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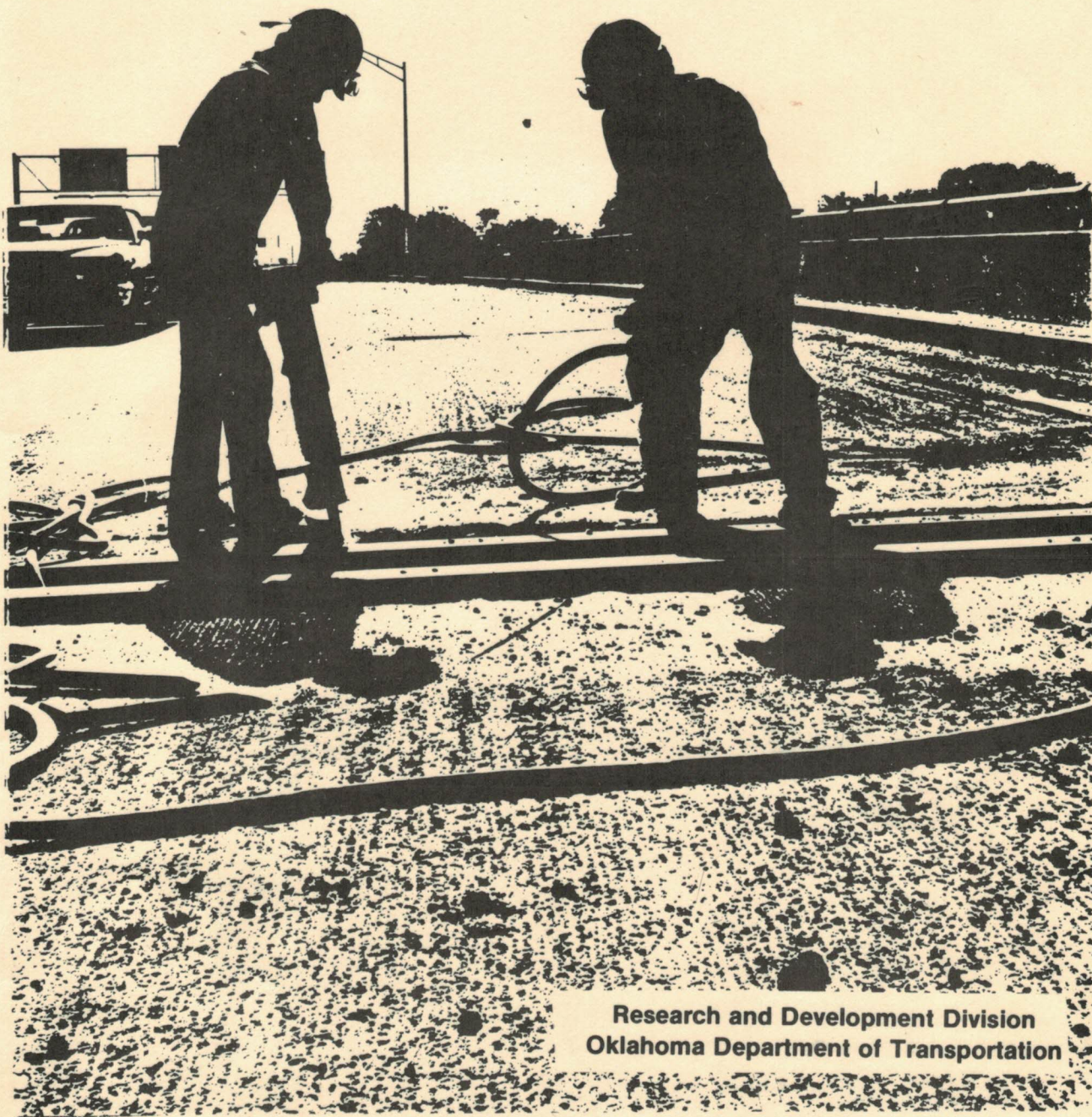
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BRIDGE DECK REHABILITATION

PART 3 Cathodic Protection

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BRIDGE DECK REHABILITATION: METHODS AND MATERIALS

PART 3

Cathodic Protection of a Reinforced Concrete Bridge Deck

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16. Abstract The objectives of this project were to study the factors involved in bridge deck deterioration and to formulate and evaluate techniques to prevent or halt such deterioration. Part III of this study addressed the use of cathodic protection to prevent NaCl induced corrosion of reinforcing steel. Construction details of an impressed current cathodic protection installation are presented in this report. Data on stability and electrical resistance of a coke breeze asphaltic overlay are included as well as data concerning voltage drops through the conductive asphaltic concrete and the concrete. Also included are data concerning the polarized potential and current density required for cathodic protection of steel imbedded in concrete.			
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INTRODUCTION

It is widely accepted that chloride induced corrosion of reinforcing steel is a principle cause of premature deterioration of reinforced concrete structures.

Interest in the area of chloride induced corrosion of steel imbedded in concrete has been evident for over half a century.¹ But recent use of large quantities of chloride salts as deicing agents on highways has brought on an outpouring of interest as well as monies in this area of investigation. There have been several proposed methods of preventing or minimizing the loss of structural usefulness caused by this corrosion. This report will present the advantages and disadvantages of one of these methods, that being cathodic protection.

DISCUSSION OF PROBLEM

In recent years spalling or delamination of the riding surface of concrete bridge decks has reached monumental proportions. This problem has been generally accepted to be the result of widespread use of deicing salts. These salts (sodium and calcium chloride) are applied to the bridge surface and slowly percolate through the concrete via cracks within the concrete or through interconnected voids until sufficient quantities are present at the level of the reinforcing to break down the passivity that steel imbedded in concrete ordinarily enjoys. Once this passivity is overcome, corrosion products begin to form on the reinforcing bars. These corrosion products occupy approximately 2.2 times the volume of the metal from which they are formed. This increase in volume creates stresses at the level of the rebar mat that soon overcome the tensile strength of concrete (indeed Stratfull² has found in laboratory specimens that one mil of corrosion was capable of fracturing 7/8" of concrete. From this same work and work by Locke³ corrosion rates of 20 to 30 mils per year are not uncommon for reinforcing bars located in salt contaminated concrete). These stresses create cracks that radiate to the surface of the bridge deck. The affects of water freezing in these cracks and the pounding of traffic soon remove the concrete and a void or spall is created in the riding surface.

The problem of chloride induced corrosion of reinforcing steel has been attacked in several ways. The attempted solutions generally fall into two categories: (1) solutions to the problem before high concentrations of chloride salts are present in the bridge deck; and (2) solutions after high concentrations of chlorides are present. Under the first category are the techniques of waterproof membranes, thin bonded concrete overlays, polymer impregnation, coated reinforcing bars, heated bridge decks, the use of non-corrosive deicers, and mixing a corrosion inhibitor with the plastic concrete. Waterproof membranes, thin bonded concrete overlays, polymer impregnation, heated decks, and the use of non-corrosive deicers attack the problem by attempting to prevent the aggressive anion from reaching the reinforcing. Coated rebars and inhibitors prevent corrosion of the bar even though high chloride concentrations exist. With the exception of non-corrosive deicers all the above problem solving techniques have met with some degree of success. Within the second category, that of solutions to the problem after substantial quantities of deicing salts have penetrated the concrete, are four techniques: (1) forced migration of the chloride ion by electro-potential gradient,^{4,5}; (2) cathodic protection,^{6,7,8}; (3) thin bonded concrete overlays,^{9,10} both modified and unmodified; and (4) attempts to tie up the chloride ion present in the concrete in a chemical product of low solubility. Of these procedures, only thin bonded concrete overlays have met with any degree of success although cathodic protection is now near to being field worthy.

Project Goals

This phase of the project was to investigate the use of cathodic protection as a means of controlling corrosion of reinforcing in bridge decks. The goals of the project were:

1. Determine the characteristics of the coke breeze asphaltic concrete used as the current conductive medium. This objective was broken into two subgoals: (a) determine the structural characteristics of the overlay; and (b) determine its current carrying characteristics.

2. Determine the affect that the Portland Cement concrete of the deck had on the distribution of current to the reinforcing.
3. Determine what criteria in the way of polarized potential and current density are required for complete protection of the imbedded reinforcing.
4. Determine the relationship between polarized surface potentials and those at the level of the upper rebar mat.

Review of Cathodic Protection Theory

Prior to the presentation of the experimental techniques and findings of this work a brief review of cathodic protection theory is in order. Cathodic protection is a technique for halting corrosion of metallic structures. The process has been used since 1824 when Sir Humphrey Davy used iron as a sacrificial anode to protect the copper clad hulls of ocean going ships. Even prior to that, in France during the 1700s, zinc dipping of metal pails was known to noticeably extend their life. However, it was not until the extensive use of buried metal pipelines in the 20th century that cathodic protection came into widespread use.

Cathodic protection operates on the principle of forcing the protected structure to be the cathode of a galvanic cell by connecting it electrically to a more active metal, called a sacrificial anode, or to a source of D.C. current that performs the same functions as an infinitely active anode. For the uninitiated this explanation may be less than straightforward. A discussion of corrosion fundamentals will be found in Appendix A. This discussion will aid the lay reader in his understanding of cathodic protection principles.

EXPERIMENTAL PROCEDURE

After a year of literature study, lab work, and design, the search began for a suitable structure upon which to place a full size cathodic protection installation. Because of the desire to leave the coke breeze asphalt overlay exposed for ease of data collection and armed with other experimenter's reports of poor stability in these overlays,¹¹ an effort was made to locate a structure that carried low traffic volumes. Such a structure was found in one of Oklahoma Department of Transportation's field maintenance facilities. The structure was a three-span, 120' x 20' (36.6 x 6.1 m), of T-beam design that was built in 1927 and removed from the highway system in 1969 due to route relocation. The structure carries only the vehicles used by the maintenance facility and it was felt that the exposed coke breeze asphalt would stand up under these low traffic volumes.

The type of cathodic protection installation chosen was of the conventional design utilizing 12" x 1 1/2" (30.5 x 3.81 cm) high silicon cast iron anodes cemented to the bridge deck. Current is supplied through a constantly charged wet cell and distributed across the deck with a coke breeze asphaltic concrete.

Prior to placement of the coke breeze overlay the deck was routinely surveyed to determine half-cell potential of the reinforcing steel, chloride content of the concrete, and concrete cover over the top steel mat. At the same time the structure was visually surveyed to locate any exposed steel that might act as a short to the coke breeze asphaltic concrete.

