

positions within the chamber may be regarded as essentially identical.

3. The repeatability or accuracy of results between runs appeared to require the use of control systems to reduce the variability. With an effective control technique, the run-to-run variation could approach the within-runs limits.

4. The correlation with the Brunswick 45° south sea-coast test-fence results was generally good, but sufficient distinct differences in correlation curves were observed among different paint systems to make the use of control systems advantageous for the detection and computation of nonlinear correlations.

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Measurement of Polarized Potentials in Concrete Bridge Decks

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An investigation was conducted to determine the best method of measuring the polarized potential of the reinforcing steel in a cathodically protected bridge deck. The use of carbon rods and copper-copper sulfate and zinc-zinc sulfate half-cells as probes was studied in laboratory

slabs and bridge decks. The carbon probes were found to be more accurate and reliable; the half-cells produced variable results. The coke layer was found to act as a half-cell and its voltage had to be taken into account when measuring the polarized potentials in the deck.

The application of cathodic protection to concrete bridge decks to mitigate the corrosion of the reinforcing steel has been shown to be successful by the work of Stratfull (1, 2) and of Fromm and Wilson (3, 4). This type of application, however, requires careful control of the potential to which the reinforcing steel is lowered with reference to the copper-copper sulfate (Cu-CuSO_4) half-cell. For pipelines, the steel is protected if the potential is maintained at less than -0.85 V (5). For reinforcing steel in concrete, the potential must not be lower than -1.1 V . It has been claimed by Scott and Hausmann (6, 7) that potentials lower than -1.1 V can cause disbonding of the steel. It is thus necessary to be able to measure and control accurately the potentials induced on the reinforcing steel.

Stratfull (2) has measured these potentials by placing a Cu-CuSO_4 half-cell on the nonconducting asphalt concrete surfacing and soaking the surfacing with a detergent solution to obtain conduction. Fromm (3, 4) has made use of the unused anodes in the conductive layer or placed special carbon probes in the conductive layer to sense the potential, which was then measured at the junction box. Others have tried to sense the potential in a deck by using half-cells cast in the upper surface of the concrete, but the results were confusing and could not be interpreted.

The purpose of this investigation was to test the method of using carbon probes and to further investigate the use of half-cells as probes and controls for the rectifier.

SURFACE MEASUREMENT OF POTENTIAL

Three types of probes have been used by the Ontario Ministry of Transportation and Communications to measure the potentials in bridge decks. On the first two bridges tested (3, 4), high-silicon-content cast-iron anodes were used to sense the potentials. Each anode was connected to the junction box by a separate wire so that each area could be measured separately. On the next two bridges (3, 4), carbon rods set in the coke layer were used to measure the potentials. Since that time, square graphite rods, $50 \times 50 \times 150\text{ mm}$ ($2 \times 2 \times 6\text{ in}$) long, have been used to measure the potentials. These graphite probes were embedded in the deck with only the surface of the probe in contact with the coke. In all cases, the potentials were measured at the junction box to which the probes were connected by separate wires.

The potential measurements made by using the anodes and the carbon probes described above are reported as being similar to those obtained by using a Cu-CuSO_4 half-cell. Typical data are given in Table 1 (the sign given before the voltage is that conventionally used in

corrosion measurements and refers to the saturated Cu-CuSO_4 half-cell). This table shows the measurements made on bridge 9, the first bridge to be protected. The anodes were spaced along the length of the deck, 3.66 m (12 ft) apart. Next to each anode, a hole 63 mm (2.5 in) in diameter was cored through the surfacing to bare the concrete deck, and a Cu-CuSO_4 half-cell was placed on the concrete in each of the holes. The difference between the mean anode voltage and the mean Cu-CuSO_4 half-cell voltage for the power-on columns is 0.16 V and that for the power-off columns is also 0.16 V . This identical difference suggests that some other factor (such as a voltage contribution due to the coke) may be involved.

