Buried Permanent Reference Cell Performance Testing—An Engineered Approach to Evaluation

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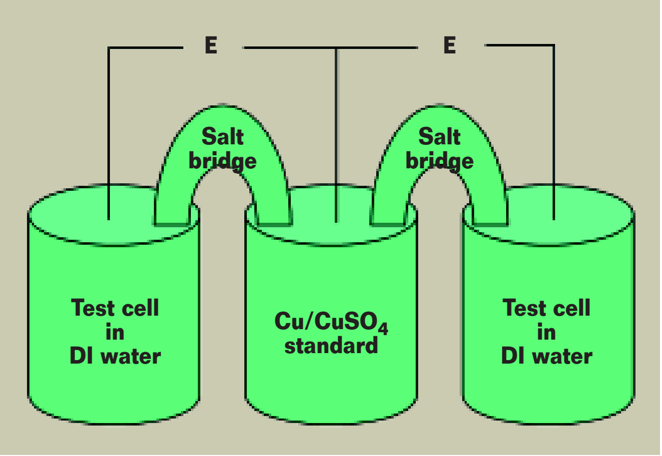
There are currently no industry-standard techniques to evaluate the long-term performance of permanent reference cells for direct-burial applications. Acceptable test methods could assist the engineer in product evaluation, qualification testing, and quality assurance testing. Recent in-house testing by some manufacturers has led to the formation of a NACE Technical Exchange Group. This article presents the results of one company's test program.

Permanent reference cells have been used for many years to monitor buried structures susceptible to corrosive elements. These reference cells were typically bagged with a backfill material that made the cells bulky. Several new reference cells have emerged with the advantages of smaller size and apparent longer life. The present work was designed to focus on copper/copper sulfate (Cu/$CuSO_4$) reference cells used in direct-burial applications. If the testing strategy proves successful, it can be applied with some modification to other cell types. The strategy includes identifying specific failure modes of the cells and developing tests that stress that cell characteristic. The tests are intended to be realistic yet sufficiently severe to cause the cells to fail in a reasonable period of time.

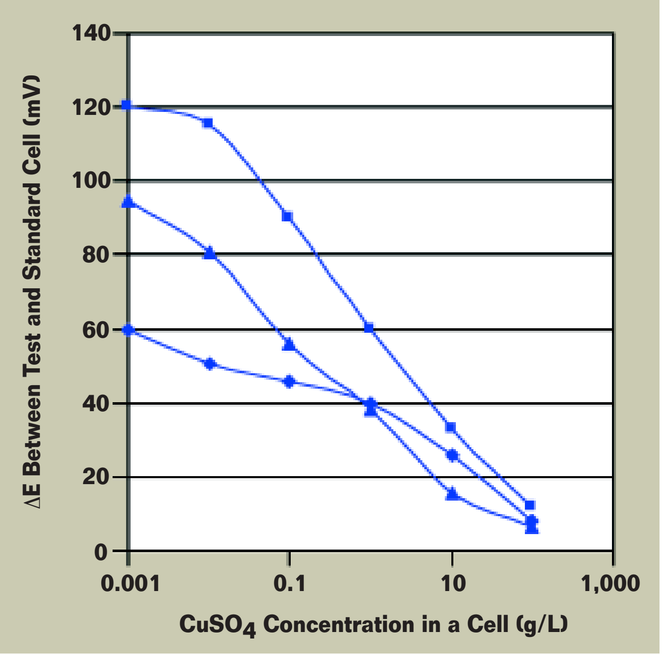
Environmental factors must be considered while performing durability testing. Previous authors have discussed possible factors resulting in erroneous potential readings from a half-cell and their relevance to permanent reference electrodes.[1-2] Variables that usually affect Cu/$CuSO_4$ reference cells include temperature and light variations. Both authors indicate that potential readings can vary by 0.9 mV/°C, and that exposure to direct sunlight can cause potential variations of up to ±20 mV. However, since permanent reference cells are typically used in locations with no direct sunlight exposure and limited temperature variations, such effects should be minimal.[1] Another environmental factor that can cause a change in potential, although not as common as temperature and sunlight, is a change in chloride concentration. As the chloride contamination increases, the potential shifts away from its reference potential (potential with no chlorides present) to ~ –123 mV in a 60,000-ppm solution.[2]

FIGURE 1



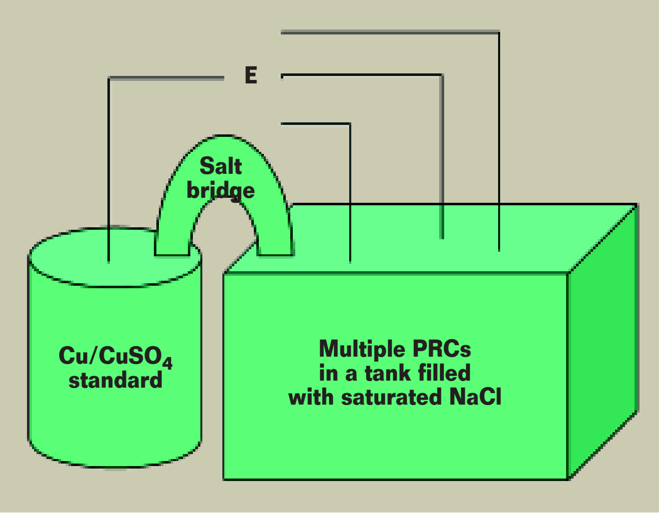
$CuSO_4$ leaching test schematic.