The half-cell survey pointed out only four readings in excess of 300 mV negative to the copper/copper sulfate electrode. Three of these four were along the curb line; the fourth was adjacent to a transverse crack. The chloride content survey indicated only one area out of the eight areas sampled that contained chloride ion in excess of two pounds/yd.³ (1.179 kg/m³) of concrete which is considered by many the chloride content threshold for corrosion. This area is an area of plus 300 mV half-cell readings. Concrete cover averaged two and five-eighths inches (6.67 cm) with rebar depths ranging from two and one-half (6.35 cm) to four and one-sixteenth (10.32 cm) inches.

Several areas along the curb face had exposed reinforcing and all drains were exposed cast iron that were grounded to the rebar mat. The exposed steel in the curb face was coated with a general purpose epoxy and the areas near the drains were excavated of conductive asphaltic concrete after the laydown operation and back filled with ordinary non-conductive asphaltic concrete.

The anodes were epoxied along the bridge's centerline at a 20 foot (6.096 m) spacing, beginning ten feet (3.048 m) into the bridge. Holes were cored in the deck to the level of the rebar mat in four locations and electrical resistance corrosion probes were placed in these holes and then backfilled with Portland Cement concrete to which five percent NaCl was added based on the cement content, Figure 1. The wiring from these anodes and probes was routed underneath the bridge through holes drilled adjacent to the respective anode or probe. From there they were routed to a control box near the south end of the structure. Figure 2 presents a diagram of the location of the cathodic protection devices.

The coke breeze asphaltic concrete was made up of approximately 60 percent bituminous coke breeze, 40 percent mineral aggregate, and 13 percent asphalt cement. Figure 3 contains the gradation and mix design. The stability as determined by the Hveem method (ASTM D 1560-71) was 33 and uncompacted thickness was four inches. Batching and placement of the overlay was relatively uneventful but difficulty was encountered during the compaction. Severe rutting of the overlay occurred when rolling was attempted before the overlay temperature dropped to 150°F (65.5°C). When rolling commenced at asphalt temperature of 150°F to 160°F (65.5°C to 71°C) and followed the normal sequence of initial rolling with a steel wheel roller followed by pneumatic rolling and a final rolling by a steel wheel, then the compaction problems were greatly alleviated. A large amount of the bituminous coke breeze was wasted while calibrating the asphalt plant and we obtained, as back up, material from a local supplier of petroleum coke breeze. This material was much more porous than the original material and the one load of asphaltic concrete utilizing this material proved to be much too low in asphalt

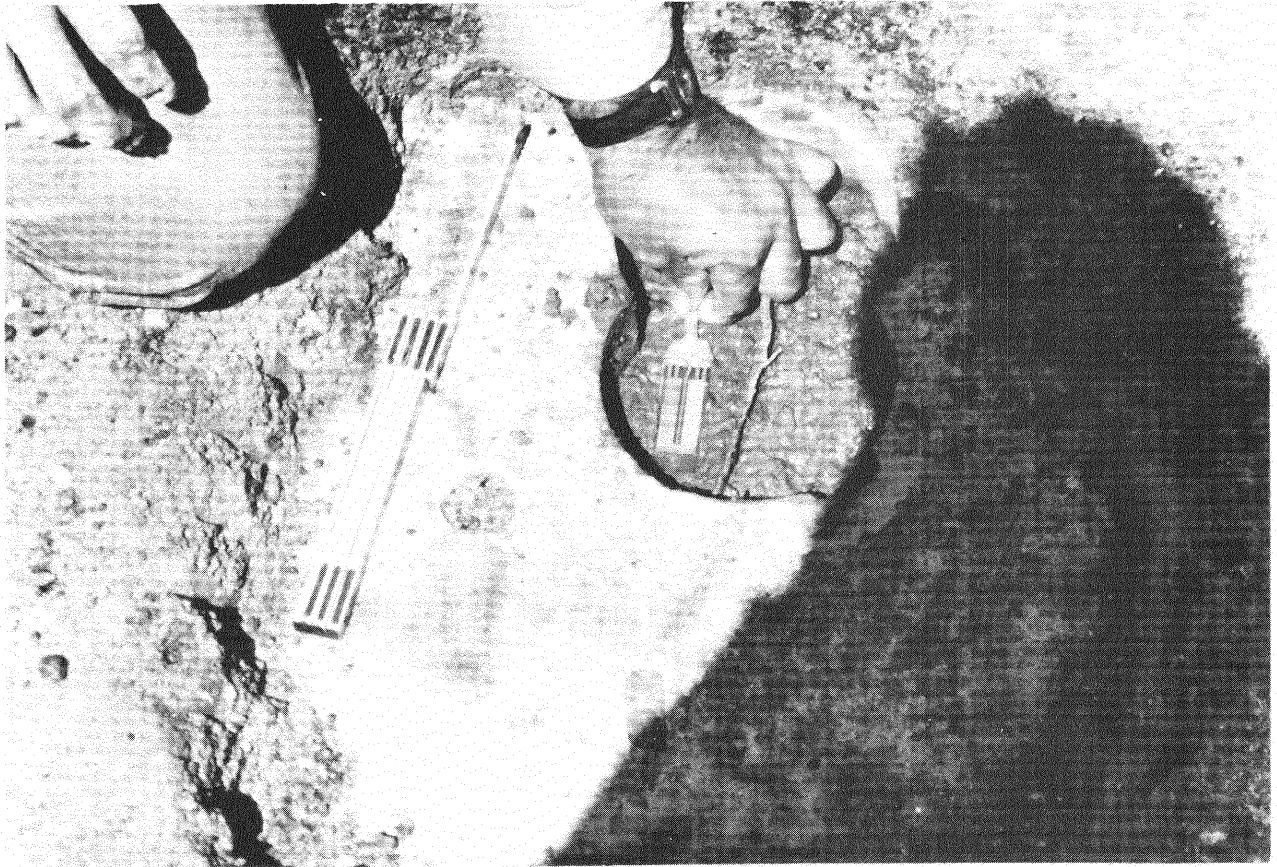


Figure 1. Placing corrosion resistance probes in the bridge deck.

General Bridge Layout

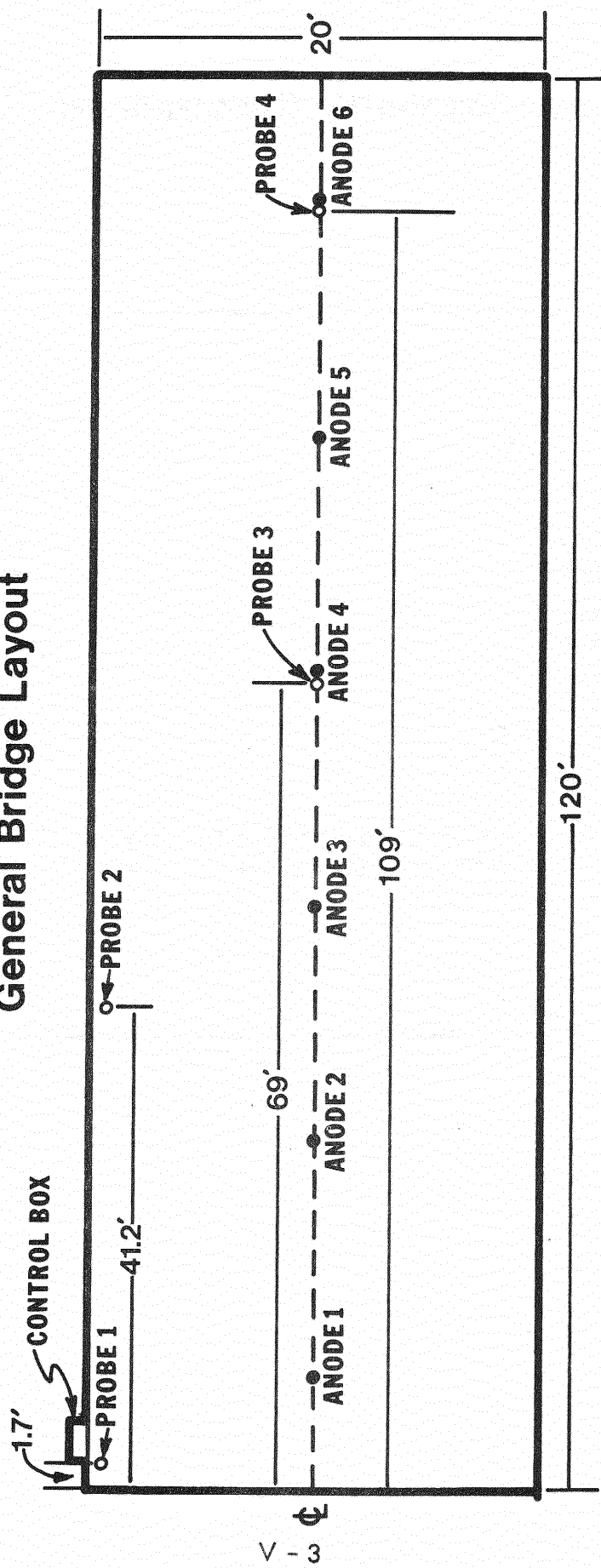


Figure 2

Coke Breeze Asphaltic Concrete Mix Design

SIEVE NO.	AGGREGATE PERCENT PASSING
1/2"	100
3/8"	99
NO. 4	79
NO. 10	49
NO. 40	17
NO. 80	6
NO. 200	1.7
% A-C3	12.8
Bulk Impregnated Specific Gravity-----1.854	
Hveem Stability Value-----33	

Figure 3

cement to provide stability. In comparing this mix design with that of Spellman's¹², it appears that this design would have benefited from a two to three percent increase in the amount of asphalt cement. Eventually an adequate surface was obtained over all the structure except where the petroleum coke breeze had been used; this area remained unstable. Figures 4 and 5 depict the overlay operation and the final appearance of the coke breeze asphaltic concrete overlay. Several days after the placement of the overlay, one and one-fourth inch (3.75) diameter holes were drilled through the overlay and the concrete to the level of the previously buried corrosion probes. These holes dead ended approximately one-fourth inch to the south of each probe and at the same level as the probe. A PVC pipe was epoxy cemented into this hole. Adjacent to this hole another was drilled, but this one was drilled only through the coke breeze overlay. Another PVC pipe was epoxied here. These pipes allowed entry of the copper/copper sulfate reference cell in order that potential measurements could be taken at the level of the reinforcing steel in the near vicinity of the electrical resistance corrosion probe and also upon the concrete bridge deck. Figure 6 is a cross section of the equipment and facilities at each probe site. These four corrosion probe sites are referred to as probe locations in the body of this paper and only as probes in the figures. Close fitting caps were placed on these pipes to prevent intrusion of debris or rainwater. The reference electrode entry pipes are pictured in Figure 7. Protection current is supplied through a constantly charged 12 volt wet cell with power potentiometers to control total applied voltage and individual anode voltage. The current is essentially DC with a 50 mV full wave ripple imposed on it from the charger. Circuitry is provided to measure total applied voltage and current, individual anode voltage and current, corrosion probe readings and current impressed on these probes. Figure 8 is a schematic of the cathodic protection power supply and Figure 9 is a schematic of the circuitry of the resistance probe monitoring system. The control box for current regulation and data gathering is pictured in Figures 10 and 11. Data on all the above functions as well as half-cell potentials at the four probe sites have been taken weekly since July, 1975.