DETERMINATION OF COKE POTENTIAL

Coke similar to that used for the conductive mix on bridge 9 was obtained, placed in a glass beaker, and moistened with 1N hydrochloric acid. A platinum connector was immersed in the coke. A Cu-CuSO_4 half-cell was then pressed onto the coke, and the voltage between the coke and the Cu-CuSO_4 cell was measured by using a $100\text{-M}\Omega$ impedance voltmeter. This procedure was repeated using a zinc-zinc sulfate (Zn-ZnSO_4) half-cell and finally using a saturated calomel electrode. The results obtained are given below:

Electrolytic Cell	Potential (V)
Coke- $\text{H}^+ \parallel \text{Cu}^+-\text{CuSO}_4$	0.31
Coke- $\text{H}^+ \parallel \text{Zn}^{2+}-\text{ZnSO}_4$	1.43
Coke- $\text{H}^+ \parallel$ Saturated calomel	0.44

The half-cell potentials for the above half-cells referenced to the standard hydrogen electrode (8) are given below:

Half-Cell	Potential (V)
$\text{Cu}^+-\text{CuSO}_4$	+0.3402
$\text{Zn}^{2+}-\text{ZnSO}_4$	-0.7628
Saturated calomel	+0.2415

Thus, the half-cell potential of the Coke- H^+ was

According to	Potential (V)
Cu-CuSO_4 half-cell	+0.65
Zn-ZnSO_4 half-cell	+0.67
Calomel electrode	+0.68
Mean	+0.67

If 1N sodium chloride solution is substituted for the 1N acid, the results are almost identical.

If only tap water is used to moisten the coke, the average carbon potential obtained by using the same techniques is 0.44 V .

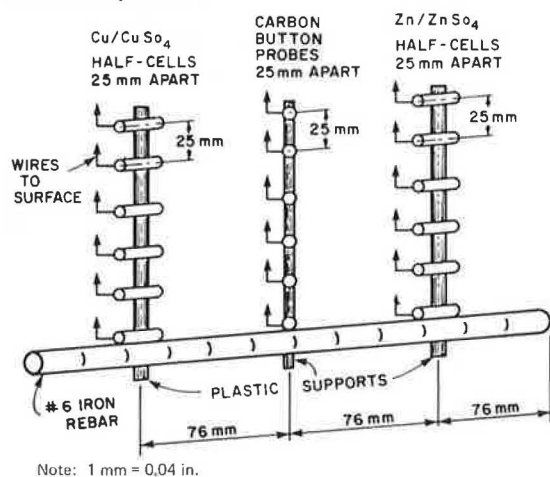
This carbon potential thus explains the higher potentials obtained when the anodes are buried in the coke compared with those obtained by using the Cu-CuSO_4 half-cell on the concrete deck. The results shown in Table 1 suggest an average carbon potential of $+0.50\text{ V}$. This value is reasonable because the readings were taken during the summer when most of the winter salt would have been flushed out of the coke layer.

When the Cu-CuSO_4 half-cell was placed in contact with the top of the coke layer on the bridge deck to read the polarization of the deck, a somewhat higher potential was obtained. Higher, that is, than if the cell had been placed directly on the concrete deck surface. This potential varied between 0.10 and 0.16 V and was due to the contribution of the coke layer.

Table 1. Comparison of voltage measurement methods: bridge 9.

Anode No.	Anode Potential (V)		Cu-CuSO ₄ Half-Cell Potential (V)	
	Power On	Power Off	Power On	Power Off
1	-0.68	-0.67	-0.56	-0.56
4	-0.70	-0.70	-0.52	-0.52
6	-0.72	-0.71	-0.57	-0.56
9	-0.76	-0.75	-0.60	-0.59
11	-0.78	-0.77	-0.58	-0.58
14	-0.80	-0.79	-0.64	-0.63
16	-0.83	-0.82	-0.67	-0.65
19	-0.87	-0.85	-0.72	-0.69
21	-0.93	-0.86	-0.82	-0.73
Avg	-0.79	-0.77	-0.63	-0.61

Figure 1. Arrangement of half-cells and carbon probes on rebar: test specimen 1.



