Embedded Reference Cells for Use in Cathodically Protected Concrete

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Reference cells are needed to measure the potential of embedded steel in cathodically protected, reinforced concrete members to ensure that the level of protection is neither too high nor too low. Embedded cells are more convenient than surface cells where access to the protected surface of the structure is difficult, and they are essential when potential-controlled rectifiers or remote monitoring systems are being used. This paper reports the results of a series of laboratory, outdoor exposure plot, and field tests to evaluate the suitability of candidate embedded reference cells for use in reinforced concrete. Zinc-zinc sulfate, silver-silver chloride, molybdenum-molybdenum oxide, lead-lead oxide cells, and graphite electrodes were evaluated. The graphite electrodes were found to be the most stable with time and the least influenced by changes in temperature or the chloride content of the concrete. They were also inexpensive. The only other cell considered suitable for embedment in concrete was a silver-silver chloride cell, although this type of cell was more affected by temperature and chloride content than was graphite. Large performance variations occurred in some cells of the same type from different sources.

A reference cell is an electrode of known electrical potential that can be used to measure the potential of embedded steel. When the steel is under cathodic protection, an accurate measurement of its potential is necessary to ensure that it is neither underprotected nor overprotected. Protection criteria may be based on absolute potential measurements or on shifts in potential with time. For exposed concrete surfaces, a surface electrode, such as the copper-copper sulfate cell (CSE), which has become the standard reference cell used on highway structures, can be used to measure potentials at different points on the structure. On decks, however, traffic control is usually required, and on substructure components, access is often difficult. Further, so that the cell potential is not influenced by its proximity to the anode, portions of the anode may have to be removed to expose the concrete surface, or the reference cell must be inserted in holes either drilled or cast into the surface of the structure. In view of the cost and practical difficulties of making surface measurements, embedded cells are more convenient. In some cases, such as in systems equipped with potential-controlled rectifiers or remote-monitoring capabilities, they are essential.

Unfortunately, the standard copper-copper sulfate electrode is unsuitable for embedding in concrete (because of leakage and damage by freezing), and a reliable embedded reference cell is needed. This paper reports data collected by the Ontario Ministry of Transportation on several types of reference cells in both the laboratory and the field over a period of about 10 years. Some of the laboratory experiments were designed to examine specific characteristics of selected reference cells. Much of the field data was collected in conjunction with ongoing efforts to monitor the performance of cathodically protected, reinforced concrete highway structures, although some installations included several types of reference cells for the specific purpose of examining the performance of the reference cells under field conditions.

It can be argued that effective cathodic protection systems that do not include reference cells can be constructed. Such an approach is consistent with attempts to reduce costs and simplify cathodic protection systems to increase their use by highway agencies. Eliminating reference cells is premature, however; and even if it were feasible, it would compromise the ability to monitor installations to ensure both effectiveness and efficiency of the cathodic protection with time. The current required to cathodically protect a reinforced concrete component is determined largely by the amount of steel receiving current and by two factors that vary with changes in environmental conditions and with time: the corrosion rate and the circuit resistance. An arbitrary protective current that is effective and does not result in overprotection, especially in complex or unusual structures where it may be difficult to determine the amount of steel receiving current, has not yet been defined. Eliminating reference cells prevents monitoring potential variation in the structure or the effect of seasonal changes (unless a survey is made with a surface cell). Further, experience with existing installations has shown that current demands decrease with time. The use of an arbitrary constant current could result, at worst, in overprotection or, at best, in reduced anode life and inefficient power use.

REQUIREMENTS AND TYPES OF REFERENCE CELLS

The requirements for a good reference electrode have been defined as follows (*1*):

1. It should be reversible and follow the Nernst equation with respect to one reacting species.
2. It should have a stable potential with time.
3. The potential should return to the reversible value after small currents are passed through the electrolyte.
4. It should remain at a constant potential in spite of temperature changes.

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5. It should not introduce any species into the system that cause adverse effects.

In addition, embedded reference cells for use in reinforced concrete highway structures need to be rugged enough to be installed by a contractor and inexpensive. A disadvantage of embedded cells, compared with surface measurements, is that they measure the potential of the steel only at the position of installation. If the cells are inexpensive, however, this disadvantage can be reduced by installing several cells at different positions in the structure.

It is convenient to divide the types of reference cells available into three types:

- Metals surrounded by an ion-rich backfill (e.g., zinc-zinc sulfate and silver-silver chloride);
- Metals with an oxide film (e.g., molybdenum and lead); and
- Solid electrodes that behave like a cell when in contact with concrete (e.g., graphite).

All cells discussed in this paper are installed in the same manner. First, sufficient concrete is removed from the structure to allow the cell to be placed adjacent to a reinforcing bar, parallel and at the same depth. A minimum of concrete is removed, avoiding disturbance of the concrete immediately surrounding the steel. Once the cell is in place, the cavity walls are dampened and the cavity is hard-packed with concrete.

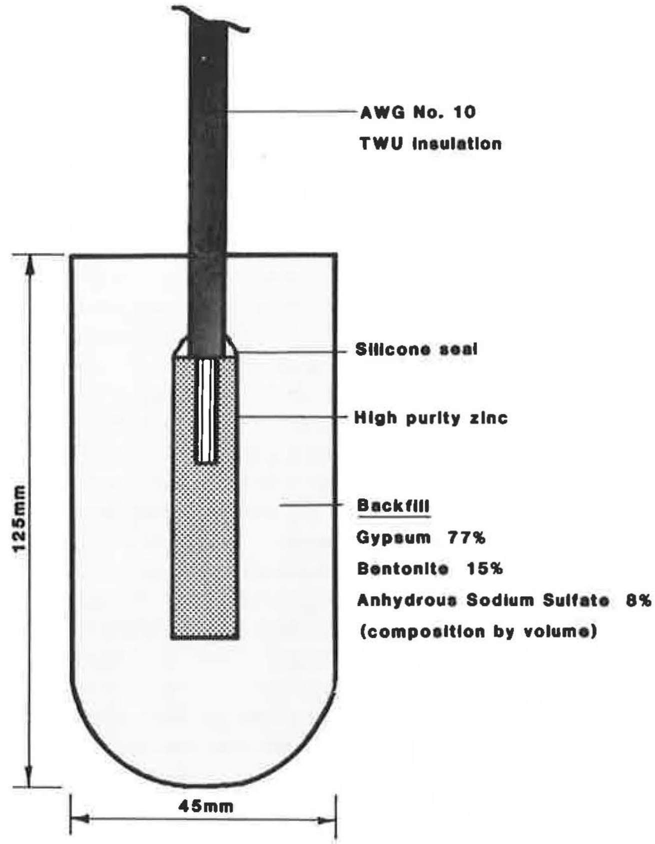

FIGURE 1 A zinc-zinc sulfate reference cell.