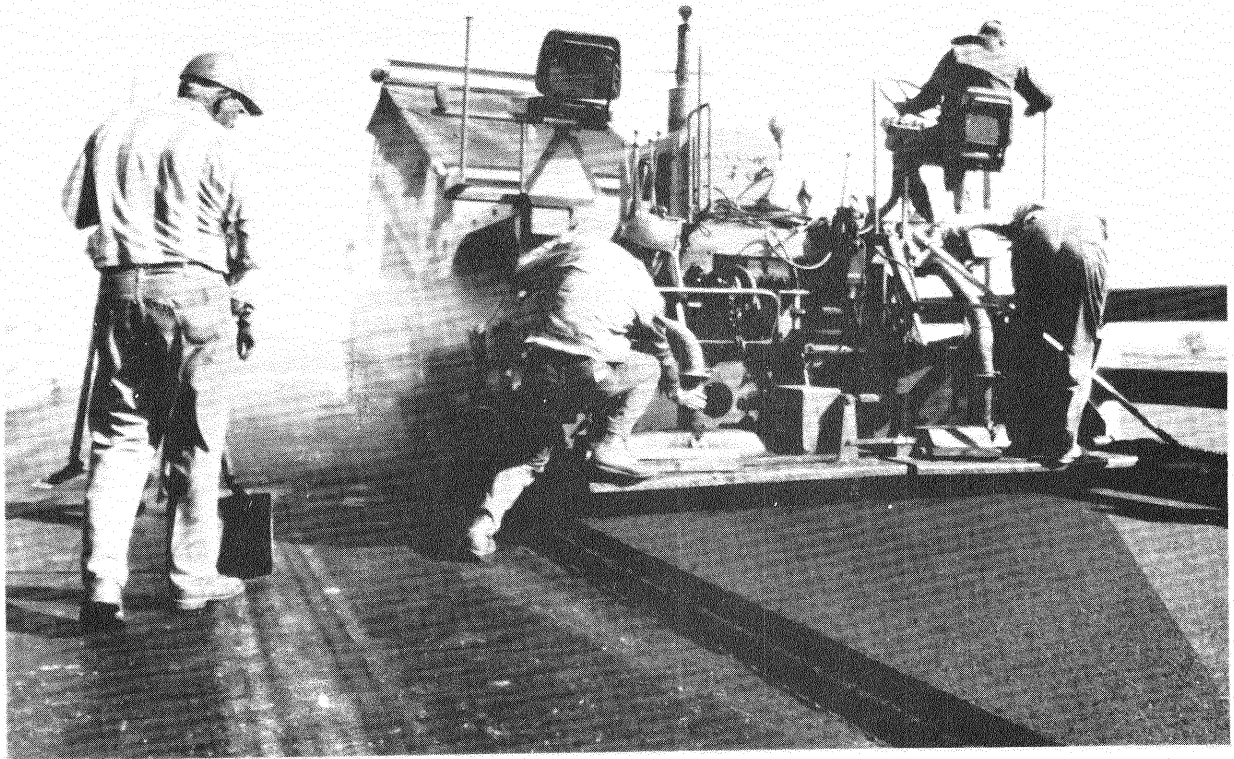


Figure 4. Placement of Coke Breeze asphaltic concrete. Note: Anodes along bridge centerline.

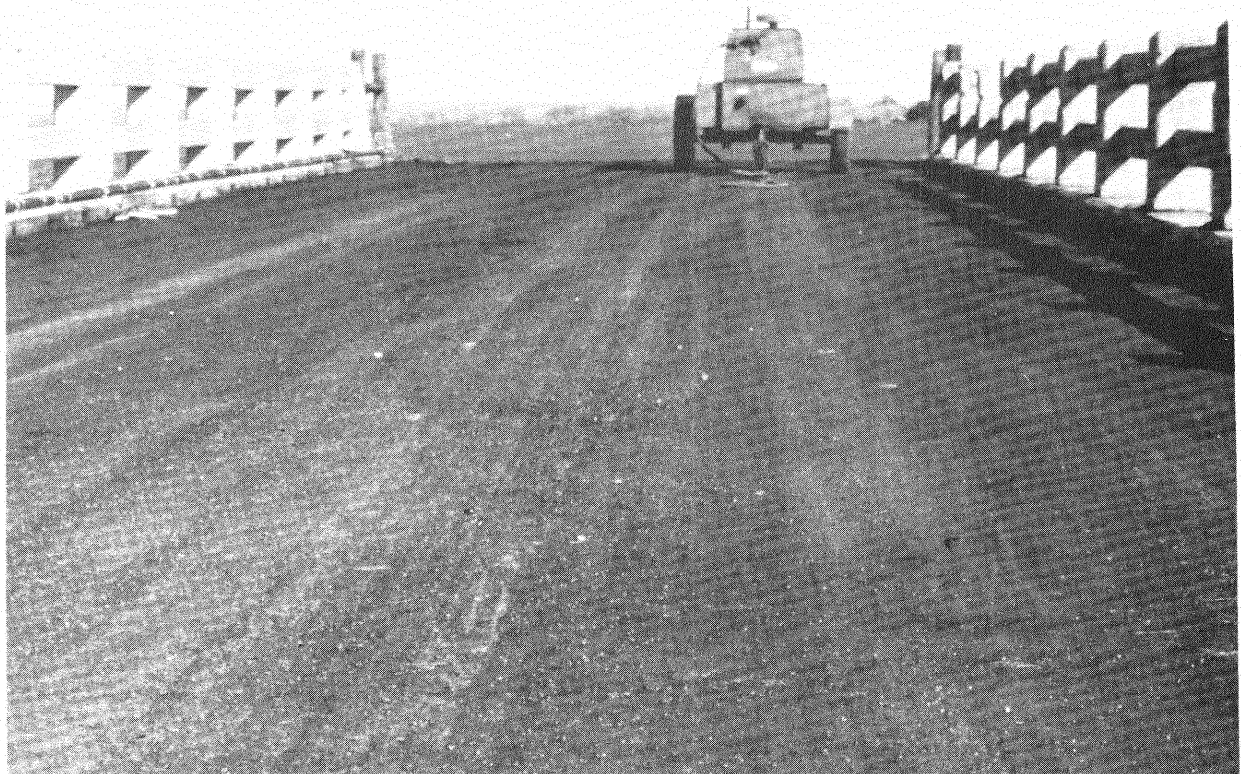
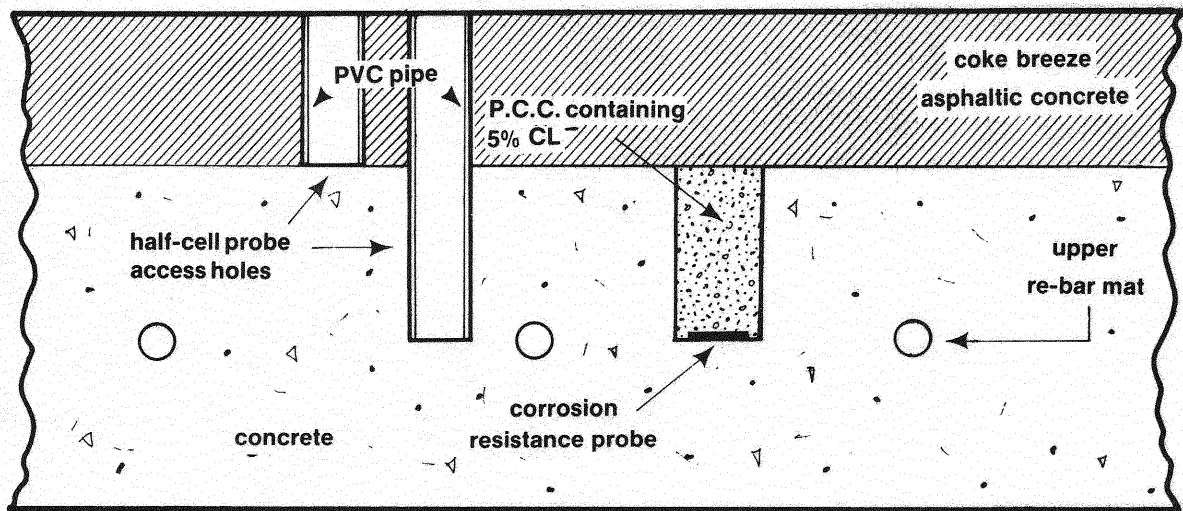


Figure 5. Appearance of completed overlay.



Cross Section at Probe Location

Figure 6



Figure 7. Access pipes for reference electrodes.

RESULTS

Coke Breeze Conducting Layer

The in-place resistivity of the coke breeze asphalt is three to six ohm-cm, as measured by the Wenner four pin method. Initially only one anode was driven in order that the relationship concerning voltage drop versus distance from the anode could be developed. Figure 12 is a plot of the data collected on two halfcell surface surveys taken approximately six weeks apart and consists of 350 data points. The parabolic curve fits the aggregate data adequately at distances from the anode of 60 to 70 feet (18.3 to 21.3 m) or less. This distance should be greater than the practical radius of protection for this type of installation.

It is not the intent of this paper to suggest that this curve represents the underlying relationship. It is simply the one that fits best out of the several we have tried.

