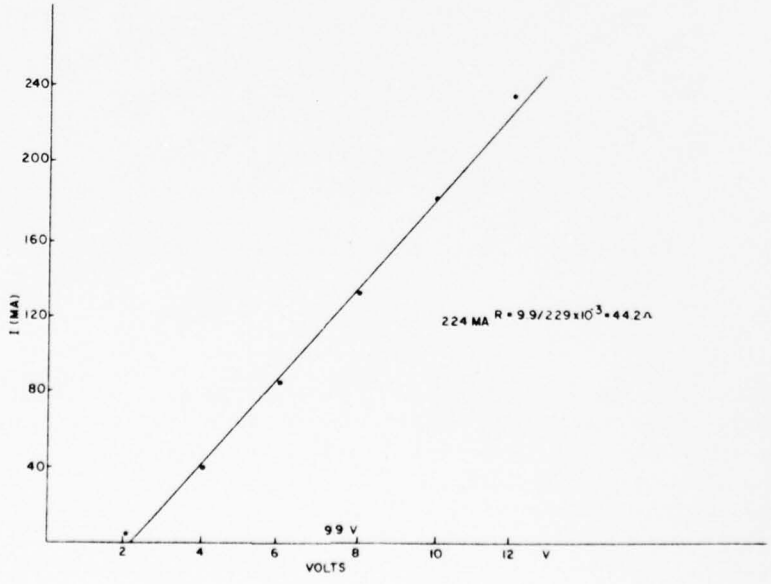


Figure B15. Anode resistance: two anodes far apart.

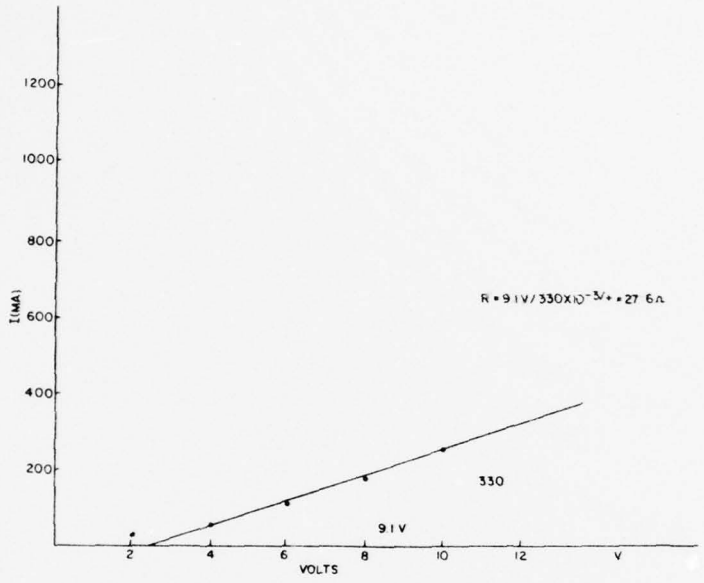


Figure B16. Anode resistance: three anodes.

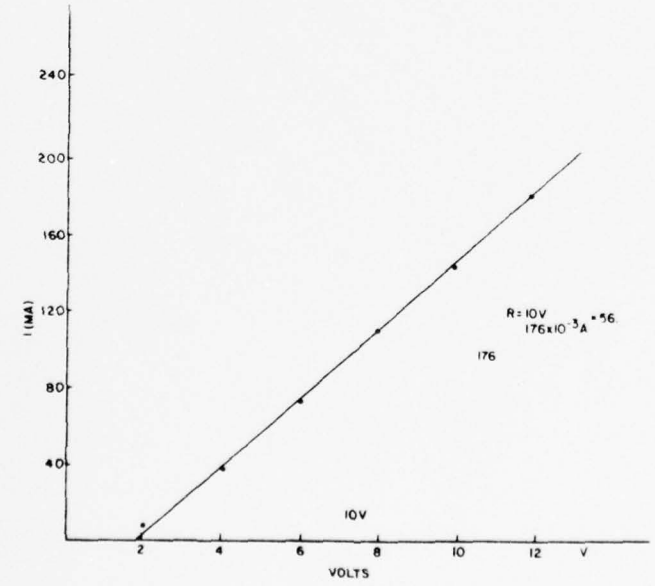


Figure B17. Anode resistance: two anodes close together.

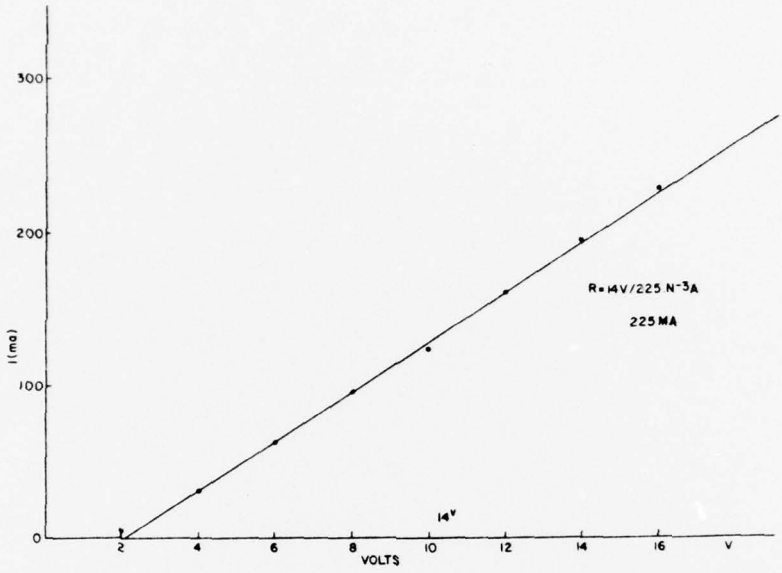


Figure B18. Anode resistance: one large anode.

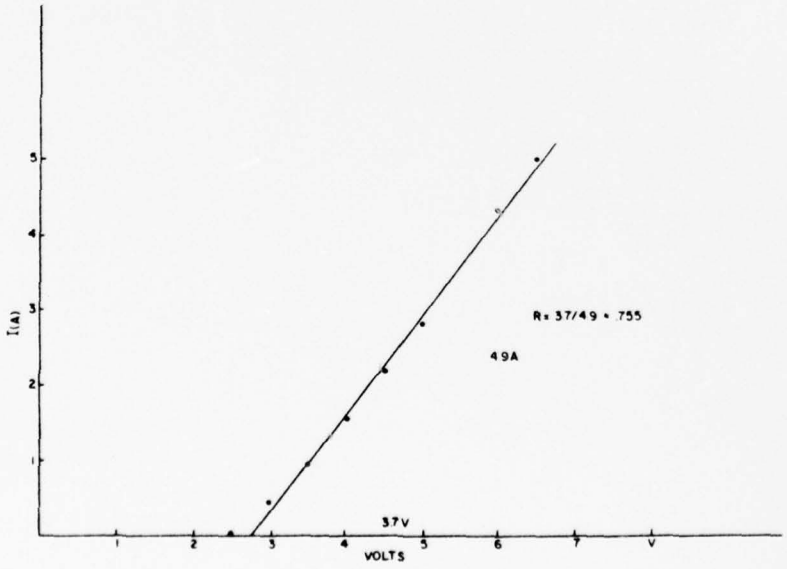


Figure B19. Anode resistance measurements: 3 percent salt water (resistivity 21.6 ohm/cm), one small anode.