FIGURE 2



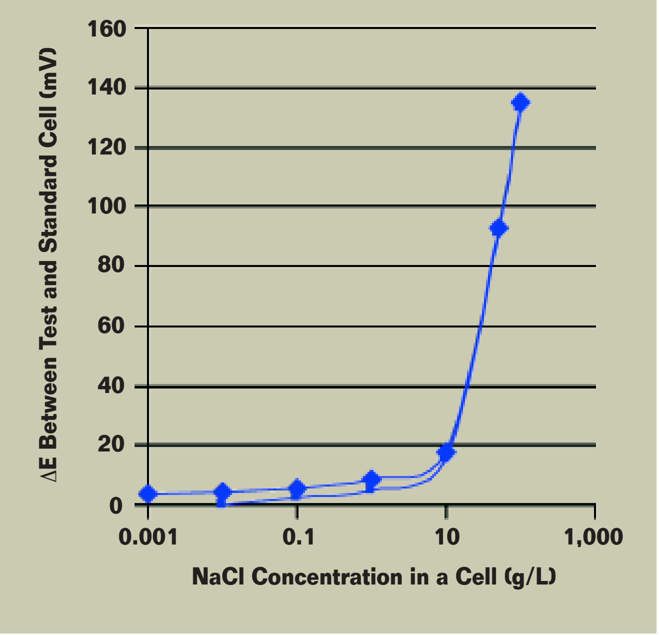
Effect of unsaturated $CuSO_4$ solution.

FIGURE 3



NaCl leaching test schematic.

FIGURE 4



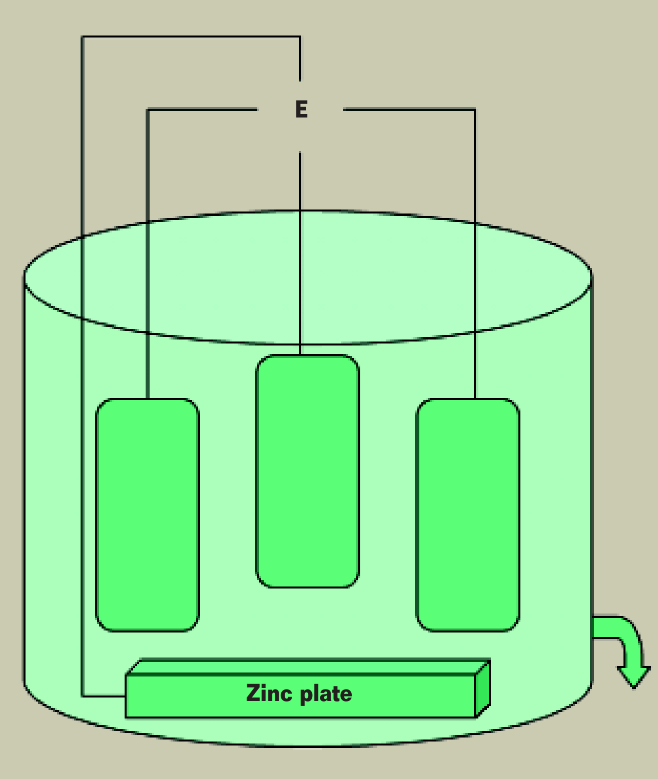
Effect of NaCl contamination in saturated $CuSO_4$ solution.

The natural tendency for the potential of a $Cu/CuSO_4$ reference cell to vary must also be considered. Some sources of this variation may include the age of the cell and differences in manufacturing. Consequently, cells have been cited as repeatable to ±0.006 V (6 mV).[3] When potentials between a known "good" and test $Cu/CuSO_4$ reference cell are outside this range, it should be considered unusable. Although this may be an acceptable range in a laboratory setting, an electrode found to be a few mV outside this range will likely be used when acquiring field data.

Testing Procedures

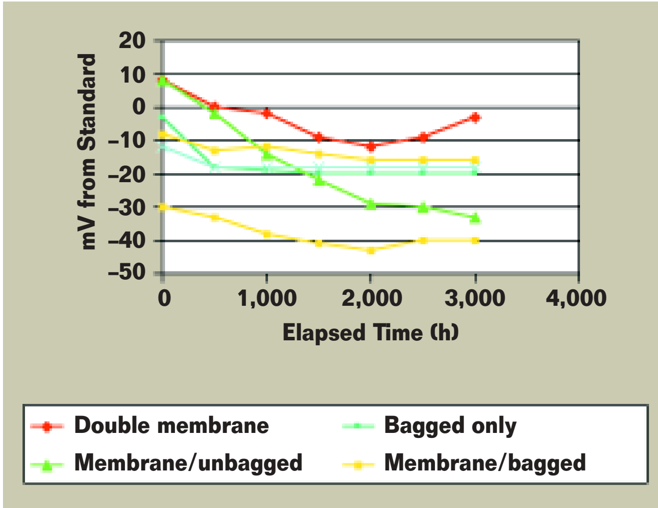
Several test procedures and evaluation techniques were developed and executed as part of the program. The durability issues for $Cu/CuSO_4$ cells that are discussed in this article include chloride ingress into the cell, $CuSO_4$ leaching out of the cell, drying of the cell electrolyte (gel), and "rewettability" of the gel. These durability issues evaluate the ability of the cell membrane to resist the transmission of ions and moisture while still allowing sufficient electrical contact to obtain an accurate measurement.