The equation for this best fitting curve is:

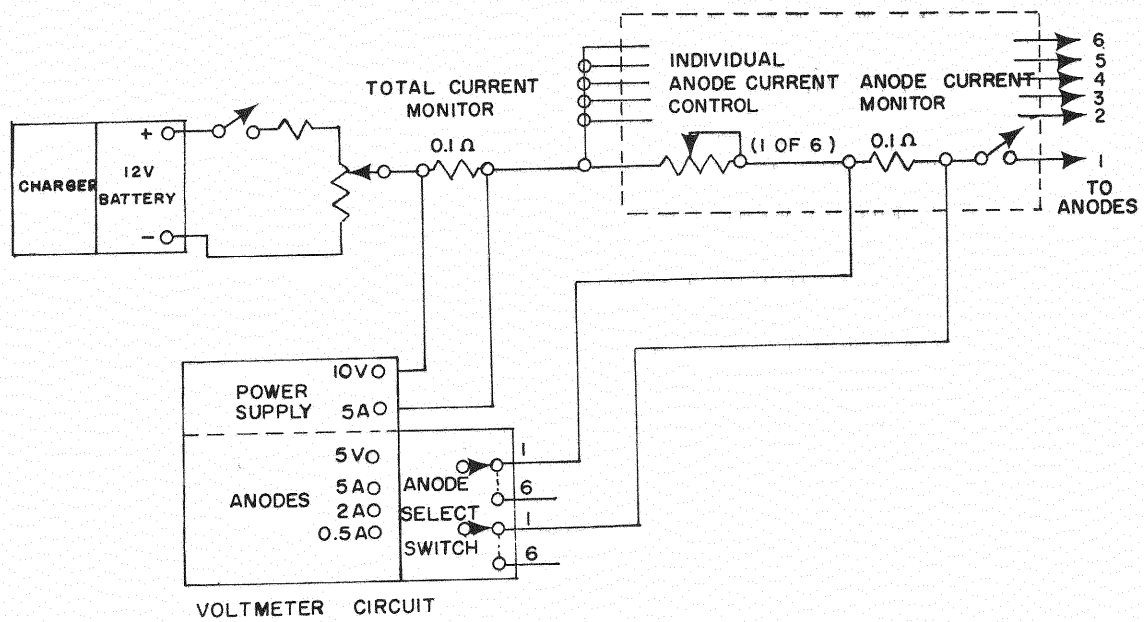
$$V = 3.153D^2 - 5.184D + 3.5182$$

where V is the potential (volts versus Cu/CuSO₄), and D is distance from the anode, ft.

More recently three anodes have been driven, giving rise to a surface potential versus distance along the structure curve as shown in Figure 13. Driving three anodes gives a much better distribution of potential along the bridge surface.

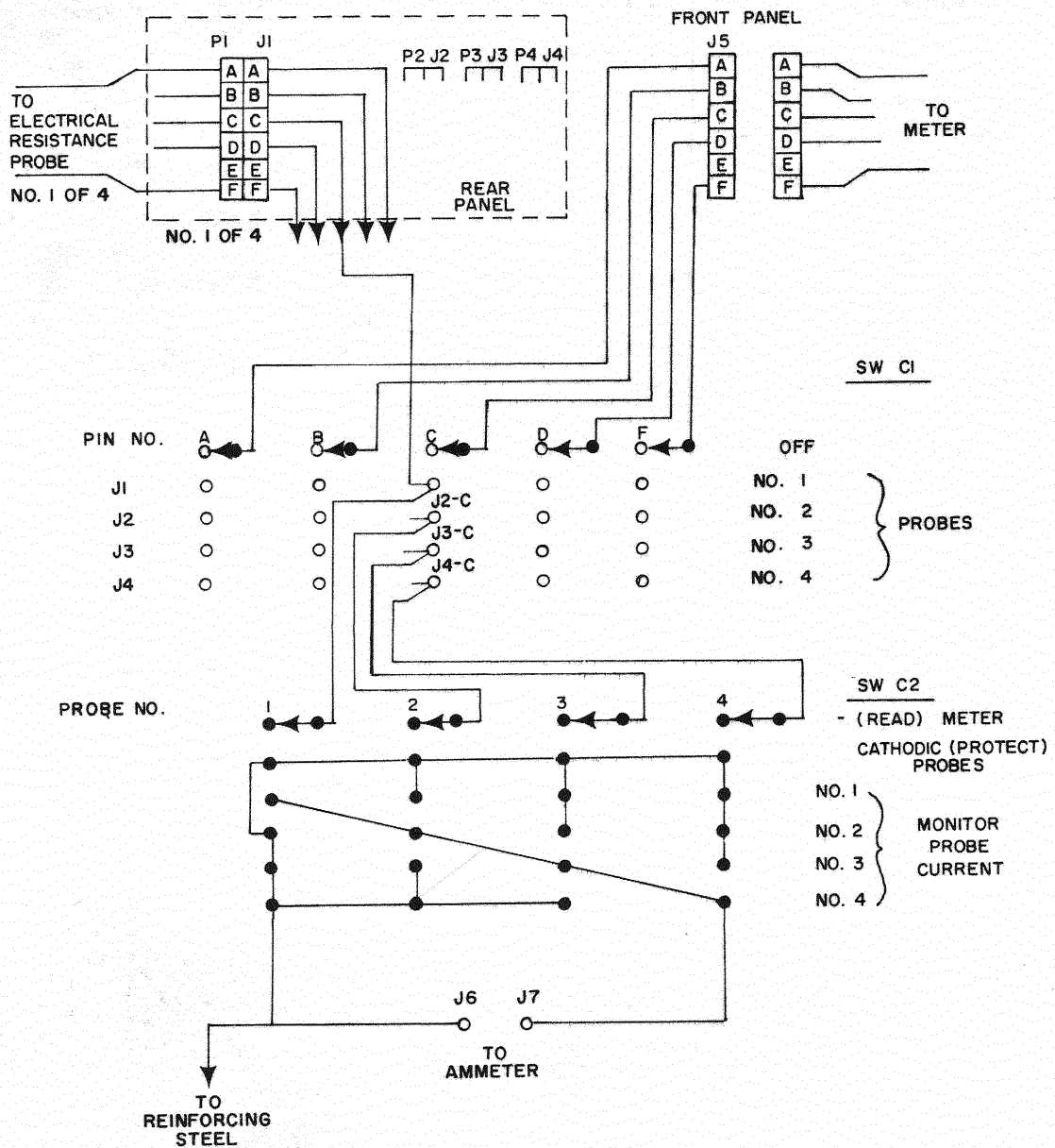
Predicting Steel Level Potential

Realizing that the most flexible method for determining the effectiveness of a cathodic protection installation was in measuring the polarized potential of the reinforcing mat, this became one of the goals of this investigation. To randomly obtain potential measurements in the near vicinity of the rebar is impossible unless holes are drilled in the deck and since the potential of reference electrodes imbedded in the deck were of questionable stability, it was decided to attempt to correlate surface potential to steel level potentials. At each of the four probe locations potential measurements were routinely taken on the coke breeze A.C. surface, on the concrete deck surface through one of two PVC access pipes and



CATHODIC PROTECTION POWER SUPPLY

Figure 8



ELECTRICAL RESISTANCE METER/PROBE FUNCTIONS

Figure 9

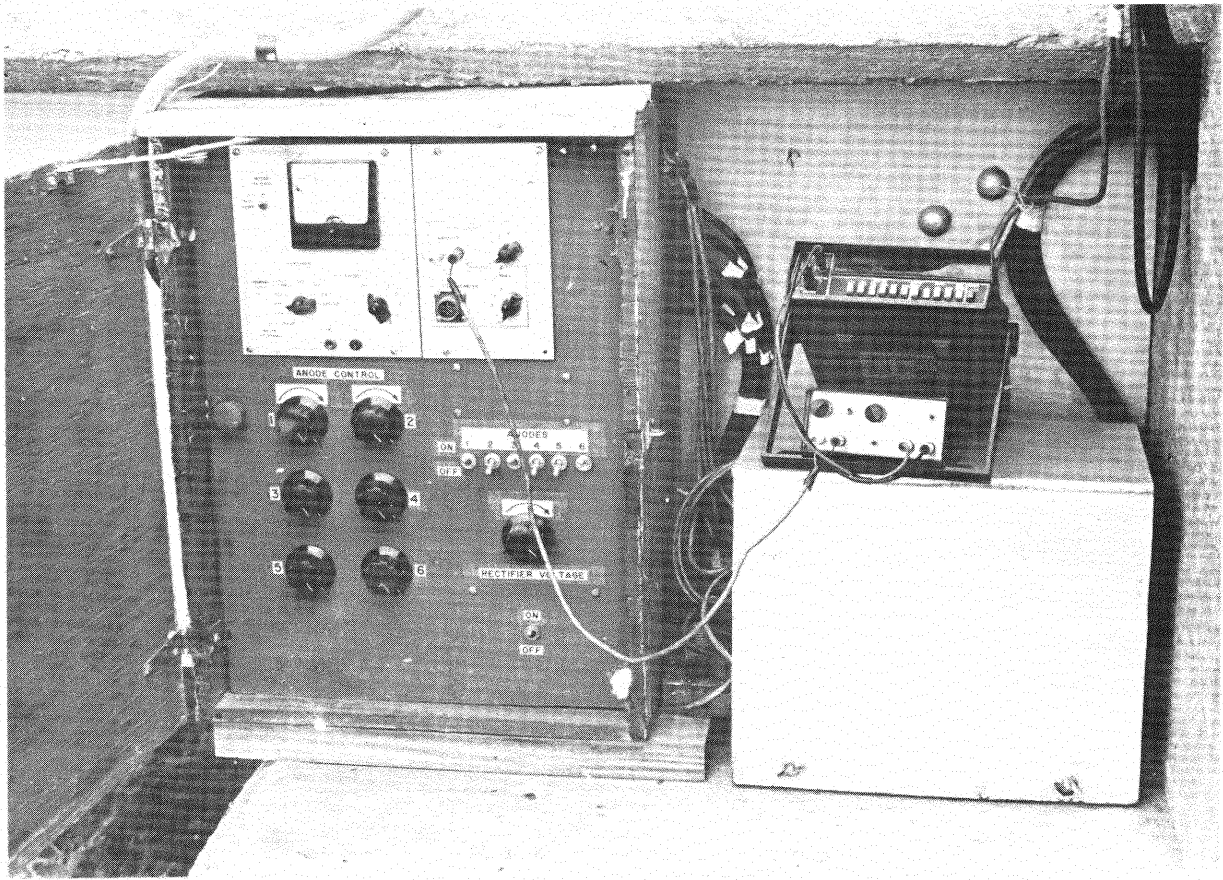


Figure 10. Control Box.