EARLY BRIDGE DECK CATHODIC PROTECTION SYSTEMS

The Ministry's first installation of cathodic protection on a bridge deck occurred in 1974, when three decks were protected (*2*). The system used a coke-asphalt anode. The experience gained from the early installations led to the system based on conductive bituminous concrete that the Ministry adopted as a standard rehabilitation procedure in 1978; it is still used today (*3*).

The early installations included zinc-zinc sulfate reference cells, as shown in Figure 1 and made in-house. The original intention was for the rectifiers to operate under potential control. A minimum of three cells were installed in each deck. The cells were used to sense the variation in potential over the deck. The most suitable cell would be chosen to control the rectifier, and the remaining two would act as spares to provide redundancy if the first cell should fail. Experience showed that the zinc-zinc sulfate cells could not be used to control the rectifiers because they were not sufficiently stable with time. In particular, their response to shifts in potential decreased with time and became erratic in cold weather.

Graphite voltage probes were also included in the early installations. The probes were embedded in the concrete flush with the deck surface and in contact with the anode. They were used to measure the anode voltage at several locations on the deck surface to ensure an even distribution of voltage. Comparisons were made between CSE measurements of the potential of the steel using a cell placed on the deck surface and voltage measurements on the probes (*4*). It was found that the graphite probes were stable and consistent; consequently, a graphite probe was used to control the rectifier. The remaining probes were used to ensure that the established protection criterion (an instant-off potential of between 0.80 V and 1.25 V measured on the voltage probe) was satisfied. The stability of the readings from the voltage probes led to the idea that graphite may be suitable for use as an embedded reference cell.

In 1986, an opportunity arose to examine the condition of zinc-zinc sulfate reference cells and graphite voltage probes after 10 years in service when joint repairs required the removal of the surfacing from a deck that had been cathodically protected in 1976 (*5*). The zinc-zinc sulfate cells had long since ceased to be useful because of instability, and the backfill was found to be deteriorated. In contrast, the graphite voltage probes showed no deterioration.

SUBSTRUCTURE CATHODIC PROTECTION FIELD TRIALS

Burlington Bay Skyway Test Site

Overall Observations

Four experimental cathodic protection systems were installed on the columns of the Burlington Bay Skyway Bridge in 1982, and four more were added in 1983. Several types of instrumentation, including a number of different reference cells,

were incorporated in the construction to monitor the effectiveness of the cathodic protection. Only zinc-zinc sulfate cells were used in 1982, but it was recognized that these were not entirely satisfactory (*6*). In 1983 a small number of molybdenum-molybdenum oxide (*7*), silver-silver chloride and lead-lead oxide cells, and graphite electrodes were installed in addition to the zinc-zinc sulfate cells. In the remainder of this paper, these cells are referred to as molybdenum, silver, lead, graphite, and zinc cells, respectively.

A paper based on data collected through July 1984 (*8*) noted that considerable variation occurred in the performance of the five types of reference cells. The zinc cells showed large differences between the potentials measured on individual cells that would have been expected to give similar readings. Cells in both powered and unpowered areas shifted with time so that measurements of absolute potential values as a protection criterion were unreliable. Most of the zinc cells, however, were consistent and reliable for measuring short-term potential shifts to determine whether the individual systems satisfied criteria (−300 mV between static and instant-off potentials or −100 mV decay from instant-off potential within 4 hours) for effective protection. The molybdenum cells were more erratic than the zinc cells and became very unstable at temperatures below 5°C. The silver cells were also erratic during periods of low temperature. The graphite cells and the lead cells were more consistent over time and showed little variation with temperature or changes in the moisture condition of the concrete.

Additional data collected through October 1986 on one of the systems that contained all five types of cells confirmed the earlier findings. Except for the zinc cells, however, there was only one sample of each type of cell. Of the three zinc cells, two became unreliable after about 1 year; the third remained stable throughout the 3-year period of observation and consistently returned to essentially the same static potential reading during periods when the power was switched off.

Comparison of Embedded Cell Potentials with Potentials Measured by a Portable Cell

The same cathodic protection system was used to monitor the performance of the embedded reference cells in comparison with CSE cells placed directly above the embedded cells. The cathodic protection system consisted of a polymer mesh anode with a 40-mm-thick covering of shotcrete. Pieces of plastic tubing were anchored to the concrete surface prior to shotcreting so the portable cell could be placed in a "well" to the original concrete surface to eliminate the effect of the anode.

Comparative readings were made by recording the potential of the embedded cells relative to ground and then placing the portable cell in the well and measuring its potential relative to ground. Finally, the potential difference between the portable cell and the corresponding embedded cell was measured. A total of eight sets of readings were made during the 18-month period after construction. The readings were made when the power was switched off and when the system was operating. In the latter case, the power supply was interrupted momentarily so that the "instant-off" potentials were measured. Unfortunately, reconstruction of the bridge deck prevented the access to the test sites that was needed to take a complete set of readings on every occasion.

Table 1 lists the measured potential differences between each cell and the portable cell and the calculated standard deviation for each embedded cell for the periods when instant-off measurements were made. The graphite and lead cells showed the least variation with respect to the portable cell; and the silver cell exhibited large fluctuations, although very limited data are available. Figure 2 compares the potentials measured on the graphite cell and one of the zinc cells (which became unstable) with the potentials measured by the portable cell at the corresponding locations. The figure shows the relatively good agreement between the graphite cell and the portable cell.