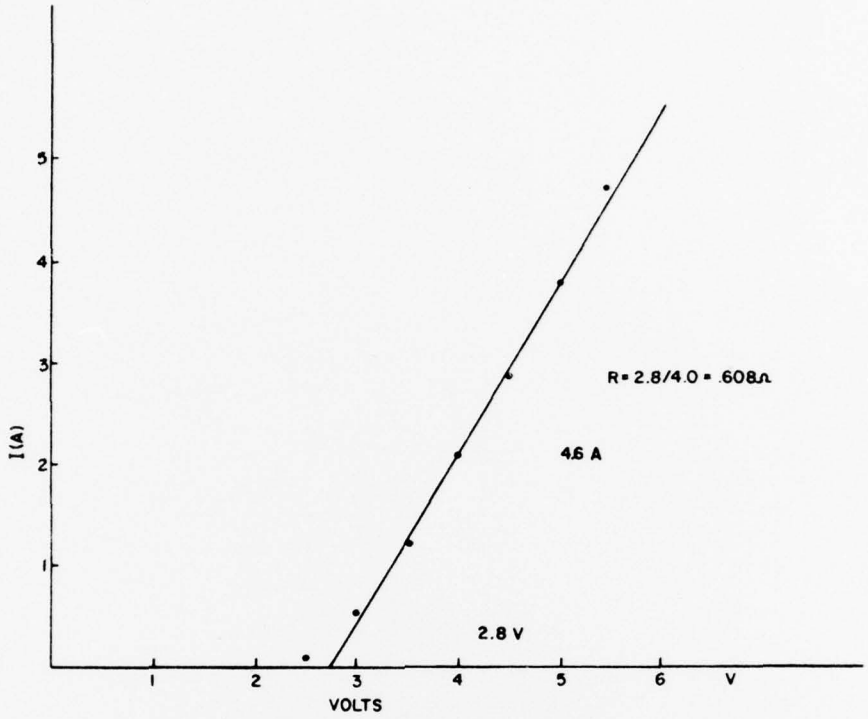


Figure B20. Anode resistance measurements: 3 percent salt water (resistivity 21.6 ohm/cm), two anodes far apart.

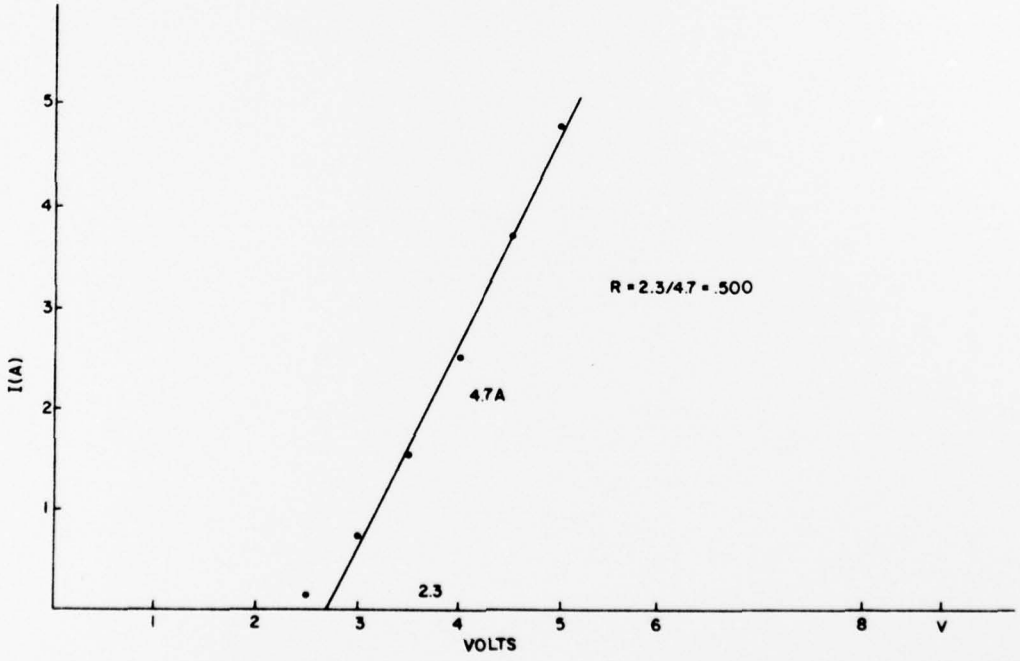


Figure B21. Anode resistance measurements: 3 percent salt water (resistivity 21.6 ohm/cm), three anodes.

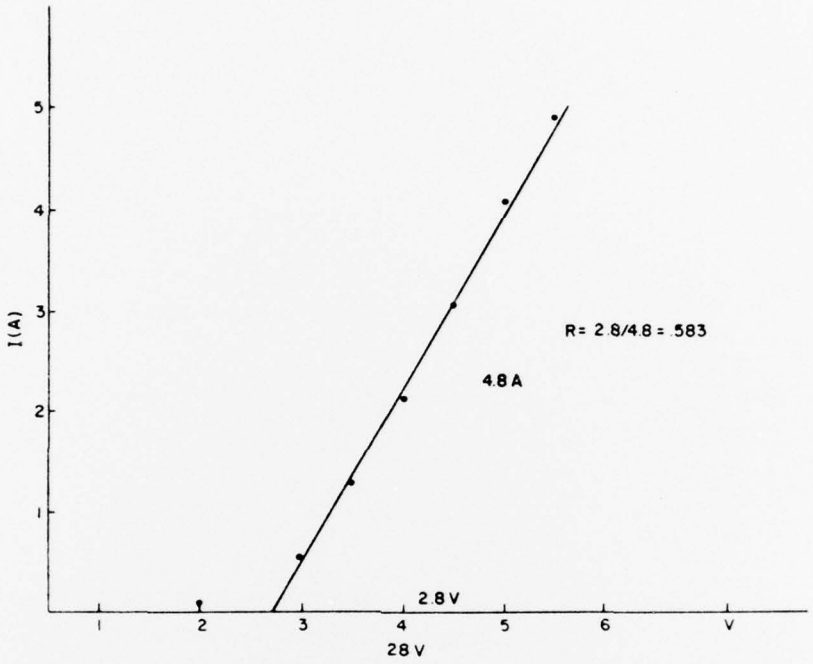


Figure B22. Anode resistance measurements: 3 percent salt water (resistivity 21.6 ohm/cm), anodes close together.