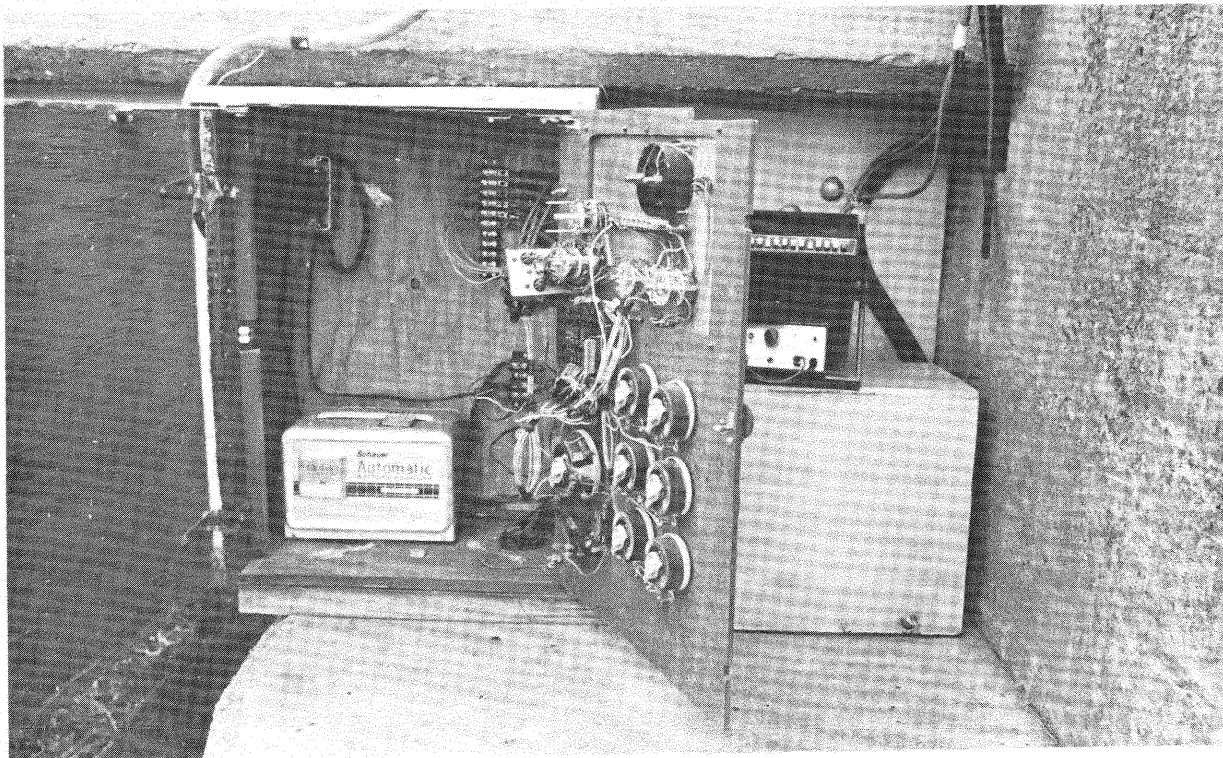


Figure 11. Control Box, Panel opened.

Surface Potential Profile ONE ANODE DRIVEN

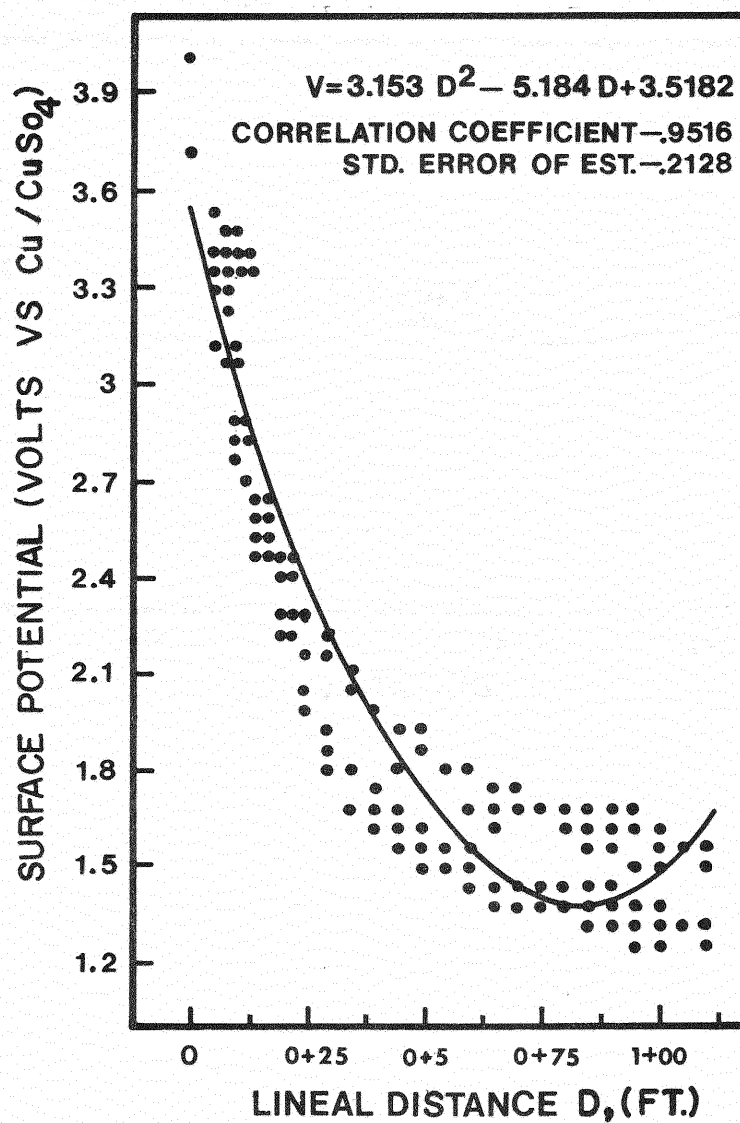


Figure 12

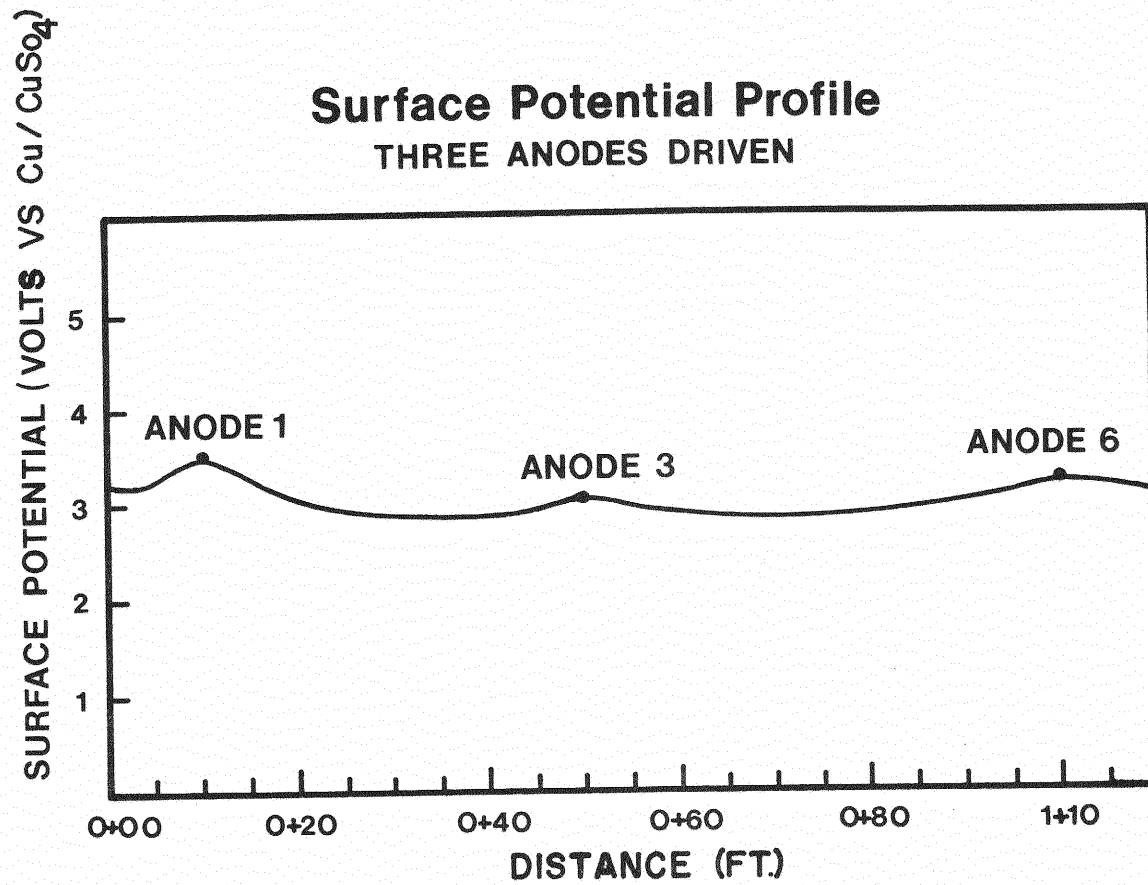


Figure 13

within the bridge deck at the level of the rebar mat through the second PVC pipe. These data were then compared through regression analyses to determine if steel level potential measurements could be predicted from the easily obtainable surface potentials.

Before the results of the regression analyses are presented, a word is in order concerning the upper and lower limits of polarized potential that bracket cathodic protection of reinforced concrete.

Many researcher's^{13, 14, 15} have found that when cathodically protecting steel in concrete, the polarized steel potential should not exceed the over-voltage for hydrogen. At the pH of concrete this critical potential is approximately 1100 mV negative to Cu/Cu SO_4 . Potentials more anodic than this will liberate hydrogen and may soften the concrete adjacent to the bar, adversely affecting bar-concrete adhesion. On the other end of the scale is the minimum potential required for protection. Researcher's^{16, 17} working with steel specimens immersed in saturated Ca(OH)_2 solutions to which NaCl was added as a corrodant have found minimum potentials for protection to be 750mV to 770mV. Data obtained from corrosion resistance probes and from cathodic polarization curves, to be presented elsewhere in this report, indicate protected potentials slightly more noble than this, in the neighborhood of 660mV to 700mV. Therefore, at most, the potential span for cathodic protection of steel imbedded in concrete is about 440mV. Whenever this potential span is exceeded by the error interval from the regression analysis, then the relation is unable to accurately predict that a rebar potential lies within the above mentioned upper and lower limits.