TABLE 1 POTENTIAL OF EMBEDDED REFERENCE CELLS RELATIVE TO A PORTABLE COPPER-COPPER SULFATE CELL

Type of Embedded Cell	Potential Difference, Cell to CSE, mV Date and System Status						Standard Deviation of Potential Difference (mV)
	Apr. 25 1984 On	May 30 1984 On	Jun 12 1984 On	Jun 14 1984 On	Sep 07 1984 On	May 16 1985 On	
Zinc (1)	887	828	830	810	825	550	120
Zinc (2)	---	555	680	---	511	540	75
Zinc (3)	598	815	795	645	630	920	128
Graphite	76	148	125	155	91	190	42
Molybdenum	604	910	---	---	563	770	160
Silver	---	985	---	---	250	365	395
Lead	---	780	---	---	884	840	52

Notes:

1. --- indicates reading not taken because access to location of the cell restricted temporarily.

2. Negative voltmeter terminal connected to embedded cell.

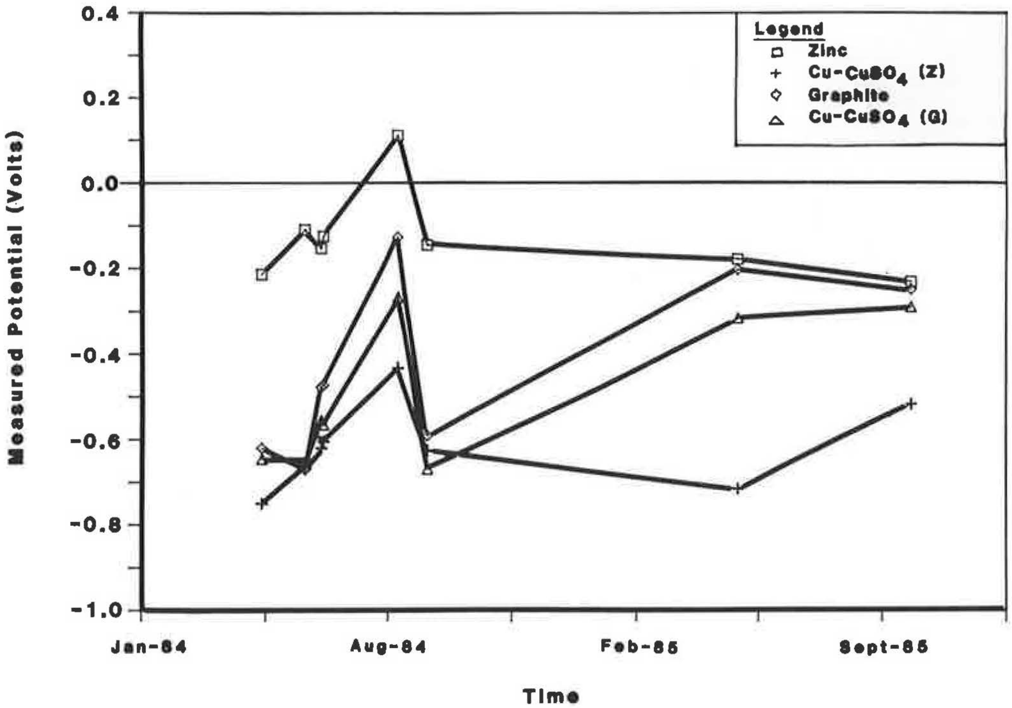

FIGURE 2 Comparison of embedded graphite and zinc cells with portable copper-copper sulfate cell under field conditions.

Although more complete field data comparing embedded cells and surface cells would be desirable, the procedure is time-consuming, especially where access is difficult, as in the case of high piers. Measurements are further complicated by the presence of a surface anode if wells are not provided to the original concrete surface.

Effect of Concrete Overcoat on Potential Measurements

Since many of the Ministry's substructure cathodic protection installations consist of a distributed anode with a concrete overcoat, readings were taken to investigate the validity of potential measurements made directly on the overcoat. The readings were taken by placing the portable CSE cell in the wells installed in the cathodic protection system already described, and then placing the cell on the shotcrete overcoat immediately adjacent to the well. Instant-off potentials were recorded on two occasions when the system was operating at normal power levels (typically 10 mA/m^2 of concrete surface) and on one occasion when the power was switched off.

The instant-off potentials measured on the shotcrete surface were from 150 mV to 200 mV more negative (i.e., indicating more protection) than the measurements in the tubes. With the power off, the surface measurements were an average of 60 mV more negative.

The measurements clearly demonstrate the influence of the anode on surface potential measurements. This effect is of particular concern when the performance of cathodic protection systems relative to an absolute potential criterion is being evaluated, but it is also important when criteria based on potential shifts are being used. Two important conclusions emerge from this test. First, the test confirms the need for a stable reference electrode that can be permanently embedded at the level of the steel. Second, it shows that where portable cells are used, direct access to the concrete in the immediate vicinity of the steel must be provided.

Measurement of AC Resistance of Cells

An additional means of evaluating the long-term stability of the reference cells is to measure the AC resistance between the cell and the reinforcing steel (often referred to as "ground") adjacent to it. While such resistance is influenced by changes in the temperature and moisture condition of the concrete, these effects are seasonal. Thus, any irreversible changes, such as deterioration of the cell backfill material or corrosion of the connecting wire, indicate changes in the reliability of the cell. Measurements were made over a 2-year period.

The graphite cell displayed the lowest resistance to ground and exhibited only a seasonal response over the 2-year period. One of the zinc cells and the lead cell also displayed a predictable response, although the resistance was higher than with the graphite cell, presumably because of the smaller size of the cells. The resistance of the silver cell was very high, especially in the winter months. The resistance of the molybdenum cell fluctuated considerably in a way that could not be predicted from changes in temperature.