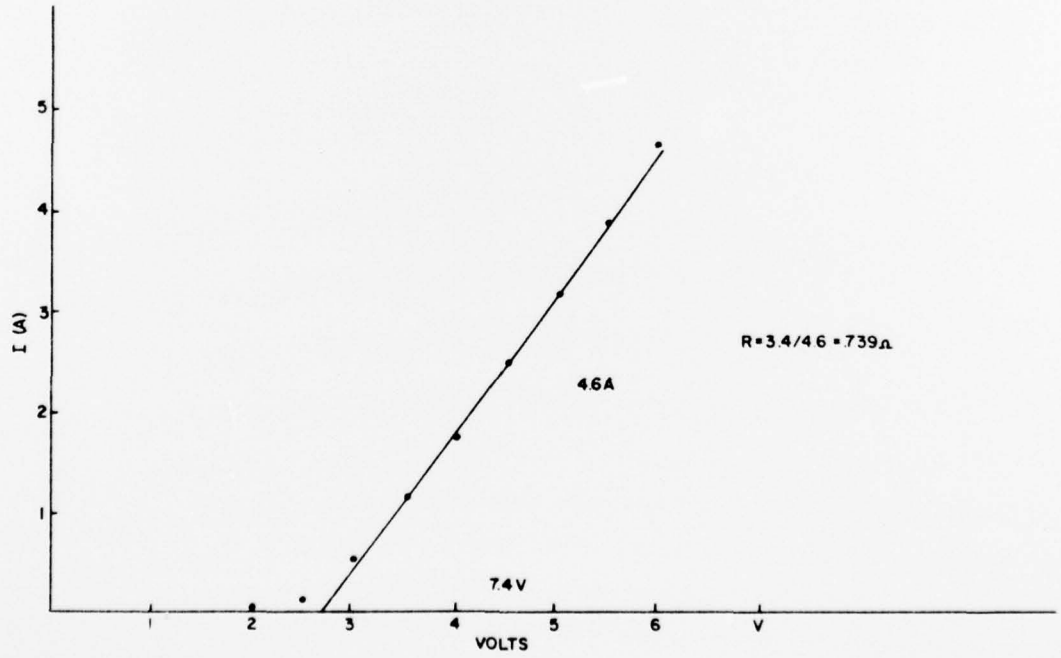


Figure B23. Anode resistance measurements: 3 percent salt water (resistivity 21.6 ohm/cm), one large anode.

Table B1

Comparative Resistances

Configuration	Resistance (ohms)	
	Freshwater	Salt Water
One anode—small diameter	92.6	0.755
Two anodes—far apart	44.2	.608
Three anodes	27.5	.500
Two anodes—close together	56	.583
One anode—large	66.2	.739

APPENDIX C:

POLARIZATION BY CATHODIC PROTECTION

C.1 Process of Polarization by Cathodic Protection

C.1.1 *General.* If an iron or steel surface is immersed in water, numerous local-action cells start producing current, as shown in Figure C1. The figure also pictures the flow of local-action direct current between individual cells. For purposes of illustration, Figure C1 exaggerates the size of the local-action cells. The fact that anode and cathode surface areas are shown to be approximately equal is also a simplification, since cathodic sites dominate in a natural-water exposure. The polarization curve in Figure C2 depicts this corrosion process, including the reversible anode and cathode potentials (ϕ_a° and ϕ_c°) and the corrosion potential or intersection of the anodic and cathodic polarization curves (ϕ_{corr}). Corrosion engineers often monitor corrosion potential because (1) it can be measured with relative ease, and (2) it relates the degree of corrosion that a particular metal experiences to changes in potential. It is assumed that the corrosion circuit exhibits insignificant electrical resistance. When this is not the case, the potentials of anodic and cathodic sides are not the same, and analysis is more complex.

C.1.2 *Circuit With Insignificant Resistance*

C.1.2.1 The effectiveness of an impressed-current cathodic-protection system installed to protect a submerged steel member depends on the steel's electrochemical or corrosion characteristics. Figure C3 shows the polarization curve from Figure C2 along with additional features necessary to explain cathodic protection in the case of insignificant electrical resistance. The steel structure effectively serves as the cathode in a galvanic couple, so its potential varies relative to its freely corroding potential (ϕ_{corr}). Thus the steel, which has no cathodic protection, is polarized in the cathodic direction. As a result, the net cathodic current across the steel-water interface (from both local-action cells and the impressed-current system) increases, and net anodic current decreases. Since corrosion occurs at sites of anodic current flow, the corrosion rate also decreases.

C.1.2.2 Figure C3 shows how these current changes grow more pronounced as the steel potential becomes increasingly negative. At potential ϕ' (where ϕ' is less than ϕ_{corr}), the total or net cathodic current at the steel is i_c' and the net anodic current is i_a'. Likewise, for ϕ'' (ϕ'' is less than ϕ' which is less than ϕ_{corr}) these values are i_c'' and i_a'', respectively, because all areas of the steel surface must necessarily reach the same potential as long as the circuit resistance is insignificant. The fact that the net anode current is now less than the net cathode current does not violate this rule, since applied current from the impressed-current system (I_{appl}) must also be considered. These various current components satisfy the relationship

$$i_c = I_{appl} + i_a \qquad \text{[Eq C1]}$$

The magnitude of applied current increases with the amount of polarization from the corrosion potential ($\triangle\phi$); i.e., I_{appl}'' is greater than I_{appl}'.

C.1.2.3 As cathodic protection polarizes the steel to increasingly negative values, the net anodic current and associated corrosion decrease. Ideally, corrosion should stop altogether when the steel potential equals the reversible anode potential (ϕ_a°), since no net current is entering the electrolyte from the structure at this point. For the case of iron or steel in natural waters or soils, corrosion generally stops at a potential of $-.85$ V with respect to a copper-copper sulfate reference electrode.

C.1.3 *Circuit With Significant Resistance*

C.1.3.1 Given a finite, significant electrical resistance in the corrosion cell, the total cell resistance consists of an anodic component (r_a) and a cathodic component (r_c). Component r_a represents resistance to current flow within the anodic portion of the circuit, and r_c represents resistance within the cathodic portion. Either resistance component may result from electrolyte resistance, films at the electrode surface, or both. For the present discussion, however, resistance through the metal itself is assumed to be unimportant.

C.1.3.2 Figure C4 shows polarization curves for a circuit with significant electrical resistance. Figure C4 is very similar to Figure C2, where zero cell resistance was specified. The anodic and cathodic curves are identical to those in Figure C2, except the two do not intersect, and the anode and cathode exhibit distinct potentials (ϕ_a and ϕ_c). The potential difference between ϕ_a and ϕ_c constitutes a voltage drop

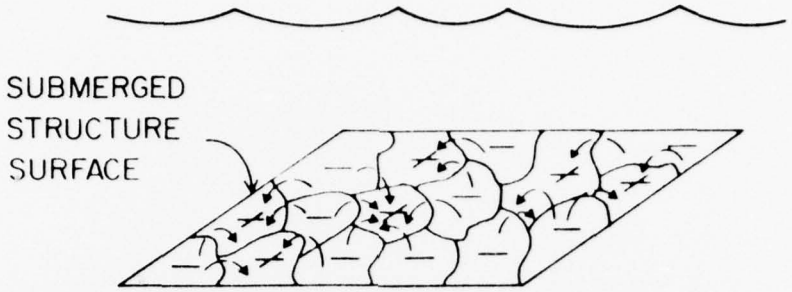


Figure C1. Polarization of iron or steel immersed in water.