MEASUREMENT OF BRIDGE-DECK POTENTIALS BY USING HALF-CELLS

Half-cells for measuring rebar potentials were buried below the surface of the concrete in four bridge decks. Two types of cells were used—Zn-ZnSO₄ and Cu-CuSO₄. The potential readings obtained by using these half-cells were difficult to interpret and did not correlate with the potentials sensed in the coke layer by electrodes or by carbon probes.

Examples from two bridge decks that illustrate this problem are given below.

Bridge	Potential (V)		
	Carbon Probe in Coke	Cu-CuSO ₄ in Deck	Zn-ZnSO ₄ in Deck
Medway Creek	-1.15	-0.86	+0.62
Paint Lake (1)	-0.95	-0.46	+0.45
Paint Lake (2)	-0.95	-0.36	+0.51

To more fully understand the meaning of the voltage readings and the variation of the readings, some concrete specimens containing half-cells and carbon probes were cast in the laboratory.

Test Specimen 1

Test specimen 1 was a block of concrete 300×300×184 mm (12×12×7.25 in) high that had a no. 6 rebar cast into it 25 mm (1 in) above the bottom. A series of Cu-CuSO₄ half-cells, a series of Zn-ZnSO₄ half-cells, and a series of carbon button probes (slices of a dry-cell carbon electrode) were arranged on plastic supports rising vertically from the bar to the top of the block. This arrangement is shown in Figure 1.

Before the block was cast, the rebar was covered with a thin coating of grout, which was allowed to dry. The first cell of each of the three series was placed in contact with the grout (thus being set very close to the rebar). The remaining five cells in each series were arranged above this bottom cell, 25 mm apart. The top cell in each series was just below the top surface of the block. The carbon-probe series was positioned between the Cu-CuSO₄ and the Zn-ZnSO₄ half-cells. Each series was separated from the adjoining one by 76 mm (3 in) on centers and each was 76 mm in from the sides of the block. The top of the block was covered with coke breeze and power was applied to the block by connecting the coke to the positive terminal of a rectifier and the

rebar to the negative terminal.

The cells in each series were numbered consecutively, no. 1 being closest to the rebar and no. 6 being at the top of the block.

After the block had cured, a 1.5-V DC potential was applied between the coke covering the block and the rebar. After a few days, some of the cells and carbon probes were found to be giving potential readings different from the others. The power was turned off, and the block was allowed to discharge until there was no further change in cell readings. (Before the block was made, all half-cells had been tested and found to produce acceptable half-cell voltages).

When the potential readings were taken at equilibrium between the rebar and the half-cells and carbon probes, it was found that the no. 1 carbon probe had shorted to the rebar and was therefore useless, and that one carbon probe, one Cu-CuSO₄ half-cell, and two Zn-ZnSO₄ half-cells were producing different readings. Correction factors for these were computed so that their readings could be used with the others.

Because all cells had been tested before use, it is thought that the differences may have been due to small local differences in composition of the concrete. This does point out, however, that caution must be exercised when relying on half-cells to control the potential in a bridge deck and that backup cells should be installed.

After the half-cells in the block had been calibrated, a 1.0-V DC potential was applied to the block. The build-up of polarized voltage in the block was monitored daily by taking potential readings between each half-cell lead and the rebar and a Cu-CuSO₄ half-cell reading between the surface coke and the rebar. The readings were taken with the applied DC current turned off. On the sixteenth day, the applied voltage was increased to 1.5 V and maintained at this level to the end of the test. The results obtained are shown in Figure 2.

The specimen potential measured by a Cu-CuSO₄ half-cell on the surface coke is shown in the lower curve of Figure 2. The next curve shows the average potential indicated by the six internal Cu-CuSO₄ half-cells. The middle curve is the mean potential of the carbon probes and the top curve is the mean potential of the Zn-ZnSO₄ half-cells.

The first portion of these curves shows the equilibrium potential as indicated by the four methods of measurement. The specimen had previously been polarized and then the current was removed and it was allowed to settle to the condition as shown. On the seventh day, a 1.0-V potential was applied. At first, the polarization overshoot the new equilibrium value by about 0.1 V. Equilibrium was achieved on the twelfth day and was held until the sixteenth day. The applied voltage was then increased to 1.5 V and, here again, there was a small overshoot before equilibrium was achieved. In the case of the polarized potential indicated by the Zn-ZnSO₄ half-cells, there was a continued slow decrease in value.