Although additional data are required to establish a normal range of values for each type of cell, the AC resistance measurements are easy to make and are a useful supplement to potential measurements in determining whether a cell remains

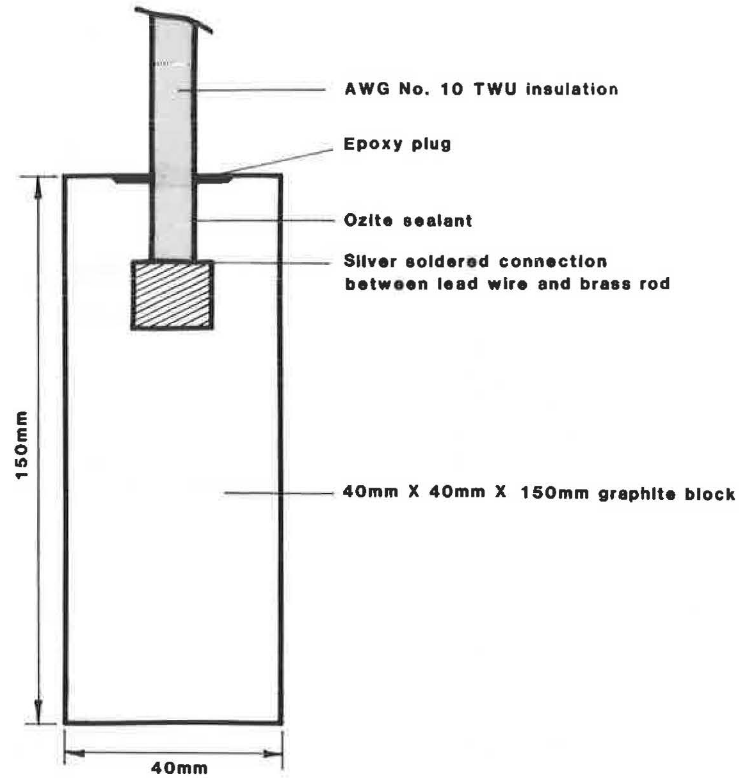

FIGURE 3 A graphite electrode.

stable. Such measurements have been made periodically on subsequent installations to define "normal" values for a stable cell.

Leslie Street Test Site

Two conductive coating systems, one using conductive paint and the other using flame-sprayed zinc, were installed on pier bents at the Leslie Street test site in 1984; a proprietary titanium mesh anode was installed in 1985 (*9*). Several types of reference cells were included in the instrumentation used to evaluate the three systems. Graphite probes, zinc, conductive polymer, and lead cells were fabricated by the Ministry, and silver cells were purchased from two commercial sources. Figure 3 illustrates schematically the graphite electrode. The cost varied considerably, ranging from $30 Canadian, which is the approximate commercial cost of the graphite cells, to $400 Canadian for the silver cells.

Initial results confirmed the findings made from measurements at the Burlington test site. The graphite cells and the lead cells were not only the most stable but also the least expensive. Although there was confidence that the graphite cells were consistent from batch to batch, this was not necessarily the case for the lead cells because of the lack of good quality-control procedures. The conductive polymer cell became unstable soon after installation and was of no further use. Mixed results were obtained from the zinc cells; some showed evidence of deterioration, while others remained stable. The silver cells became unstable at temperatures below 5°C and also had the disadvantage of high cost. In view of the deterioration of the backfill in the zinc cells used at other sites, concern existed about the long-term durability of the backfill used with the silver cells. This could not be evaluated, however, because deterioration of one of the cathodic protection systems precluded a thorough assessment of the instrumentation. A decision was made to augment field experience by testing selected cells under more controlled conditions.

TESTING UNDER CONTROLLED CONDITIONS

Laboratory and exposure plot studies of the performance of reference cells were carried out by Ministry staff and, through a research contract, under exposure plot conditions at a facility in Virginia.

Ministry of Transportation Tests

Exposure Plot Testing

Tests were performed between 1984 and 1986 using small concrete specimens containing embedded reference cells, which were exposed first under laboratory conditions and later in an outdoor environment. Four types of reference cells were fabricated in the Ministry's laboratories (graphite, lead, molybdenum, and zinc); molybdenum cells were also purchased commercially. Two cells of each type were included in the study.

The cells were placed adjacent to reinforcing bars cast in the specimens, as illustrated in Figure 4. Wells were con-

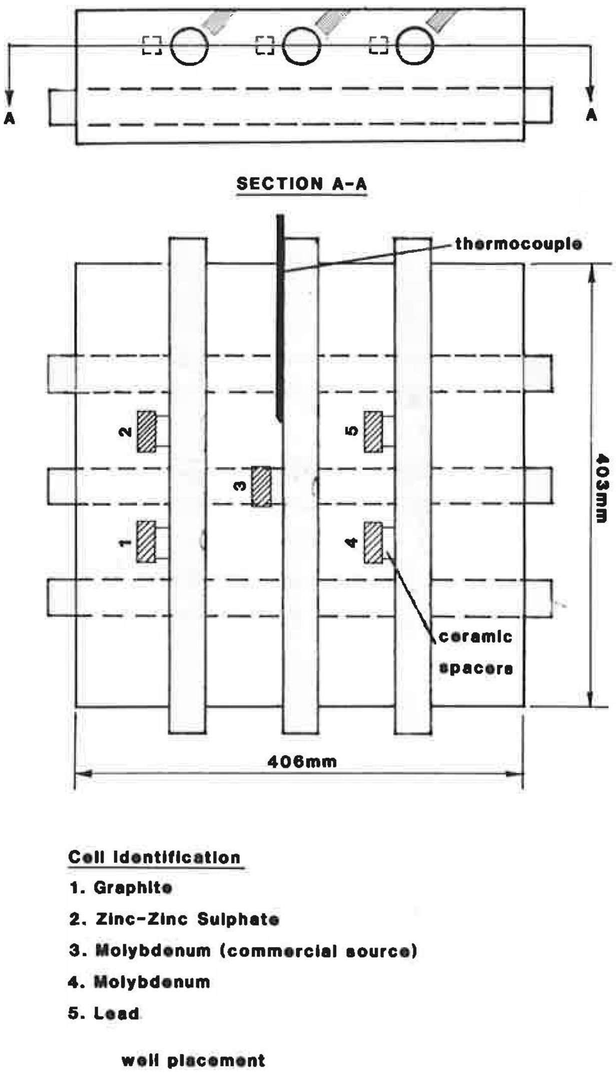

FIGURE 4 Test specimen in the Ministry of Transportation laboratory and exposure plot study.

structed using plastic tubing positioned over the reinforcing bars and close to the embedded cells to allow potential measurements using a portable CSE cell. The potential of the steel was measured using the embedded cells and the portable (external) cell. The potential difference between the embedded cells and the external cell was measured by placing the external cell on the surface of the concrete directly above each embedded cell in turn.