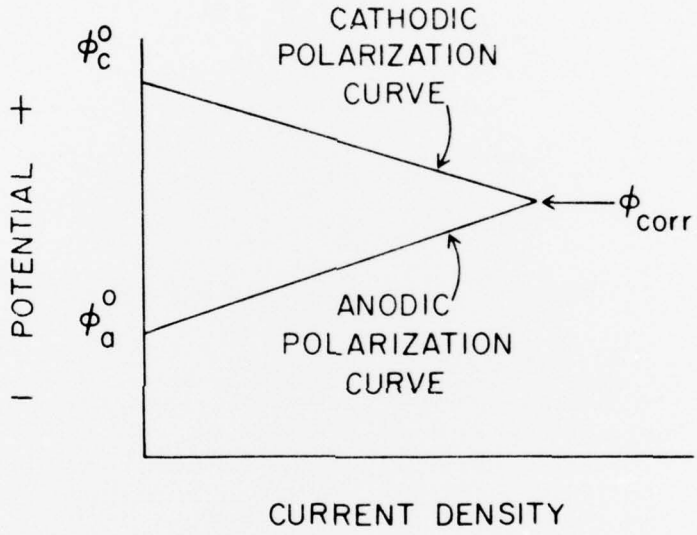


Figure C2. Polarization curve for iron or steel in water.

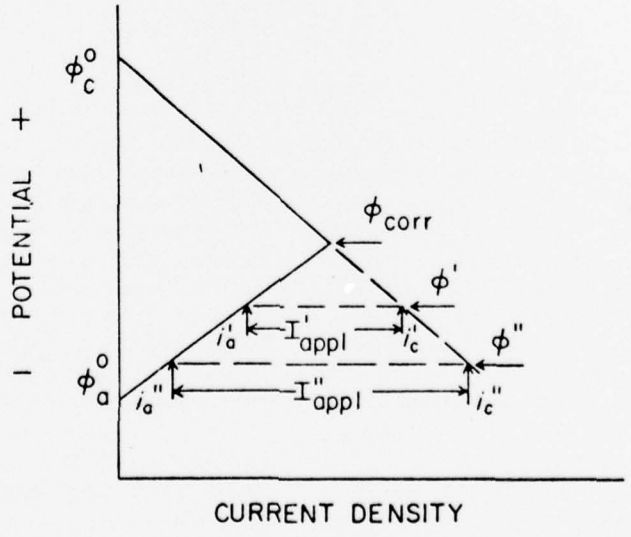


Figure C3. Polarization curves for a corrosion circuit with insignificant electrical resistance.

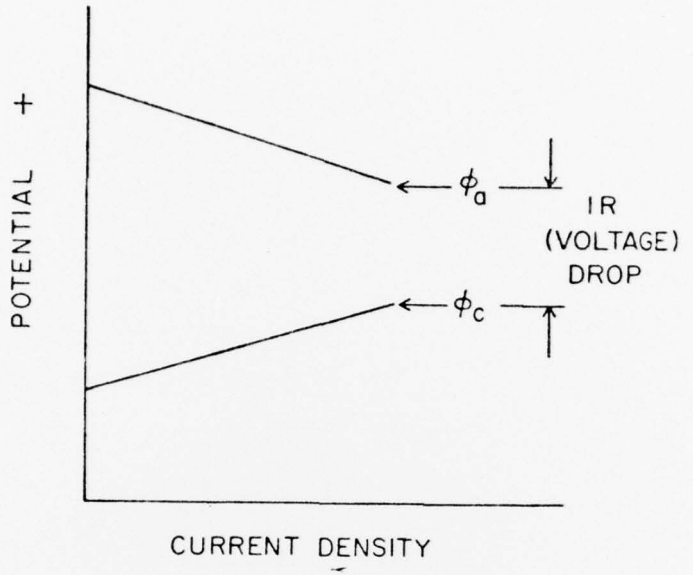


Figure C4. Polarization curves for a corrosion circuit with significant electrical resistance.

(IR). Since r_a and r_c, the two resistance components, are in series, the IR term equals I_{corr}, which is the sum of r_a and r_c. A corrosion cell with significant internal resistance will exhibit a lower value of I_{corr} and, correspondingly, a reduced corrosion rate, than one in which resistance approaches zero (Figure C2). A fundamental law of electricity states that the sum of all voltage drops about a circuit must be zero, so

$$\phi_c - \phi_a - I_{corr} \cdot r_a - I_{corr} \cdot r_c = 0 \qquad \text{[Eq C2]}$$

C.1.3.3 Thus, a reference electrode connected through a high-resistance voltmeter to the corrosion cell and placed in the electrolyte near the cell will be affected not only by the true or actual anode and cathode potentials (ϕ_a and ϕ_c), but also by the voltage drop in the electrolyte. A sufficiently small reference electrode placed directly at the anode or cathode surfaces would allow the voltmeter to measure ϕ_a and ϕ_c exactly, without electrolyte voltage drop. At any other position within the current-carrying portion of the electrolyte, the observed voltage would be a function of both the anode and cathode potentials and the electrolyte voltage drop associated with I_{corr}.

C.1.3.4 Figure C5, which pictures a corrosion cell consisting of an anode and a cathode, illustrates the term "current-carrying portion." The dashed line encircling the anode and cathode depicts that volume of electrolyte within which I_{corr} flows. The voltage drop occurs only within this region. With the reference electrode positioned anywhere along a planar surface in the electrolyte exactly separating anode resistance and cathode resistance (r_a and r_c), the measured potential is constant and equal to $\phi_c - (I_{corr} \cdot r_c)$ or $\phi_a + (I_{corr} \cdot r_a)$. With the reference electrode at any point outside the dashed line, the same potential is recorded ($\phi_c - [I_{corr} \cdot r_c] = \phi_a + [I_{corr} \cdot r_a]$).