The polarization indicated by the Cu-CuSO₄ half-cell on the surface of the coke was lower than that indicated by the upper Cu-CuSO₄ half-cells in the block. This was due to the half-cell effect of the coke layer.

The mean voltages for the half-cells and probes at equilibrium are given in Table 2, and the results are shown in Figures 3, 4, and 5.

Figure 3 shows the potential gradient that existed within the block when power was applied at both 1 and 1.5 V as indicated by the Cu-CuSO₄ half-cells. A definite potential gradient existed within the block, decreasing as the rebar was approached. The polarized potential measured by the Cu-CuSO₄ cells throughout the block was the same because no current was being ap-

Figure 2. Change of polarized voltage in test specimen with time.

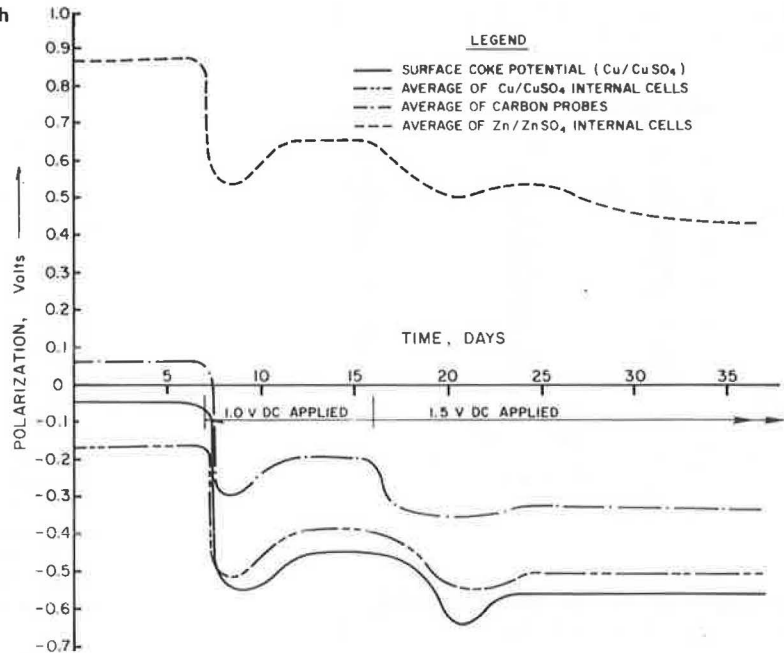


Table 2. Mean polarized potentials in test specimen 1.

Type of Cell	Cell No. ^a	Applied Potential (V)			
		1.0 V		1.5 V	
		Power On	Power Off	Power On	Power Off
Cu-CuSO ₄	1	-0.42	-0.40	-0.58	-0.52
	2	-0.51	-0.43	-0.78	-0.57
	3 ^b	-0.51	-0.40	-0.81	-0.53
	4	-0.55	-0.42	-0.90	-0.55
	5	-0.56	-0.40	-0.96	-0.55
	6	-0.56	-0.38	-1.00	-0.52
Zn-ZnSO ₄	1 ^b	+0.76	+0.78	+0.50	+0.56
	2	+0.57	+0.66	+0.29	+0.52
	3 ^b	+0.55	+0.68	- ^c	- ^d
	4	+0.54	+0.68	+0.19	+0.56
	5	+0.57	+0.73	+0.19	+0.60
	6	+0.58	+0.74	+0.16	+0.90
Carbon probe	1 ^d				
	2 ^b	-0.37	-0.19	-0.79	-0.32
	3	-0.34	-0.18	-0.76	-0.34
	4	-0.34	-0.23	-0.72	-0.35
	5	-0.35	-0.23	-0.68	-0.36
	6	-0.35	-0.25	-0.66	-0.40

^aNo. 1 cells located at the rebar and no. 6 cells located at the top of the specimen.

^bValues adjusted as per calibration.

^cHalf-cell failed.