Measurements were made during 4 months in the laboratory, followed by 2 years in the exposure plot. During the winter, when cold temperatures prevented the use of a portable cell, the potentials measured by the embedded cells were recorded periodically using a remote data logger.

The stability of the cells was evaluated by calculating the standard deviations of the cell-to-rebar potential with time. The results are shown in Table 2 for three exposure periods: the initial 4 months in the laboratory and two 5-month periods corresponding to the spring and summer of each year in the outdoor exposure plot.

The graphite cells consistently displayed the lowest standard deviation throughout the evaluation period. Individual lead, zinc, and molybdenum cells that displayed good performance in the laboratory and during the first year of outdoor exposure became unstable during the second year, and potential measurements fluctuated widely. Table 2 also includes the standard deviation of the potentials measured by the copper-copper sulfate cell for purposes of comparison.

The cold weather performance of reference cells was of particular interest in view of the Ontario climate and the need for year-round reliability of instrumentation used to monitor and control installations of cathodic protection. Readings taken during a 5-day period beginning February 7, 1985, are shown for the two samples of each cell in Figures 5a and 5b. The standard deviation of the readings during the period is provided in Table 3. Concrete temperatures recorded during the period were consistently lower than 0°C, and the lowest temperature recorded was −18°C. Another set of readings was made over a 5-day period of cool weather beginning March 21, 1985. During this period, the average concrete tempera-

TABLE 2 STANDARD DEVIATION OF CELL-TO-REBAR POTENTIAL READINGS

Cell Type	Indoor Exposure (16 weeks)		Outdoor Exposure Year 1 (22 weeks)		Outdoor Exposure Year 2 (22 weeks)	
	#1	#2	#1	#2	#1	#2
Lead	28	50	161	27	125	243
Zinc	72	63	73	48	178	92
Graphite	25	30	28	25	10	21
Molybdenum (1)	72	47	34	58	23	78
Molybdenum (2)	78	43	38	50	16	140
Copper-Copper Sulfate (on concrete surface)	35	59	43	43	15	23

Notes:

1. Molybdenum (2) cells were purchased commercially.
2. All values are in millivolts.

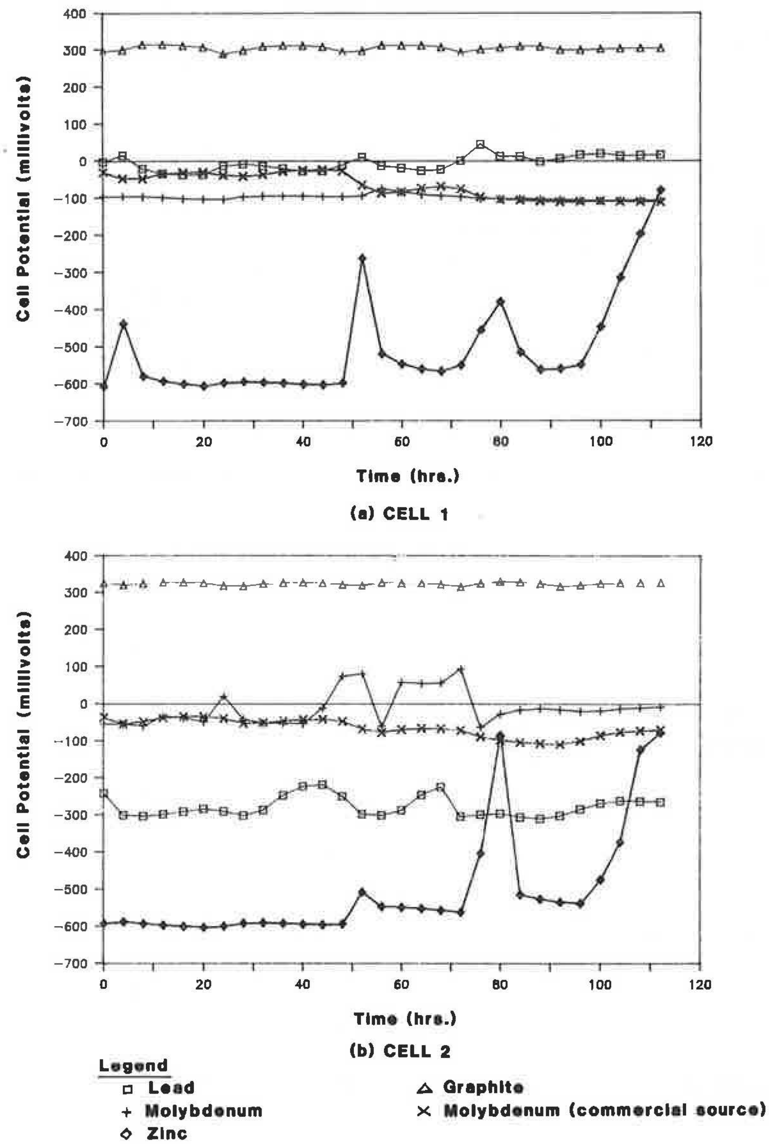

FIGURE 5 Cell performance in cold weather, February 7, 1985: (a) cell 1, (b) cell 2.

TABLE 3 STANDARD DEVIATIONS OF CELL-TO-REBAR POTENTIAL READINGS DURING COLD AND COOL WEATHER INVESTIGATIONS

Cell Type	Test Period Beginning February 7, 1985		March 2, 1987	
	#1	#2	#1	#2
Lead	21	27	27	16
Zinc	175	181	167	129
Graphite	7	4	5	5
Molybdenum (1)	7	48	14	45
Molybdenum (2)	35	23	4	5

Notes:
1. Molybdenum (2) cells were purchased commercially.
2. All values are in millivolts.