C.1.3.5 Ideally, the local-cell "boundary" can be determined by placing the reference electrode very close to the corrosion cell and then moving it outward along any path other than one within the plane that divides r_a and r_c. As the reference cell moves, the point at which the voltmeter indicates a constant potential value defines a point of the local-cell boundary. If the corrosion cell consists of dissimilar metals immersed in water (e.g., a small steel plate with a large copper rivet in the center), this technique can determine the cell boundary. The observed potential at any location beyond the cell boundary or within the plane partitioning r_a and r_c is the corrosion potential (ϕ_{corr}). Expressed mathematically,

$$\phi_{corr} = \phi_a + (I_{corr} \cdot r_a) = \phi_c - (I_{corr} \cdot r_c) \qquad \text{[Eq C3]}$$

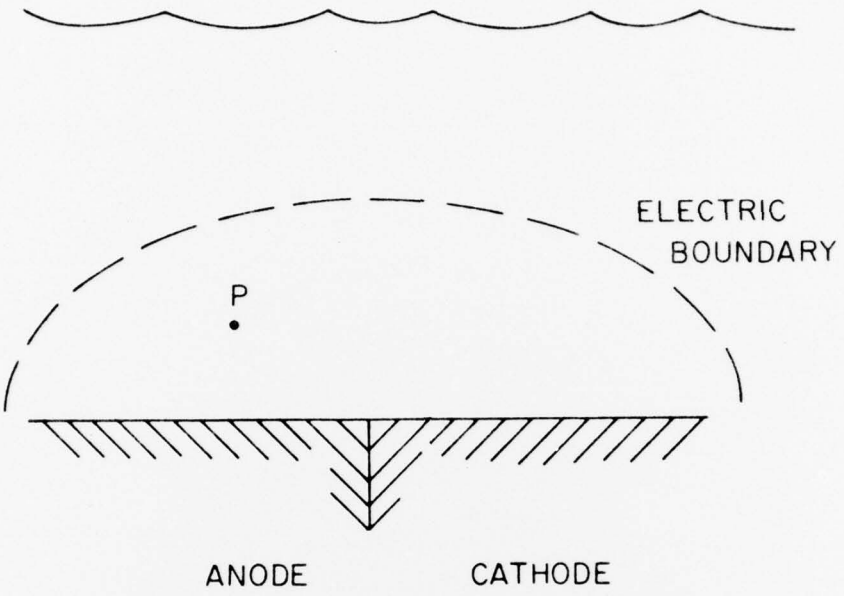


Figure C5. Typical corrosion cell with electrolyte boundary.

If, for example, ϕ_a equals $-.75$ V and ϕ_c equals $-.60$ V (with respect to a copper-copper sulfate reference electrode), and r_c equals $2r_a$, then $I_{corr} \cdot r_c$ is equal to $2I_{corr} \cdot r_a$, and ϕ_{corr} is $-.65$ V. In general, the value of ϕ_{corr} will be other than that obtained by simply extrapolating the anodic and cathodic polarization curves to intersection, as is appropriate when no voltage drop is apparent. The term "corrosion potential" applies only if the reference cell is located so that the measured potential is $\phi_a + (I_{corr} \cdot r_a) = \phi_c - (I_{corr} \cdot r_c)$. With the reference electrode at an alternate location, the measured potential differs from ϕ_{corr}.

C.1.3.6 There is a relationship, however, for any point inside the cell boundary. For example, in Figure C5, the potential at point P (ϕ_p) is

$$\phi_p = \phi_a + (I_{corr} \cdot r_x) = \phi_c - (I_{corr} \cdot r_y) \quad \text{[Eq C4]}$$

where $I_{corr} \cdot r_x$ = the voltage drop in the electrolyte between point P and the anode

$I_{corr} \cdot r_y$ = the corresponding voltage drop to the cathode.

C.1.3.7 Eqs C3 and C4 apply only when the resistance of the external portion of the cell circuit is insignificant compared to the internal electrode resistance.

C.2 Effects of External Cathodic Current

C.2.1 In the discussion of corrosion cells of negligible electrolytic and metallic circuit resistance, an important assumption is that external current enters the structure to be protected at the cathodic sites of the local-action cells. If the current delivered via the external anode (Figure 5 of the main body of the report) is initially zero and then increases incrementally, the cathodic microelectrodes on the steel surface are polarized to progressively more negative values. The polarization curve in Figure 6 depicts this situation. Since there can be no potential or voltage difference from one part of the metal surface to another for a zero-resistance corrosion cell, the anode and cathode potentials are necessarily the same (i.e., ϕ_a equals ϕ_c). Although a zero-resistance electrical or electrochemical circuit cannot actually exist, most metals in high conductivity media (e.g., steel in seawater) approach this situation. Increasing cathodic currents polarizes cathodic sites to a more negative potential, but altering anode potential to this same value reduces anodic current. According to Faraday's law, a reduction in anodic current results in a proportionately smaller loss of metal weight and a reduction in corrosion rate. Figure C3 demonstrates this relationship. Corrosion stops altogether when the structure is polarized to the open circuit anode potential (ϕ_a). The potential condition corresponding to this state is