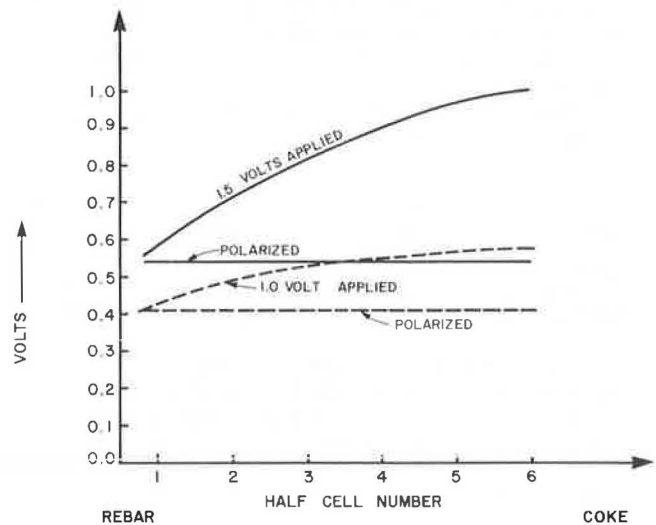
^dProbe shorted to rebar.

plied and no current was being drawn. The polarized potential is shown here as the meter reading and not with the sign reversed as is customary in corrosion measurements. This was done to better illustrate the potential gradient that existed when a positive voltage was applied to the surface. Figure 4 shows the same effect as indicated by the Zn-ZnSO₄ half-cells.

The carbon probes (Figure 5) behaved in a way that could not be explained. When power was applied at 1.0 V, they showed no gradient, and at 1.5 V, they showed a reverse gradient. They did, however, indicate the polarization level as expected.

The potential gradients shown in Figures 3 and 4 indicate that, as the amount of cover of concrete over the rebars increases, higher applied potentials will be necessary to attain the desired polarization voltage.

Figure 3. Applied and polarized potential gradients: Cu-CuSO₄ half-cells.



Relationship Between Voltages Indicated by Different Half-Cells

It is common practice to determine the polarized potential on pipelines and bridge decks by using the Cu-CuSO₄ half-cell. The maximum and minimum limits placed on the polarized potential for bridge decks have always been stated as volts negative to this half-cell. When other cells are used to sense the polarized potential in the deck, it is necessary to change the values thus obtained to values in terms of the Cu-CuSO₄ cell. It is also normal practice to connect the measuring half-cell to the positive terminal of the voltmeter and to report the voltage as positive or negative with regard to this alignment.

The relationship between the Cu-CuSO₄ voltage and the other half-cell voltages is the following:

$$V_{Cu(R)} - V_{X(R)} = V_{Cu(M)} - V_{X(M)} \quad (1)$$

where

- $V_{Cu(R)}$ = Cu-CuSO₄ equilibrium reduction potential (+0.34 V),
 $V_{X(R)}$ = equilibrium reduction potential of half-cell in question,
 $V_{Cu(M)}$ = polarized potential of the slab as measured by the Cu-CuSO₄ half-cell, and
 $V_{X(M)}$ = polarized potential of the slab as measured by the half-cell in question.

Equation 1 can be rearranged as follows:

$$[V_{Cu(R)} - V_{X(R)}] + V_{X(M)} = V_{Cu(M)} \quad (2)$$

which gives the voltage that a Cu-CuSO₄ half-cell would read if used in place of the half-cell in question.

This method was tested on the polarized-potential results obtained from test specimen 1; the procedure is illustrated below.

Item	Applied Potential (V)	
	1.00	1.50
1. Cu-CuSO ₄ cell	0.41	0.54
2. Zn-ZnSO ₄ cell	-0.69	-0.57
3. Carbon probe	0.22	0.35
Item 1 - item 3	0.19	0.19
Item 1 - item 2	1.10	1.11
Item 2 - item 3	-0.91	-0.92

Figure 4. Applied and polarized potential gradients: Zn-ZnSO₄ half-cells.