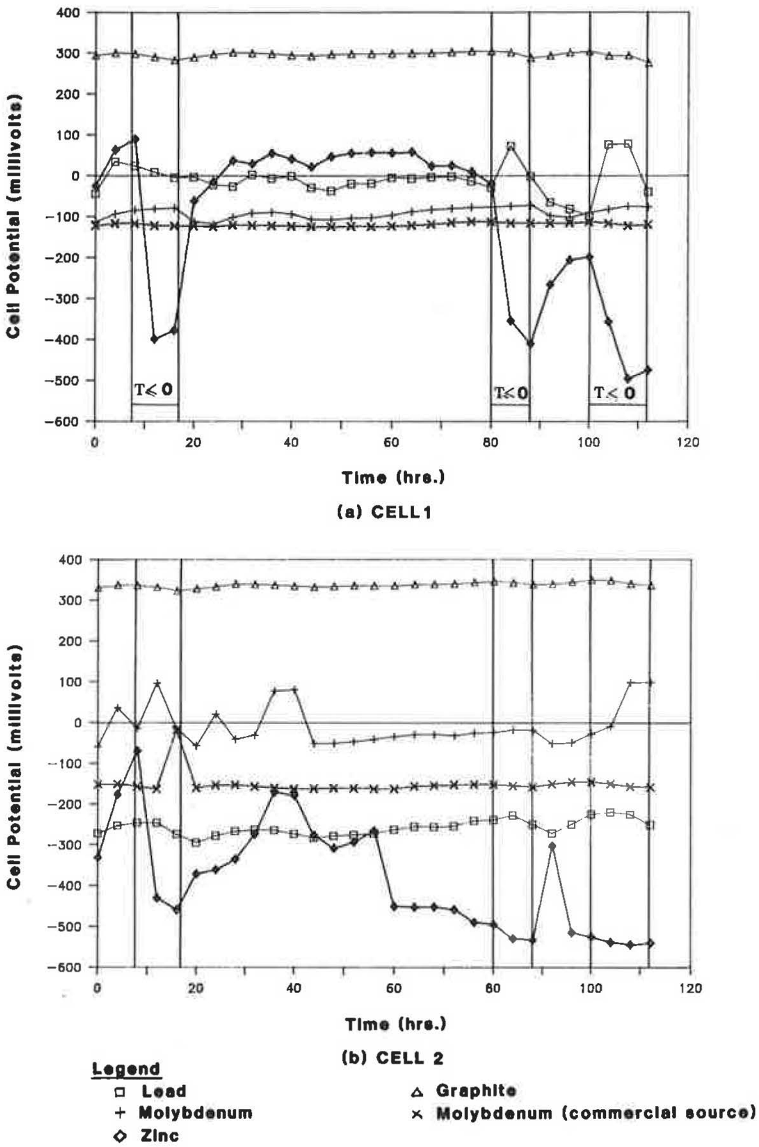

FIGURE 6 Cell performance in cool weather, March 21, 1985: (a) cell 1, (b) cell 2.

ture was 3°C, and the range was from −5°C to 14°C. Results appear in Figures 6a and 6b, and Table 3 provides the standard deviations.

The zinc cells were most affected by periods of low temperature, probably because of effects on the backfill material that resulted in poor contact between the zinc and the backfill. Lead cells and the laboratory-made molybdenum cells also fluctuated with low temperatures. Although the fluctuations were less severe than those of the zinc cells, these cells would not be suitable for use with a potential-controlled rectifier. The graphite cells had the lowest standard deviation and showed very little response to changes in temperature.

An indication of an acceptable standard deviation for a reference cell can be obtained by considering a rectifier under potential control and a protection criterion of, for example, −770 mV to −1100 mV (CSE). If the rectifier is adjusted to the midpoint of the band (−935 mV), the reference cell could shift by 165 mV before the protection criterion was violated. If the cell output is assumed to follow a normal distribution and acceptable readings are defined as those within three standard deviations of the mean (i.e., a 99.74 percent chance of satisfying the protection criterion), then the reference cell must have a standard deviation no greater than 55 mV.

The results of these experiments increased confidence in the ability of the graphite cells to provide stable, long-term performance. The zinc cells clearly were unsuitable in the form used. Variations between the individual samples of the lead cells and molybdenum cells made in the laboratory indicated that if the cells were to be used, the effect of various aspects of the manufacturing process (particularly the rate of cooling) on cell performance would have to be investigated fully, and rigorous quality control procedures would have to be implemented.

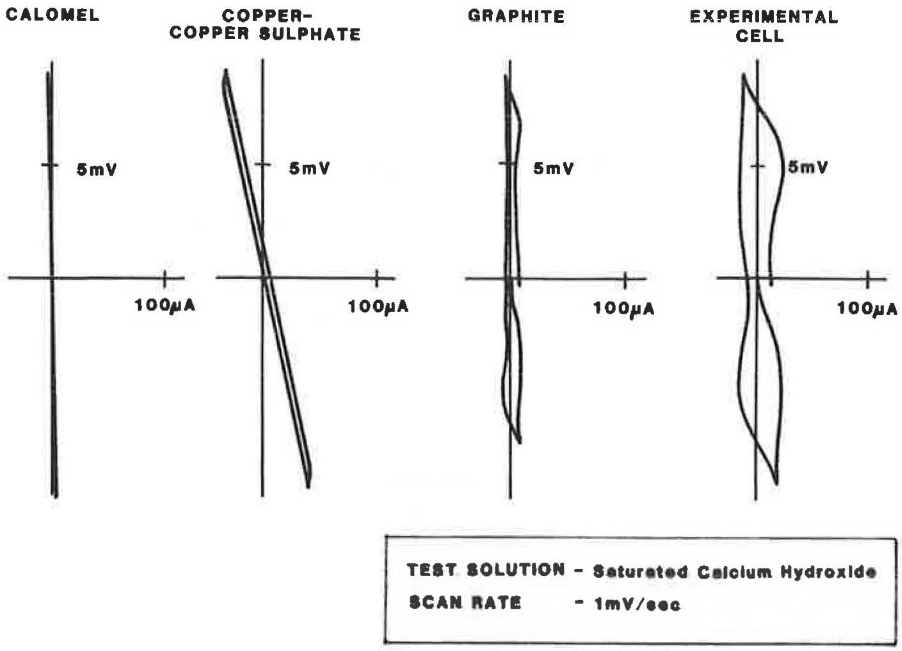

FIGURE 7 Micropolarization tests on selected reference cells.