Coke Breeze Potential vs. Steel Level Potential (Current On)

The results of this correlation are shown in tabular form in the top section of Figure 14. The standard errors of estimate are disappointingly large ranging from 84mV to 134mV. The data for all probes, which more nearly represents the situation encountered in the random testing of a structure, yield a standard error of 128mV. This translates to a 95 percent confidence interval that is 502mV wide. This interval greatly exceeds the 440mV range for steel in concrete indicating an

CORRELATION	PROBE NO.	EQUATION	CORR. COEFF.	STD. ERR. OF EST. (VOLT)	STD. DEVIATION (VOLT)	WIDTH OF 95 % CONF INTERVAL (VOLT)
COKE BREEZE A.C. VS STEEL LEVEL (CURRENT ON)	1	$P_{sl} = 0.015P_{cb} + 0.703$	0.1668	0.0848	0.085	0.332
	2	$P_{sl} = 0.084P_{cb} + 0.543$	0.6724	0.1178	0.158	0.458
	3	$P_{sl} = 0.077P_{cb} + 0.433$	0.6648	0.1166	0.155	0.458
	4	$P_{sl} = 0.107P_{cb} + 0.382$	0.7596	0.1345	0.205	0.527
	ALL	$P_{sl} = 0.081P_{cb} + 0.475$	0.6339	0.1284	0.166	0.503
CONCRETE DECK SURFACE VS STEEL LEVEL (CURRENT ON)	2	$P_{sl} = 0.427P_c + 0.359$	0.9249	0.0605	0.157	0.237
	3	$P_{sl} = 0.285P_c + 0.402$	0.7816	0.0973	0.155	0.381
	4	$P_{sl} = 0.076P_c + 0.555$	0.5275	0.1760	0.205	0.690
	ALL	$P_{sl} = 0.087P_c + 0.603$	0.4645	0.1609	0.181	0.631
	2 3	$P_{sl} = 0.366P_c + 0.378$	0.8317	0.0961	0.1724	0.377
STEEL LEVEL (INSTANT OFF) VS STEEL LEVEL (CURRENT ON)	1	$P_{on} = 1.541P_{off} - 0.166$	0.7374	0.0581	0.086	0.227
	2	$P_{on} = 1.864P_{off} - 0.2926$	0.9201	0.0623	0.158	0.243
	3	$P_{on} = 1.617P_{off} - 0.1765$	0.8803	0.0740	0.155	0.290
	4	$P_{on} = 1.786P_{off} - 0.288$	0.9512	0.0638	0.205	0.251
	ALL	$P_{on} = 1.703P_{off} - 0.231$	0.9095	0.0691	0.166	0.270

Figure 14

inability to predict steel level potential with sufficient accuracy to prevent over or under protection.

Bridge Deck Potential vs. Steel Level Potential (Current On)

Because of mechanical difficulty, insufficient data at probe location one is available for a meaningful analysis. The standard errors for the regression analyses of the other three probes range from 61mV to 176mV, with a standard error for all probe locations of 161mV. Again, this standard error is much too great to predict steel level potential with the required accuracy. However, probe location 4 is quite near a driving anode (approximately 3"). It is very likely that steel level predictions may be very difficult so close to a driving anode. If data from this probe is deleted from the analysis, the overall regression analysis is much better. When the data from probe 2 and 3 are lumped the span of the 95% confidence interval is 384mV. If this relationship holds true for areas sufficiently far away from an anode, steel level potentials' could be predicted with suitable accuracy from the concrete bridge deck surface.

Regression analyses of current interrupted potential readings were performed on "instant off" potential measurements on coke Breeze A.C. surface and on the deck surface vs. "instant off" as well as "current on" potential at the level of the reinforcing. These analyses had poorer correlation parameters than the "current on" analysis reported above. Virtually all of the analyses yielded standard errors of estimate that were very close to the standard deviations of the raw data indicating little or no improvement in estimating steel level potential was provided by the regression line. These data are not presented here.

Steel Level Potential (Instant Off) vs. Steel Level Potential (Current on)

The data for these regression analyses are presented in the lower section of Figure 14. As might have been expected, these analyses provided a much better estimate of "current on" potential than any other analysis with standard errors being 50 percent or less of the standard deviations. The width of the 95 percent confidence interval is 270mV for all probes. This, however, provides little relief from the awkward task of obtaining current on steel level potential readings.

PREDICTIONS OF PROTECTED POTENTIAL AND CURRENT DENSITY

Polarized Potential Required for Protection

Estimates of the polarized potential required for halting corrosion were attempted in two ways. (1) From plots of change in resistance (ΔR) vs. polarized potential of the corrosion resistance probes and (2) from plots of current flow direction vs. polarized potential of these same probes. For several weeks after imbedding of the corrosion resistance probes, plots were made of the resistance. During this time the resistance steadily climbed on all probes. As soon as trends were established, cathodic protection current was applied and the potential was adjusted until the ΔR became zero. This was somewhat difficult because each probe had a different potential for protection but the range was from 600mV to 710mV vs. Cu/CuSO₄.

The second method used to ascertain the over voltage required for protection was to plot the current direction in the corrosion resistance probes against their polarized potential. This method is less clear cut than the former, however, at potentials more negative than 750mV, 100 percent of the current readings were in the cathodic direction while at the next lowest potential with a sufficient number of points (625mV) only 50percent of the readings were in the cathodic direction. This would indicate the protected potential would lie in the region bracketed by 625mV and 750mV.

Current Density Required for Cathodic Protection

Two methods were used to arrive at the current density required for obtaining cathodic protection; (1) divide total current applied to the bridge deck by the total area of the rebar mat and (2) by analysing cathodic polarization curves on the corrosion resistance probes.

The former method requires the assumption that all applied current will be used to protect the upper rebar mat and that none will go to the lower mat or reach ground by some other method. With these assumptions in mind the 533 sq. ft. of

rebar mat surface has been protected with 1.1 to 1.3 amps for a current density of 2.06 to 2.44 mA/ft.². These readings were taken approximately 20 months after application of cathodic current. Unfortunately no such data is available on the total rebar mat during the early phases of the project. The reason for this lack of data was that the entire structure was not under total protection until after some areas had already been polarized.

Recently a galvanostat was utilized to obtain cathodic polarization curves at two of the four corrosion resistance probes. These curves were unable to provide reliable data concerning potential because the probes were still polarized cathodically (after current had been interrupted for 6 weeks!) However, both curves approached the linear tafel region at current densities of 0.8 mA/ft.² at 100mV more negative (a potential more likely to coincide with the $\text{Fe} \rightarrow \text{Fe}^{++}$ reversible potential). The current density was approximately 1.35 mA/ft.². The densities agree quite well with the densities obtained from total applied current, particularly when the difference in geometry of the probes vs. reinforcing mat are considered.

DISCUSSION

Coke Breeze Asphaltic Concrete Conductive Layer

The coke breeze asphaltic concrete developed and used on this project has provided a suitable stability for the low traffic volumes it has had to serve. With the exception of one truck load of high porosity coke breeze, the surface is visually without flaws. Further efforts at modification of the mix design and/or asphaltic cement should yield a mix suitably stable for high traffic volumes while still maintaining a reasonable low resistivity. The resistivity of this mix is quite low and reasonably uniform as evidenced by the relatively small amount of data scattering in Figure 12. The problem with this conductive layer, one that is shared by most asphaltic concretes, is the blanketing effect they provide for the bridge decks on which they are placed. This blanketing effect becomes manifest when rain water or melted snow percolates through the asphaltic concrete or down the asphaltic concrete-parapet interface to puddle on the concrete deck surface. The asphaltic concrete overlay then acts as a blanket or semi-permeable barrier to inhibit evaporation. This fact provides long soak times for the concrete and may very likely accelerate freeze thaw deterioration to the bridge deck. On nonair-entrained decks this will assuredly happen. On properly air-entrained structures, this may not be such an urgent problem. It is the author's opinion that discretion should be used before placing an asphaltic concrete overlay over any structure in areas where freeze-thaw damage has been or could be a problem.

In addition, in all likelihood, overlays will accelerate penetration of deicing salts to the bottom mat of reinforcing steel, thus creating the additional and more difficult task of protecting this mat.

The Oklahoma Department of Transportation is presently investigating the use of conductive concrete and waterproofing materials in an attempt to circumvent the problems with conductive asphaltic concrete overlays.

Predicting Steel Level Potentials

The inability to accurately predict rebar potential from the coke breeze asphaltic concrete surface has certainly created a bit of inconvenience in the monitoring of future cathodic protection installations. The possibility that sufficiently accurate predictions can be made from the concrete surface yields little relief from the inconvenience of drilling holes in the riding surface. This may be a necessary inconvenience. However, it can be made as painless as possible if these holes are chosen properly to provide information about areas that are most likely to be over and under protected. Under investigation at the University of Oklahoma are imbeddable reference electrodes that can be placed at the level of the upper rebar mat and used to monitor potential from outside the roadway. These electrodes would eliminate the problems of traffic control and access holes, and open the possibility of using the rebar potential to automatically adjust the level of impressed current.

Polarized Potential and Current Density for Cathodic Protection of Reinforcing

The data presented earlier concerning these two most important criteria should be viewed as what they are; a set of criteria that applies to a particular structure (the corrosion resistance probe) and a particular electrolyte (0 to 2 years old backfill concrete to which 5 percent NaCl was added). This may or may not hold true for other rebar concrete situations. Much work has been done on saturated Ca(OH)_2 solutions, but what is needed now is data obtained from actual field installations. The author has future work planned to isolate sections of rebar and attempt to determine through cathodic polarization just how wide is the range of these two most important parameters of cathodic protection.

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APPENDIX A

Corrosion Process

Corrosion is the combining of a metal with oxygen, the OH^- radical, or other anions to form a compound in which the cation is at a lower energy state than in the uncombined form. All metals except the precious metals, i.e., gold and platinum, corrode spontaneously. Thermodynamically, they possess lower free energy in the combined state than in the uncombined state.