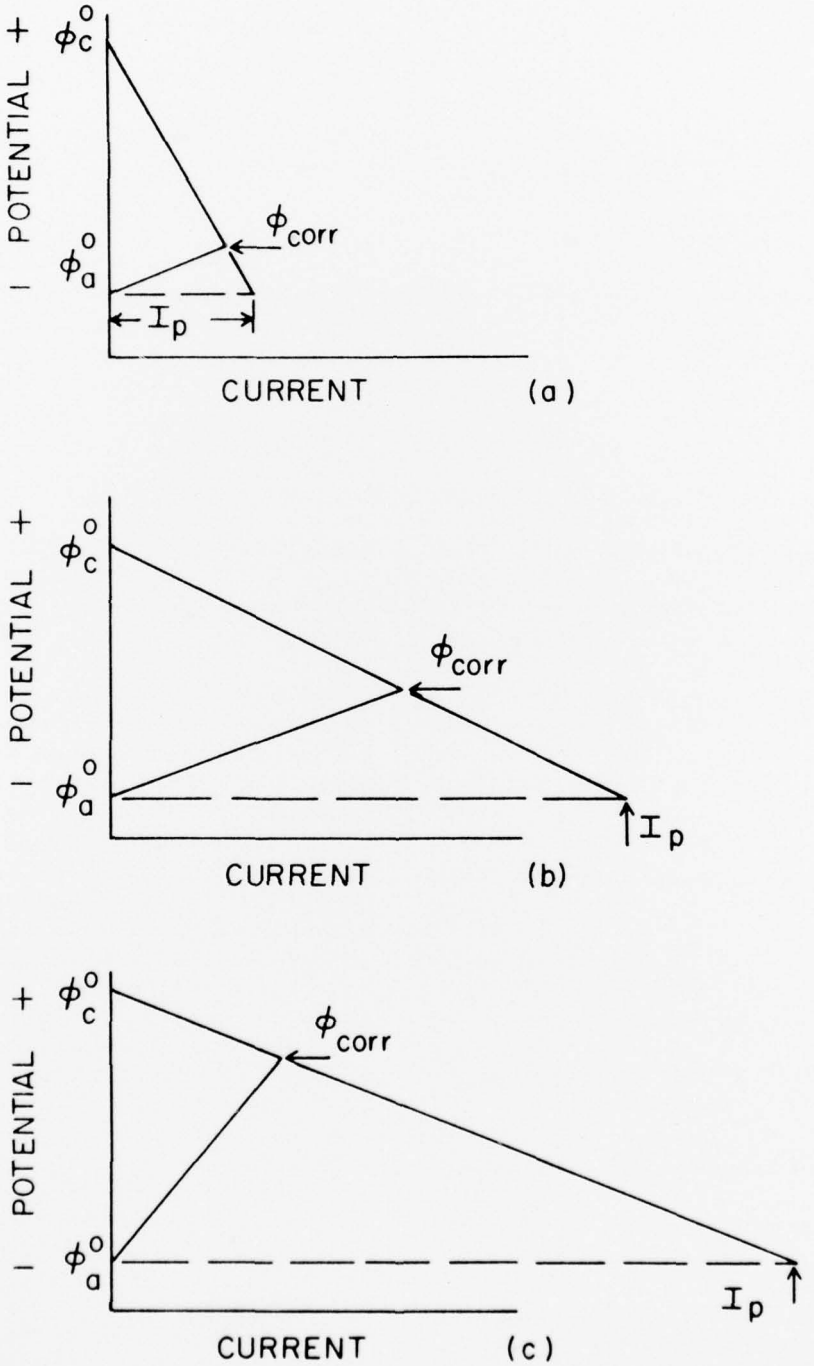


Figure C6. Degrees of cathodic polarization.

$$\phi_a = \phi_c = \phi' = \phi_a^\circ \qquad \text{[Eq C5]}$$

C.2.2 In cells with high-resistance electrolytes (e.g., freshwaters and many soils), local-action cells may be under resistance control. In such a cell the voltage drop can limit polarization of anodic and cathodic sites, so that ϕ_a and ϕ_c are decidedly different, as shown in Figure C4; thus, the magnitudes of $I_{corr} \cdot r_a$ and $I_{corr} \cdot r_c$ become highly significant. With increasing increments of external cathodic protection current supplied to a cell of significant electrolytic resistance, the general mechanism of establishing protection is quite similar to that for a cell of zero resistance. A negative shift in ϕ_c causes depolarization of microanodes of the corrosion cell toward their open-circuit potential (ϕ_a), and the structure potential becomes more negative.

C.2.3 Although the true potential of the local cathode (measured at the electrode-electrolyte interface to avoid voltage drop) does change in the anodic direction, it does not reach the open-circuit potential of the local anode (ϕ_a°) because a potential difference necessarily must exist between ϕ_a and ϕ_c. The true cathode potential can reach ϕ_a° only under conditions of excessive cathodic protection, where ϕ_a is less than ϕ_a°. As local anodes polarize to ϕ_a°, the potentials of local cathodes will be more positive by an amount equal to $I_p \cdot r_c$, where I_p is the total external current from the cathodic-protection system. When ϕ_a equals ϕ_a°, no local-cell current flows from microanodes into the electrolyte and no externally applied protective current flows to the local anode sites, so $I_{corr} \cdot r_a$ equals 0. If all external current enters the structure at cathodic sites, there should be no voltage drop at the original anodic locations. When the structure surface reaches this state, corrosion stops and cathodic protection is complete.

C.2.4 For a zero-resistance cell, complete protection occurs when the potential of local anodic sites reaches the open-circuit value (i.e., $\phi_a = \phi_a^\circ$). Since the cathode and specimen potentials are the same as ϕ_a,

$$\phi_a = \phi_c = \phi' = \phi_a^\circ \qquad \text{[Eq C5]}$$

C.2.5 Eq C5 does not hold for the case of non-zero cells, since ϕ_a is not equal to ϕ_c. In this case cathodic protection occurs when the structure potential (ϕ') reaches the open-circuit anode value. At the point of protection (ϕ_a equals ϕ_a°), local anodes have no net current across their surface and hence exhibit no voltage drop. Expressed mathematically

$$\phi_a = \phi' = \phi_a^\circ \neq \phi_c \qquad \text{[Eq C6]}$$

C.2.6 Because the only voltage drop in the corrosion cell now occurs at the cathode, this drop equals $I_p \cdot r_c$, so

$$\phi_a^\circ = \phi' = \phi_c - I_p \cdot r_c \qquad \text{[Eq C7]}$$

Eq C7 is simply a variation of

$$\phi_a + (I_{corr} \cdot r_a) = \phi_c - (I_{corr} \cdot r_c) = \phi_{corr} \qquad \text{[Eq C3]}$$

For a general cathodically protected corrosion cell, ϕ_a° is equal to $\phi_a + (I_{corr} \cdot r_a)$, since $I_{corr} \cdot r_a$ equals 0 and ϕ_a has depolarized to ϕ_a°. The cell potential (ϕ') is also identical with ϕ_a°, and $\phi_c^\circ - I_p r_c$ is the same as $\phi_c - I_{corr} \cdot r_c$.

C.3 Effect of the Degree of Polarization on Cathodic Protection

C.3.1 The shape of the cathodic polarization curve determines the current required for cathodic protection. As Figure C3 depicts, the external current needed to maintain a certain cathodic potential ϕ' varies inversely with the steepness of the cathodic polarization curve. When local anodes polarize to their open-circuit potential (ϕ_a equals ϕ_a°), the protection current and cathodic current are the same (i.e., I_p equals i_c). Figure C6 presents several examples of varying degrees of cathodic polarization. Figure C6a shows the most pronounced cathodic polarization and Figure C6c the least. Similarly, the situation shown in Figure C6a requires less cathodic protection current, I_p, to polarize the cell to its open circuit potential than does that shown in C6c. Generally, it follows that the less cathodic-protection current needed, the more pronounced the polarization at the cathode is.

C.3.2 In most practical underground and immersion environments, corrosion approaches being under cathodic control (Figure C6a), and the ratio of I_p/I_{corr} ranges from 1.1 to 1.3. In other words, for conditions of cathodic-reaction control, the cathodic-protection current (I_p) is very nearly the same as the corrosion potential (I_{corr}). On the other hand, corrosion reactions under predominantly anodic control may require such high values of external current to polarize to ϕ_a° (Figure C6c) that cathodic protection becomes uneconomical.