Micropolarization Tests

Another series of laboratory tests was performed to investigate the reversibility of reference cells. This is important because reference cells embedded in cathodically protected, reinforced concrete must respond consistently to changes in steel potential, even after repeated changes in power levels. To investigate this effect, a micropolarization technique was used (*10*) that involved repeated application of very small positive and negative currents to a reference cell and measurement of the resulting potential.

Figure 7 presents a plot of micropolarization tests performed on four reference cells. A maximum potential shift of ±10 mV was applied, and the scan rate was 1 mV/second. The calomel cell showed no hysteresis effects, which is the behavior expected of an ideal cell. The copper-copper sulfate cell exhibited some hysteresis; the graphite cell and an experimental titanium cell showed progressively greater hysteresis. As expected, the calomel and copper-copper sulfate cells, the standard portable reference cells for laboratory and field studies, respectively, performed well. It appears that the penalty to be paid for more rugged cells that are suitable for permanent embedment in concrete may be a greater departure from idealized behavior. In addition to providing information on the characteristics of different types of cells and the screening of new reference cells, micropolarization tests may prove to be useful in a routine quality assurance system for reference cells.

Although the graphite cells have performed well in concrete, use of these cells has been questioned because the ionic species involved is uncertain and cell reactions may be influenced by the composition of the concrete porewater surrounding the cell. To investigate these effects, laboratory studies have been initiated to examine the long-term performance of graphite cells in different solutions. Cells have been placed sequentially in distilled water and solutions of calcium hydroxide and calcium hydroxide plus different concentrations of sodium chloride. Study is continuing.

Other Exposure Plot Tests

Following initiation of the small-scale internal study of laboratory and exposure plot testing, a more comprehensive study was begun in 1984, by means of a research contract, to investigate the suitability of embedded reference cells for monitoring and controlling cathodic protection systems on reinforced concrete structures. All types of reference cells available commercially or made by the Ministry when the study began were included. Eight different cells were tested: two zinc-zinc sulfate cells, one graphite electrode, two silver-silver chloride cells, one lead cell, and two molybdenum-molybdenum oxide cells.

Specimens measuring 600 mm × 300 mm × 150 mm thick were made from two types of concrete: one salt-free and the other containing 0.30 percent chloride ion by mass of concrete. Each specimen contained two identical reference cells, short lengths of platinized niobium wire, reinforcing steel, and a thermocouple, as shown in Figure 8.

After curing, the specimens were stored in an outdoor exposure site in Virginia. The following measurements were made periodically over a period of 20 months:

- Potential of each embedded cell relative to the embedded reinforcing steel;
- Potential difference between each embedded cell and a portable cell (calomel and CSE) placed on the concrete surface immediately over each embedded cell;
- Potential of each embedded cell relative to the platinum wire;

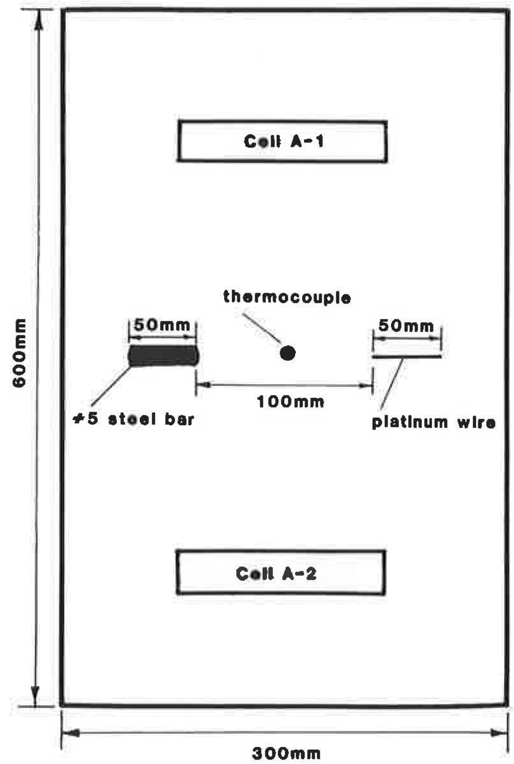

FIGURE 8 Test specimen in the Virginia outdoor exposure study.

- AC resistance of each embedded cell to the embedded steel and platinum; and
- Concrete temperature.

The concrete temperatures during data collection ranged from −1°C to 43°C. The data are available in the final report on the project (*11*); the most meaningful data are summarized in Table 4.

Both the laboratory and commercial zinc cells were found to be unstable. The standard deviation of the laboratory cells was approximately 100 mV. The standard deviation of the commercial zinc cells ranged from 94 mV to 207 mV, and the AC resistance in the salt-laden concrete was extremely high throughout most of the test period.

The four lead cells also had a standard deviation exceeding 100 mV. The cells were relatively stable during the first 300 days after the slabs were fabricated, but the readings became erratic for the rest of the test period.

The molybdenum cells from both commercial sources were judged to be unacceptably unstable. The cells from the first source underwent significant potential shifts during the first 150 days after embedment but subsequently became more stable. The standard deviation of the potential difference varied from 63 mV to 82 mV. The standard deviation of the potential difference of the cells from the second source ranged from 37 mV to 129 mV. These cells were relatively stable in the salt-free concrete for the first 300 days, after which one cell became very unstable. On the other hand, in the salt-laden concrete, the cells were very unstable during the first 150 days, and there were significant differences between the two cells throughout the remainder of the test period. The AC resistance of the cells from both sources was relatively low.

The silver cells from both commercial sources performed quite well, although the AC resistance of the cells from one of the sources was high, and this could create difficulties if they were used in conjunction with a potential-controlled rectifier. The average potential differences of the cells from the second source versus CSE were −45 mV and −26 mV in salt-free concrete, but 31 mV and 20 mV in concrete containing salt. The standard deviation of the potential difference ranged from 22 mV to 52 mV. Although the cells were stable, the measured potential was found to depend quite heavily on the chloride content of the surrounding concrete.