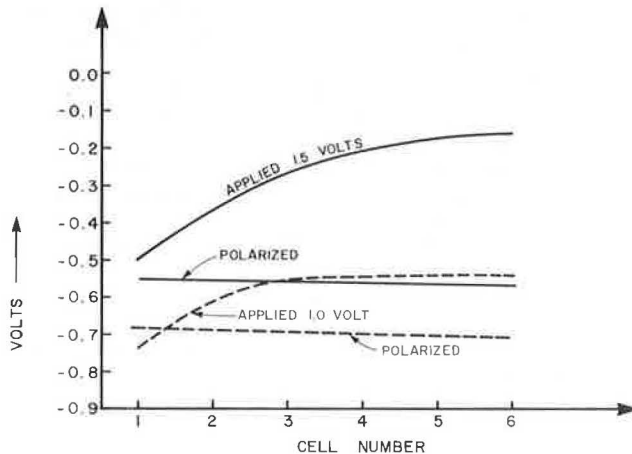
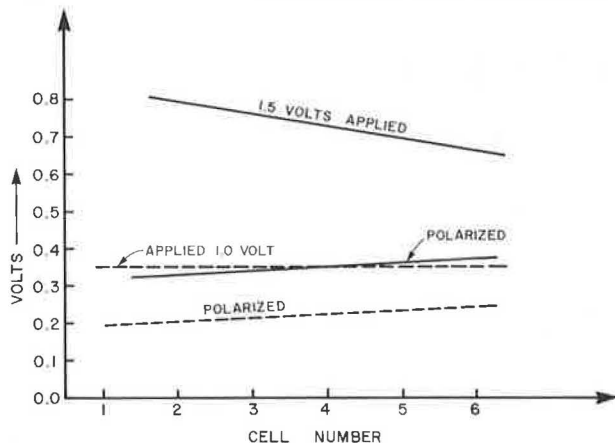


Figure 5. Applied and polarized potential gradients: carbon probes.



(The signs used do not follow the usual corrosion convention for signs. Here the polarized potential is shown as +0.41 for the Cu-CuSO₄ half-cell. This is the value as read on the meter. These values were used to be consistent with the standard half-cell-reduction potential values.) By using the half-cell potentials, we have

$$V_{Cu(R)} - V_{Zn(R)} = 0.34 + 0.76 = 1.10 \text{ V} \quad (1a)$$

and the Zn-ZnSO₄ half-cell reading of -0.69 V can be converted to the equivalent Cu-CuSO₄ half-cell reading by using Equation 2.

$$1.10 \text{ V} + (-0.69) = 0.41 \text{ V} \quad (2a)$$

This is the same value as that measured by the Cu-CuSO₄ half-cell (see table above). Similarly, the Zn-ZnSO₄ half-cell value of -0.57 V is equivalent to 0.53 V for the corresponding Cu-CuSO₄ half-cell, which agreed with the measured value of 0.54 V within experimental error.

If a value shown in the table above for the Zn-ZnSO₄ is subtracted from the corresponding value for the Cu-CuSO₄ cell, the result should be the potential of the combined electrolytic cell. These results (i.e., item 2 - item 1) are the same as the theoretical results for the Cu-Zn cell couple, i.e., 1.10 V. Similarly, the differences between items 1 and 3 and between items 2 and 3 of the table above can be used to estimate the potential of the carbon half-cell. The half-cell potential calculates to be 0.15 V. The result is considerably lower than the value reported in the first part of this paper for carbon in a solution of ions of unit activity. In the reinforced concrete slab, the carbon probe is surrounded by concrete that contains a saturated solution of calcium hydroxide (which is a weak electrolyte). This could account for the much lower potential.

The procedure shown above can be used to convert the potential shown by any half-cell, such as the Ag-AgCl half-cell, to a value in terms of the Cu-CuSO₄ half-cell. After the calculation is made, the sign for the equivalent Cu-CuSO₄ half-cell must be reversed to conform to the conventional notation.