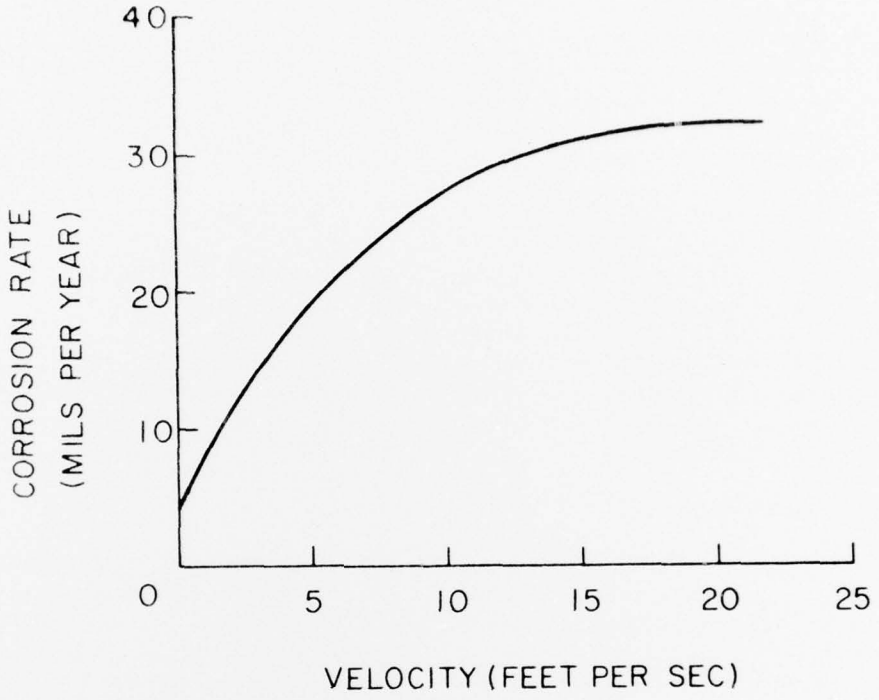


Figure C7. Seawater corrosion rate for steel as a function of water velocity.

C.3.3 The effect of water velocity on the current required for cathodic protection is especially interesting. Figure C7 charts the seawater corrosion rate for steel as a function of water velocities of 0 to 15 ft/sec (0 to 4.6 m/sec). The results are consistent with the fact that oxygen availability controls the corrosion rate of iron and steel in natural waters and soils. Water flow reduces the thickness of the stagnant water layer at the metal surface and thereby supplies more oxygen to cathodic sites. Figure C6a presents a typical polarization curve for steel in quiet, natural water. Figure C8a shows how the nonavailability of oxygen in quiet waters appears as pronounced cathodic polarization. The other parts of Figure C8 show the variation in cathodic polarization as water flow increases. At a flow of 5 ft/sec (1.5 m/sec) (Figure C8b), the oxygen supply to microcathodes increases and cathodic polarization decreases. Figure C8c shows the situation at 10 ft/sec (3.0 m/sec) and Figure C8d that at 15 ft/sec (4.6 m/sec). Figure C8 also illustrates the impressed cathodic current necessary to polarize each corrosion cell to its open-circuit anode potential. Since the horizontal current axis in potential-current plots is generally a log scale, the current requirements for cathodic protection increase quite markedly with water velocity.

C.4 Cathodic Protection of Passive Metals

C.4.1 The inherent corrosion resistance of certain engineering metals and alloys is due to a protective film that forms on their surfaces, effectively isolating the metal from the environment. Important examples of such metals include aluminum, nickel, titanium, chromium, and many of their alloys. Stainless steels—iron-chromium and iron-chromium-nickel alloys—are also passive. Whether a metal is passive depends not only on its composition, but also on its environment.

C.4.2 Cathodic polarization to the open-circuit anode potential (i.e., to ϕ' equals ϕ_a^o) provides cathodic protection for passive metals and alloys. The primary function of cathodic protection systems, however, is simply to insure that the corrosion potential (ϕ_{corr}) stays within the passive region. Figure C9, which gives the anodic-polarization curve for a passive metal, shows the three distinct regions: active, passive, and transpassive. For the active and trans-

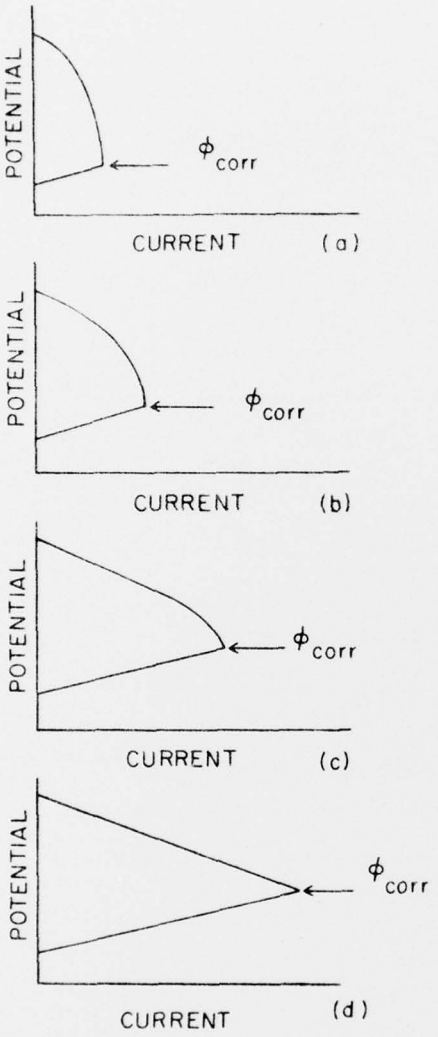


Figure C8. Variation of cathodic polarization with water velocity. Velocity increases from (a) to (d).

passive cases, the corrosion rate is quite sensitive to potential. If corrosion potential lies within either of these regions, the dissolution rate is normally high, as illustrated by the cathodic polarization curves labeled (a) and (t_p). On the other hand, curve (p) intersects the anodic curve in the passive region, and the corrosion current is relatively low. Figure C10, which considers the curve in its passive region in detail, shows the external cathodic current needed to achieve a potential of ϕ' as I'_p. Because such a potential is maintained, the corrosion rate is low (probably less than 1 mpy (25.4 μm/yr) in the case of the engineering metals and alloys listed above. The only other way to polarize the metal in Figure C10 to its open-circuit potential is by applying current I''_p, which may be orders of magnitude greater than current required in the first method. Figure C11 shows anodic polarization curves of 430 stainless steel as examples of actual passivation behavior. Note the drastic shift in the curve with a change of environment.

C.4.3 Amphoteric metals cannot be polarized to very negative potentials because an alkaline environment attacks them irrespective of their electrochemical potential. Such alkalinity occurs at cathodic sites, and the reaction produces hydroxyl (OH^-) ions. Consequently, aluminum, for example, cannot be protected by cathodic polarization to its open-circuit anode potential (ϕ_a° of aluminum is about -1.75 V), but a potential of approximately -1.1 V with respect to a copper-copper sulfate reference electrode, which is within the passive region, assures a low corrosion rate.