The graphite cells were the most stable cells tested. The average potential differences of the four cells with respect to the CSE electrode were −8 mV and −15 mV in salt-free concrete and 8 mV and 8 mV in salt-laden concrete. The standard deviation of the potential difference ranged from 27 mV to 50 mV, and AC resistance between the cells and the reinforcing steel was low.

The results showed that many of the cells available when the study began were unsuitable for the control and long-term monitoring of cathodic protection installations. Not only were the graphite cells the most stable, they also required no special backfill material and were inexpensive. The study reported that the potential difference to the CSE was small, meaning that potentials measured with the graphite cells and with the copper-copper sulfate half-cells could be used interchangeably. Much larger differences were recorded, however, in the Ministry tests reported in Table 1. The sources of the graphite used in the two series of tests were not the same; and until the effect of the grade and type of graphite is better documented, graphite electrodes should not be used without calibration. Despite the good performance, the average standard deviation relative to a calibrated CSE of the four graphite cells over 20 months was 40 mV. Consequently, the cells need periodic recalibration if they are used with cathodic protection systems for which the protection criterion is based on an absolute measurement of potential. They are well suited, however, for use with systems that have a criterion based on potential shifts.

The next most stable cells were the low-resistance silver cells. Their performance was similar to that of the graphite probes, but they were more strongly affected by the chloride content of the surrounding concrete. Since the standard deviations of the potential difference were lower in salt-free concrete than in salt-laden concrete, it was concluded that the common practice of surrounding the cells with a backfill of chloride-bearing concrete or mortar provided no benefit.

The study judged all the other cells to be unacceptably unstable. It must also be noted, however, that the lowest temperature recorded during the study was −1°C. Measurements taken by Ministry staff have shown that silver-silver chloride cells have consistently exhibited erratic behavior at colder temperatures.

CURRENT AND FUTURE MINISTRY ACTIVITIES

Embedded graphite reference electrodes have been installed in the Ministry's most recent deck cathodic protection sys-

TABLE 4 SUMMARY OF RESULTS OF EXPOSURE PLOT TESTING IN VIRGINIA

Cell	Average Pot. Diff. Cell-to-CSE, mV		Standard Dev. of Pot. Diff., mV		Average AC Res. to Pt., kΩ	
	#1	#2	#1	#2	#1	#2
Salt-Free Concrete						
Zinc (L)	728	523	109	103	1.7	1.8
Zinc (C)	566	568	94	129	2.5	2.5
Lead (L)	640	540	130	267	2.3	2.5
Graphite (L)	- 8	-15	27	35	1.6	1.5
Silver (C)	-45	-26	43	32	58.9	45.5
Silver (C)	-55	-54	22	36	1.6	1.6
Molybdenum (C)	202	165	82	63	3.7	3.8
Molybdenum (C)	451	375	37	129	3.5	3.7
Concrete Containing Salt						
Zinc (L)	718	659	130	117	1.7	2.0
Zinc (C)	435	546	173	207	279	231
Lead (L)	581	646	142	238	2.2	2.3
Graphite (L)	8	8	50	47	1.3	1.3
Silver (C)	8	12	41	51	21.2	29.7
Silver (C)	31	20	52	42	1.7	1.5
Molybdenum (C)	191	196	66	70	3.1	2.9
Molybdenum (C)	203	277	120	112	5.8	4.6

Notes:

1. L - Cells made in Ministry laboratories.
   C - Cells purchased commercially. More than one cell of each type indicates different sources.

2. Negative voltmeter terminal connected to embedded cell.

tems. Measurements are being taken to correlate readings from the embedded cells with those from the voltage probes on the concrete surface in contact with the conductive bituminous concrete. A considerable quantity of data has been collected on the surface probes over a period of 12 years, and the protection criterion of −0.80 V to −1.25 V is based on measurements made on the voltage probe. This testing is intended to ensure that any reference-cell-based criterion adopted for decks will result in protection that is equivalent to that supplied by using the existing criterion. It is also meant to ensure that the criterion of 100 mV depolarization in 4 hours, which has been adopted for substructure installation, is consistent with the criterion for decks. Although only two sets of data have been recorded, initial results are encouraging. Both the criteria based on voltage probe potentials and those based on reference cell depolarization were satisfied, but the reference cell measurements exhibit greater variation than do the probe measurements. Additional data will be collected as part of the regular monitoring program for cathodically protected decks.

Two reference cells manufactured in the United Kingdom are now being evaluated in the laboratory and the field. One is a silver-silver chloride cell that has been reported to be very stable and to have performed well under field conditions (*12*). The second cell is an experimental, titanium-based cell.

A university research contract to investigate hydrogen embrittlement in prestressed concrete elements has resulted in the development of very small graphite electrodes that should permit potential measurements at very precise locations. If successful under laboratory conditions, these electrodes will also be evaluated in the field.

CONCLUDING REMARKS

A series of measurements from laboratory, exposure plot, and field tests has identified graphite electrodes as the most suitable kind for use as a reference cell embedded in concrete. Graphite electrodes have been shown to be stable under conditions of changing temperature and to be only slightly influenced by the chloride content of the concrete.

Further, the electrodes are inexpensive and the potentials measured are sufficiently close to the potentials relative to a standard copper-copper sulfate cell that the values can be used interchangeably.

The only other cell tested that was found suitable for use in reinforced concrete was a commercial silver-silver chloride cell. That cell, however, was evaluated only at temperatures of −1°C and more and was found to be quite strongly influenced by the chloride content of the concrete. Other silver-silver chloride cells exhibited unacceptably high resistance in concrete containing chlorides and became unstable at temperatures below freezing.

Graphite probes, despite their several advantages, cannot be considered the ideal reference cell for use in concrete. They are not perfectly reversible, and questions remain with respect to the reactions involved and the extent to which those reactions are influenced by ions present in concrete. Further,

the standard deviation of potential measurements made with respect to a standard surface electrode indicated that graphite electrodes are better suited for use in conjunction with protection criteria based on potential shift rather than on absolute potentials unless they are calibrated periodically. Consequently, graphite electrodes are being installed and evaluated at the same time that the suitability of other reference cells is being evaluated.

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