Cu-CuSO₄ and Zn-ZnSO₄ half-cells were placed in four bridge decks in slits cut in the deck and covered so that they were about 25 mm below the surface. For the most part, these cells produced readings that did not agree with those given by voltage probes distributed throughout the coke layer. Similar half-cells were used to control the potential-controlled rectifiers used on these bridges. The rectifiers were adjusted to produce the desired voltage as sensed in the coke layer by the probes. The actual readings of the half-cells were disregarded. The curves shown in Figure 2 and the data given in Table 2 confirm the validity of this approach. The data for only one test specimen are reported here. Several other specimens have been made and tested in the laboratory; the results have been the similar.

DISCUSSION OF RESULTS

The results of this investigation have shown that an acceptable way to monitor the potential in a cathodically protected bridge deck is to use voltage probes in the coke layer. This investigation has also shown that the coke and electrolyte act as a half-cell and that its potential must be taken into account when evaluating results. Experience has shown that the voltage sensed in the coke is 0.1 to 0.16 V higher than that sensed by a Cu-CuSO₄ half-cell on the concrete deck surface. Therefore, the minimum and maximum limits for the degree of polarization required to give protection to the bridge deck steel

must be changed accordingly. It was found (3) that corrosion did not begin to occur in a bridge deck until the polarized voltage had dropped to -0.55 V, which shows that the recommended -0.85 -V minimum (5) has a considerable margin of safety built into it. As a result, the minimum and maximum polarized voltages sensed by carbon probes in the coke layer are recommended as -0.80 and -1.25 V. These values still contain a safety factor.

Half-cells buried in concrete are subject to failure or erratic behavior. This was shown in test specimen 1 in which the failure rate was quite high. Similarly, in bridge decks, these cells showed variable results. The reason for this behavior is not known.

Some results have been obtained from the bridges treated with cathodic protection that suggest that half-cells located close to rebars tend to give higher readings than those located farther away from the bars. This result may appear to contradict that obtained in the laboratory test specimen in which there was no potential gradient when, with no current being applied, the polarized potential was measured by several half-cells located at different distances from the bar. This may be explained by the fact that the laboratory specimen was electrically isolated and had no connection to ground, so that the polarized voltage could not leak off. In the case of a bridge deck, this is not the case. There is always some connection through the concrete and rebars to ground, so that the voltage can leak off, slowly or rapidly, and this will give rise to a potential gradient in the deck. This effect could also be the cause of lower polarized potentials that have been measured on the undersides of bridge decks.

The use of a carbon probe in the coke and in contact with the deck tends to average the potential and removes the effect of the distance from a rebar. This averaging effect is not found when a half-cell is buried in the concrete; this cell reads only the potential at that point. Thus, the carbon probe in the coke is the preferred way to determine the polarized potential.

The amount of power required to protect a bridge deck will vary with the amount of cover over the rebars and the electrical leakage from the deck. Higher amounts of cover will require a higher applied voltage.

CONCLUSIONS

1. Carbon probes located in the coke layer and in

contact with the deck provide a good method of measuring the polarized potential on the reinforcing steel.

2. The moist coke layer acts as a half-cell and its voltage must be taken into account when measuring the polarized potential of deck rebars.

3. The recommended range of polarized potential to provide protection to the reinforcing steel is -0.80 to -1.25 V, when read by carbon probes located in the coke layer and in contact with the concrete deck.

4. Half-cells buried in the deck and used as voltage probes produce variable results and should be used cautiously.

5. Various types of half-cells can be used to control the potential-controlled rectifiers on bridges. Here the rectifier must be set, not on the theoretical value of the half-cell, but to the calibration that will provide the desired potential on the deck steel.

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Methods of Determining Corrosion Susceptibility of Steel in Concrete

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Several test methods were used to study the effectiveness of calcium nitrite as a corrosion inhibitor in concrete. Measurements of open-circuit potential and of polarization in concrete were found to be useful, provided the steel area studied was completely covered by concrete. Tests in which limewater was used as a substitute for concrete yielded similar results. Induced electrolysis was found to be misleading because of other reactions that occurred. Tests on large slabs [$1.8 \times 0.6 \times 0.15$ m (6×2

$\times 0.5$ ft)] that were salted daily showed that calcium nitrite reduced the corrosion susceptibility more than fourfold.

Corrosion is an electrochemical phenomenon (1). An oxide coating does not form on iron in a dry atmosphere.