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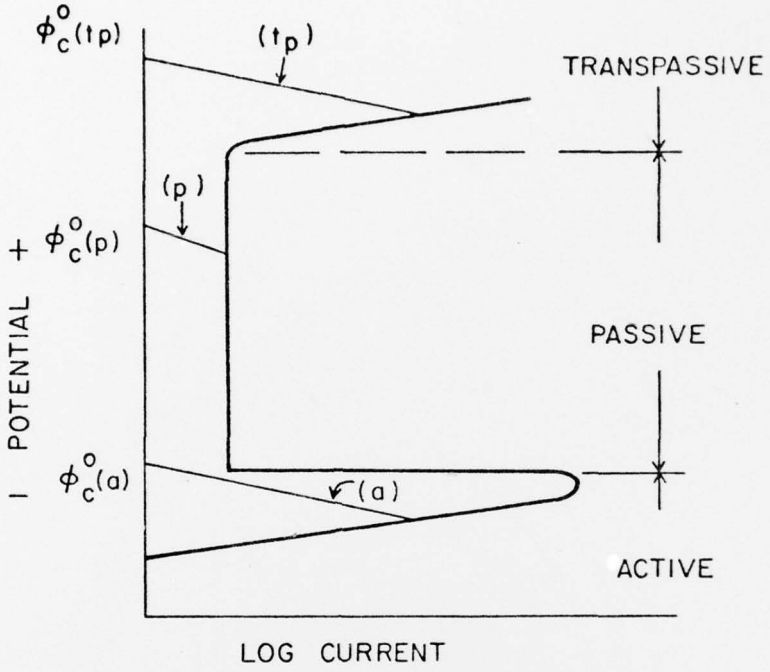

Figure C9. Anodic polarization curve for a passive metal.

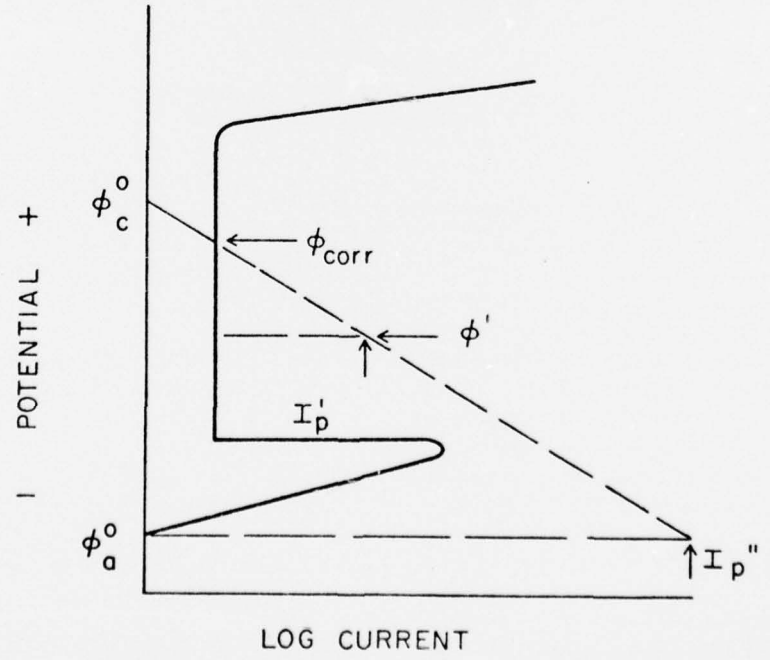

Figure C10. Anodic polarization curve in the passive region.

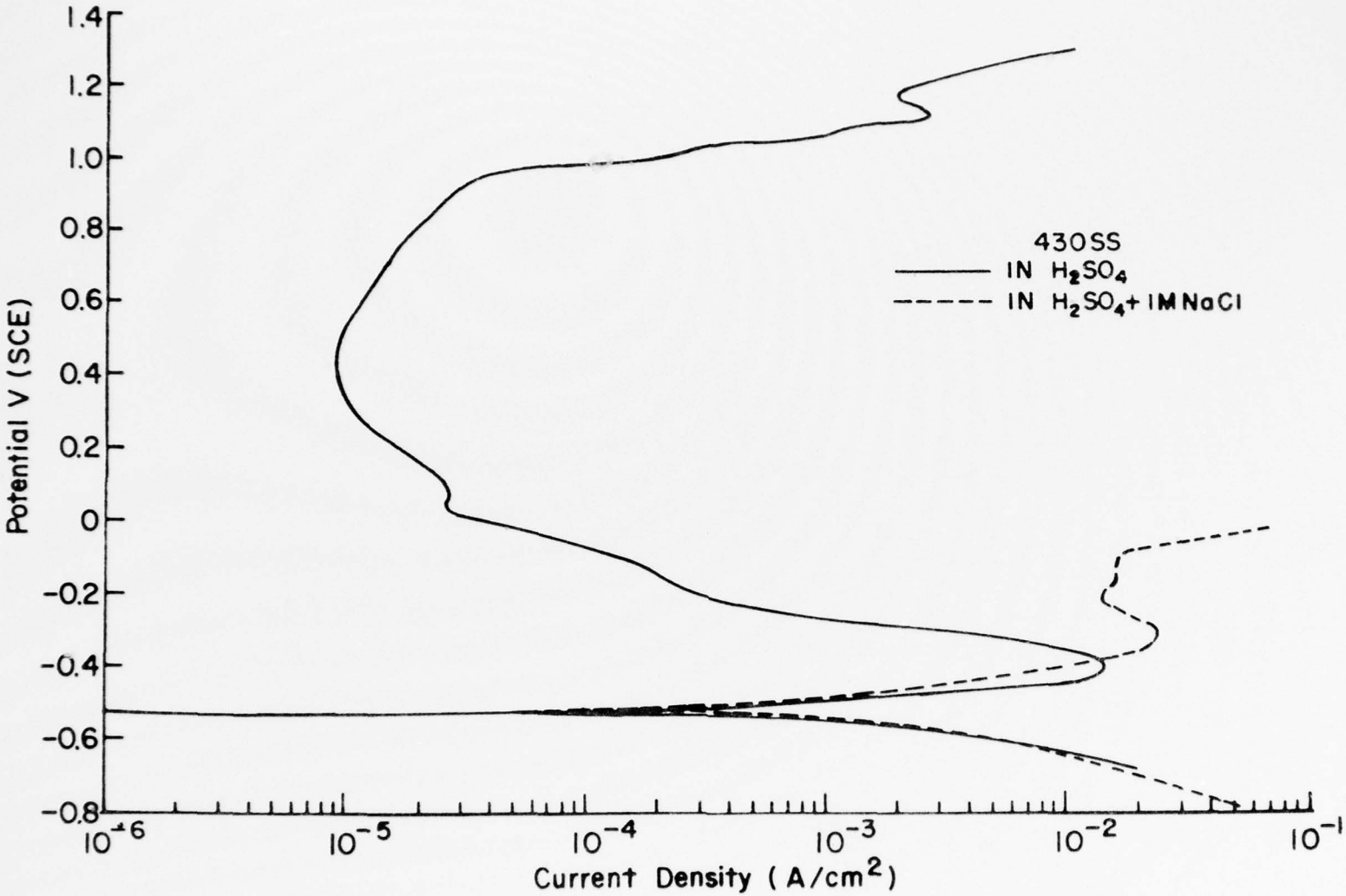

Figure C11. Anodic polarization curve for 430 stainless steel in two environments.

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