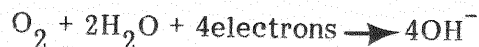
Corrosion is an electro-chemical process which means that, although the process is a chemical one, it also involves the transfer of electrons. This transfer of electrons and the potential difference that drives the transfer provides the best means of monitoring corrosion. The phenomena of corrosion, although quite complex, contains four essential elements, the loss of any one halting the process. The elements are:

1. An Anode - Generally a metal or an area of a metal that goes from nonionic to ionic metal, very often forming a corrosion product in the process. The chemical notation for this reaction is



This release of electrons creates an excess of electrons on the anode. A chemical process of this type where the electrons are released is called oxidation.

2. A Cathode - A metal or an area on a metal where the excess electrons generated at the anode can be consumed. In alkaline solutions such as Portland Cement concrete the electrons are consumed in a chemical reaction of the type:



A reaction where electrons are consumed is called reduction.

3. A metallic conductor for the electrons to flow from the anode to the cathode.

4. An electrolyte that is continuous between the anode and cathode. This electrolyte completes the circuit allowing movement of ions or ion exchange between anode and cathode to prevent an overall charge build up at either.

Each metal has its own characteristic driving force to corrode. The relative driving force between metals can be and has been measured. A listing of metals and their driving force is called an electromotive (EMF) force listing. This listing is arrived at by immersing each metal in a very specific electrolyte and then measuring the potential difference between each metal electrolyte and that of the hydrogen cell that has been arbitrarily chosen to be the standard and assigned a potential of zero. This potential difference is referred to as the cell's half-cell potential.

These metals are then listed, along with their standard half-cell potential, in descending order of activity or propensity to corrode in an electromotive force listing. See Figure A1. The metals near the bottom of the list corrode quite readily and are referred to as active or anodic metals. Metals near the top of the list corrode very slowly or not at all and are referred to as noble metals. The metal-electrolyte cell is actually referred to as a half-cell because it comprises one-half of the total measuring cell, the other half-cell being the standard, or reference cell. The hydrogen half-cell is rather inconvenient to use in routine field measurements; therefore, other more convenient half-cells have been developed. The most common of these cells are the copper/copper sulfate half-cell and the saturated calomel electrode. Silver/silver chloride and molybdenum/molybdenum oxide cells are also used in some instances. These half-cells offer the advantages of portability and ruggedness.

If one were to connect any two half-cells from the EMF series together with a continuous external conductor and a provision for a continuous electrolyte, the metal lower in the listing would corrode (anode) while a reduction reaction would occur on the surface of the metal higher in the listing (cathode). Should a high impedance voltmeter be connected in series between the half-cells, the voltage read would be the algebraic difference between the two standard half-cell potentials.

ELECTROMOTIVE FORCE SERIES

	Volts*
$\text{Au} = \text{Au}^{+3} + 3\text{e}$	+ 1.498
$\text{O}_2 + 4\text{H} + 4\text{e} = 2\text{H}_2\text{O}$	+ 1.229
$\text{Pt} = \text{Pt}^{+2} + 2\text{e}$	+ 1.2
$\text{Pd} = \text{Pd}^{++} + 2\text{e}$	+ 0.987
$\text{Ag} = \text{Ag}^{+} + \text{e}$	+ 0.799
$2\text{Hg} = \text{Hg}_2^{++} + 2\text{e}$	+ 0.788
$\text{Fe}^{+3} + \text{e} = \text{Fe}^{+2}$	+ 0.771
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} = 4 \text{OH}$	+ 0.401
$\text{Cu} = \text{Cu}^{+2} + 2\text{e}$	+ 0.337
$\text{Sn}^{+4} + 2\text{e} = \text{Sn}^{+2}$	+ 0.15
$2\text{H}^{+} + 2\text{e} = \text{H}_2$	0.000
$\text{Pb} = \text{Pb}^{+2} + 2\text{e}$	- 0.126
$\text{Sn} = \text{Sn}^{+2} + 2\text{e}$	- 0.136
$\text{Ni} = \text{Ni}^{+2} + 2\text{e}$	- 0.250
$\text{Co} = \text{Co}^{+2} + 2\text{e}$	- 0.277
$\text{Cd} = \text{Cd}^{+2} + 2\text{e}$	- 0.403
$\text{Fe} = \text{Fe}^{+2} + 2\text{e}$	- 0.440
$\text{Cr} = \text{Cr}^{+3} + 3\text{e}$	- 0.744
$\text{Zn} = \text{Zn}^{+2} + 2\text{e}$	- 0.763
$\text{Al} = \text{Al}^{+3} + 3\text{e}$	- 1.662
$\text{Mg} = \text{Mg}^{+2} + 2\text{e}$	- 2.363
$\text{Na} = \text{Na}^{+} + \text{e}$	- 2.714
$\text{K} = \text{K}^{+} + \text{e}$	- 2.925

*25⁰ C, volts vs. normal hydrogen electrode.

Figure A1

Figure A-2 depicts such a cell, coupling the standard half-cell of iron and copper through a porous membrane and an external conductor. In this instance Fe, being lower (more negative half-cell potential) in the EMF series, would corrode while the copper would be reduced. The potential difference between these two half-cells would be $-0.440\text{V} - (+0.337\text{V}) = 0.777\text{V}$. It is this potential difference that creates the driving force for electrons to flow from anode to the cathode. Without this potential difference and electron flow, corrosion would quickly halt. This concept of potential difference forms the foundation for understanding corrosion.

Galvanic Cells

In this discussion the coupling of an anode and a cathode through a continuous electrolyte and external conductor will be referred to as a corrosion cell. A corrosion cell, such as the one discussed above that is initiated by the coupling of two dissimilar metals, is called a galvanic corrosion cell. Galvanic corrosion cells are one of the two major types of corrosion cells. The second type is the result of differences in electrolyte surrounding one metal and are called electrolytic cells. Electrolytic corrosion cells will be discussed later.

Although galvanic corrosion cells are created when dissimilar metals are connected in an electrolyte, they can also occur on the surface of a single metal piece. This occurs because of the non-homogeneity of most metals. Metals, even nearly pure ones, are not homogeneous. They have microscopic as well as macroscopic surface differences. These non-homogeneities create galvanic corrosion cells.

The following is a partial listing of surface non-homogeneities that can create galvanic corrosion on a single metal surface. Areas on a hot rolled metal bar that are covered with mill scale are cathodic to other areas on the same bar that do not possess this covering. Bright metal surfaces are anodic to surfaces on the same metal that have a light corrosion covering. Stressed areas of metals are anodic to unstressed areas on the same metal. Most objects are made from alloys or mixtures of metals so chosen to provide the physical characteristics required of

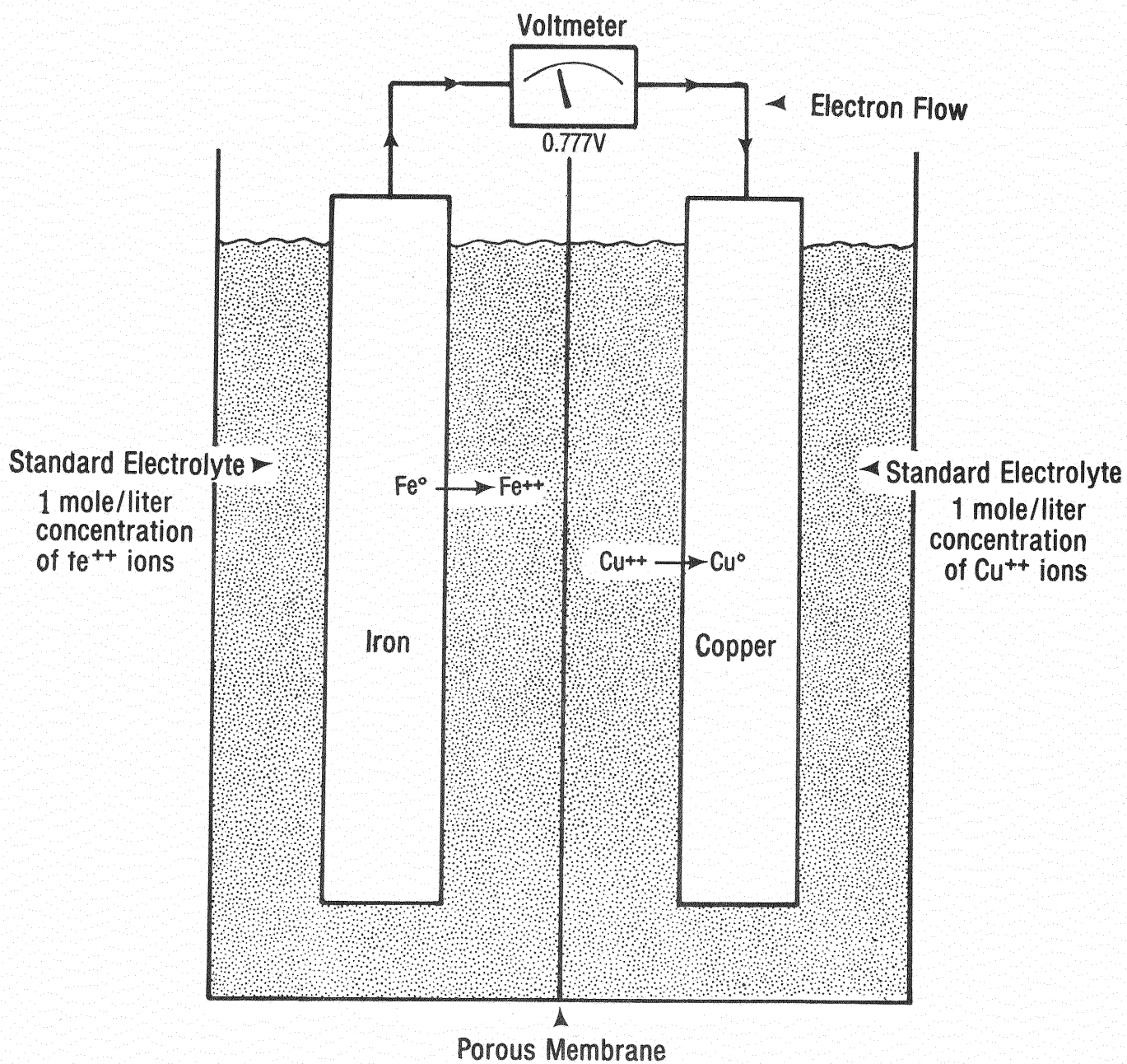


Figure A2

Standard Half-Cells of $\text{Cu}^{\circ} \rightarrow \text{Cu}^{++}$ and $\text{Fe}^{\circ} \rightarrow \text{Fe}^{++}$ Forming a Galvanic Cell

that object. This non-homogeneity quite naturally gives rise to galvanic corrosion cells. As an example of this type of cell, steel pieces are microscopically composed of grains of relatively homogeneous ferrite surrounded by grain boundaries containing ferric carbide, sulphur, and other constituents that give rise to microscopic galvanic cells in the presence of an electrolyte. These are but some of the ways galvanic coupling is accomplished on the surface of only one or like metals.

Electrolytic Cell

The second form of corrosion cell is the electrolytic or differential concentration cell. As pointed out in the discussion of the EMF series, connecting any two metal half-cells together that possess different cell potentials will theoretically create a corrosion cell. With dissimilar metals and their characteristic half-cell potentials, their connection in galvanic cells and resultant corrosion is relatively easy to understand. Differential concentration cells are little less straightforward. In the development of the EMF series the relative ranking of the various metals is dependent upon their standard half-cell potential. It was found that this potential varied widely with different electrolytes; therefore, the standard electrolyte was established. This standard electrolyte has an ionic concentration of one molecular weight per liter of the oxidized species of the metal electrode in question. For instance the $\text{Fe}^0 \rightarrow \text{Fe}^{++}$ standard half-cell electrolyte contains one mole per liter Fe^{++} ions. The $\text{Cu}^0 \rightarrow \text{Cu}^{++}$ half-cell electrolyte contains one mole per liter Cu^{++} ion and so on. The change in half-cell potential, with varying ionic concentration of the oxidized metal in the electrolyte, can be determined by the Nernst equation.

$$E = E_0 + 2.3 \frac{RT}{nF} \log \frac{a_{\text{oxid}}}{a_{\text{red}}}$$

where: E is the actual half-cell potential, E_0 is the standard half-cell potential from the EMF series, R is the gas constant, T is absolute temperature, n is the number of electrons transferred, F is the Faraday constant and a_{oxid} and a_{red} are the activities (concentrations) of oxidized and reduced species of the metal. In

essence what the Nernst equation states is that the electrode potential of a metal is directly proportional to the Logarithm of the concentration of the ions of the metal in the surrounding electrolyte. Virtually any change in the electrolyte will modify the half-cell potential either by altering the concentration or the solubility of the metal ions in solution, or the concentration or solubility of other critical constituents such as oxygen.

In general, the electrolytes such as soils, concrete, sea water, etc., are much less homogeneous than the metals themselves. Therefore, one would expect to find a great deal of corrosion caused by the potential differences created between differential concentration cells on the surfaces of these metals. Differential concentrations of dissolved and suspended constituents of all types create differential concentration cells, but among the most common of these constituents are oxygen, metal ions, oxidizing agents, hydrogen ion, and certain depassivating agents such as the chloride ion.

Corrosion of Reinforcing Steel

Passivation is a peculiarity of some metals that permits them under certain circumstances to resist corrosion. Iron and many of its alloys are passivated in highly alkaline environments. Concrete has the required high alkalinity for passivating steel, generally possessing a pH between 12 and 13. Although reinforcing is passive in sound uncontaminated concrete, with the addition of sufficient quantities of chloride salts it becomes active. It is believed as little as .04 percent chloride based on the weight of concrete can initiate corrosion in reinforcing. Researchers^{18,19} have found that when imbedded steel changes from a passive to an active state that its half-cell potential takes a large negative jump. Normally passivated reinforcing steel will have a half-cell potential of 100 to 250 mV negative to the Cu/CuSO_4 electrode. However when passivation is destroyed the potential climbs above 300 mV and may exceed 600 mV.

It is this potential difference that provides the driving voltage for an electrolytic cell. An electrolytic cell with the anode being a depassivated area of

rebar and the cathode being a still passive, or more properly, less active area. See Figure A-3. Cathodic protection can prevent corrosion of such a cell by opposing the flow of anodic current with a stronger anode such as aluminum, zinc, magnesium, or through the utilization of D.C. current. In this way the reinforcing becomes a cathode to a more active anode and, as pointed out, oxidation cannot take place at a cathode. Figure A-4 is a schematic of a typical impressed current cathodic protection system.

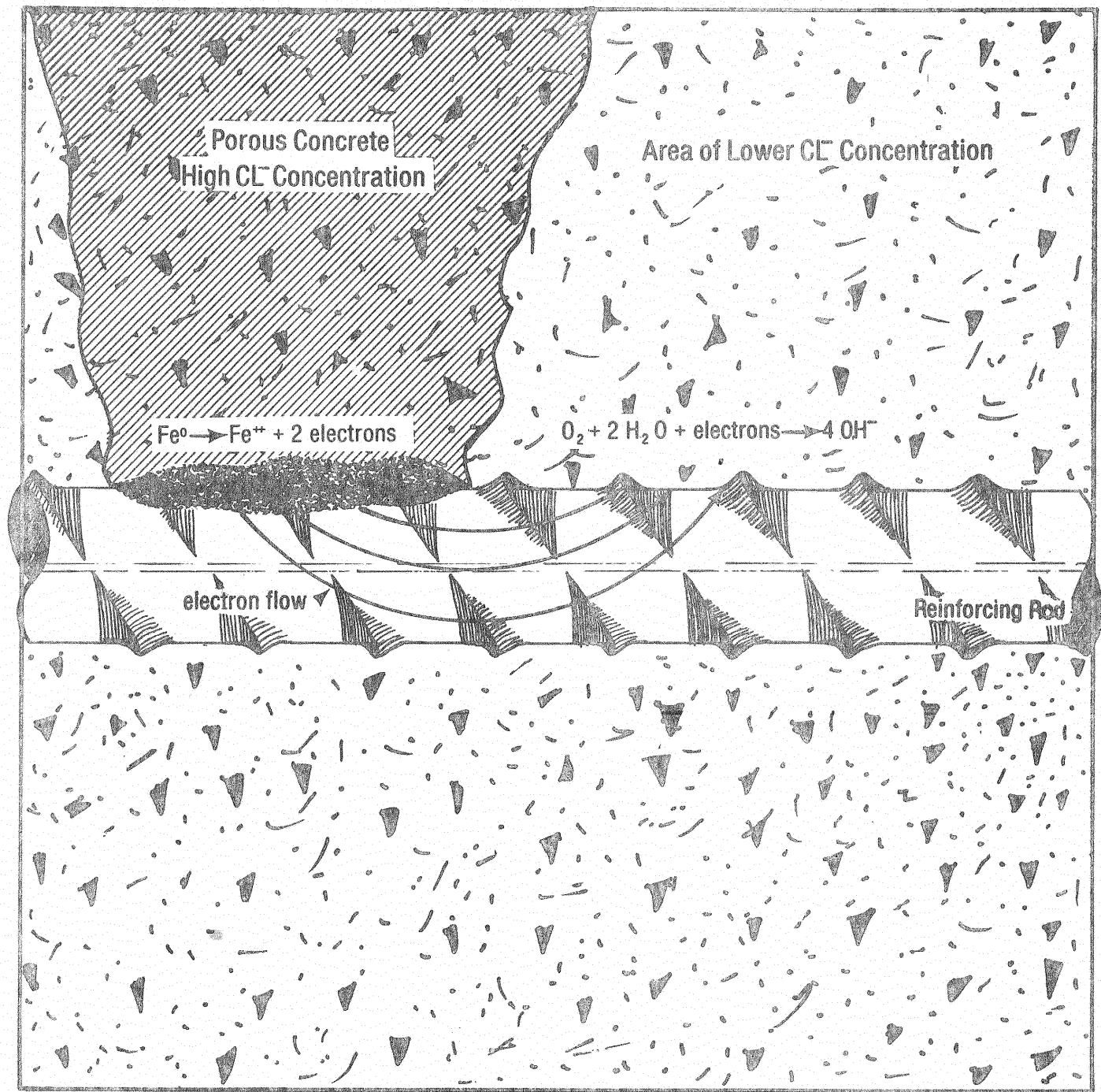
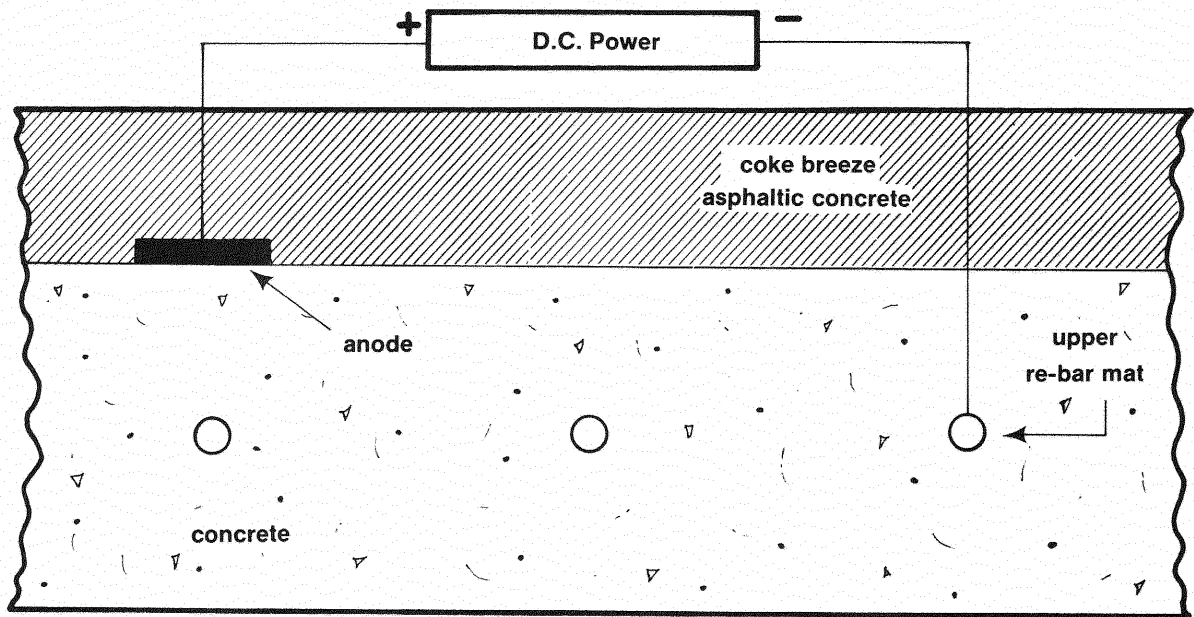


Figure A3

Reinforcing Steel in Concrete Containing unequal concentrations of Chloride ion



Conventional Cathodic Protection Configuration for Reinforced Concrete Bridge Decks

Figure A4