FIGURE 5



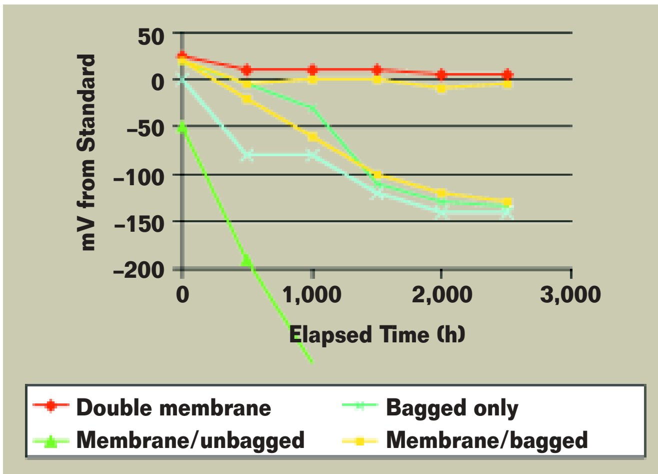
Cell drying test schematic.

FIGURE 6



Effect of $CuSO_4$ leaching on various cells.

FIGURE 7



Effect of NaCl leaching on various cells.

$CuSO_4$ LEACHING TEST

This test involves exposing a cell in deionized (DI) water and monitoring the time for $CuSO_4$ to leach from the gel until the potential shifts. Figure 1 is a schematic of the test setup. Each test cell is placed in an individual container with ~16 L of deionized water. The deionized water is replaced when the resistivity falls below 4,000 Ω-cm. That resistivity corresponds to a concentration of 11.5 g/L of $CuSO_4$ in the water. The potential difference between the test cell and a Cu/$CuSO_4$ standard coupled via a salt bridge is tracked with time. Periodically, the standard is checked against a refreshed portable Cu/$CuSO_4$ cell placed in one of the test chambers.

Figure 2 demonstrates the effect of $CuSO_4$ concentration in a cell. Saturated deionized water contains 133 g/L $CuSO_4$. The figure indicates that the $CuSO_4$ concentration in a cell must be at least 100 g/L to be within 10 mV of a saturated cell.

SODIUM CHLORIDE LEACHING TEST

This test involves exposing test cells in deionized water saturated with sodium chloride (NaCl) and monitoring the time for chloride to leach into the gel, shifting the potential. Figure 3 is a schematic of the test setup. All test cells are in one container. Deionized water is replaced as necessary. Saturation is maintained by ensuring NaCl crystals remain in the tank. The potential difference between the test cell and a Cu/$CuSO_4$ standard coupled via a salt bridge is tracked with time. Periodically, the standard is checked against a refreshed portable Cu/$CuSO_4$ cell placed in the test tank.

Figure 4 demonstrates the effect of NaCl in a saturated $CuSO_4$ solution. The contaminated Cu/$CuSO_4$ reference may shift by 10 mV with 1 g/L NaCl concentration. The data show that NaCl concentration >10 g/L will shift reference by more than 10 mV vs a standard.

CELL DRYING TEST

This test involves exposing the test cells in washed sand that can be alternately wetted and dried. Figure 5 is a schematic of the test setup. As shown, all of the test cells are placed in one container that is filled with sand. The sand is alternately wetted with tap

TABLE 1

SUMMARY OF CELLS TESTED

Cell	Supplier	Cell Type
A	A	Bagged only (no inner membrane)
C	B	Bagged only (no inner membrane)
B	A	Double membrane
D	C	Membrane/bagged
E	D	Membrane/bagged
F	E	Membrane/unbagged

water and allowed to dry. The potential of the test cells vs a Zn plate is tracked as a function of time. The rate of potential shift during drying and wetting is used to determine the response of the test cells.

Reference Cells Tested

Six permanent reference cell (PRC) models were obtained from five manufacturers (Table 1). Cells A and C were bagged with plaster/bentonite and no membrane separating the $CuSO_4$ from the backfill. Cell F was supplied unbagged but had a ceramic membrane. Cells D and E were bagged with plaster/bentonite and also had a membrane isolating the $CuSO_4$ from the backfill. Finally, Cell B was constructed with a double-membrane configuration that included a ceramic membrane containing the Cu element and $CuSO_4$ gel. Cell B's membrane was packaged within a geomembrane that also contained a $CuSO_4$ gel.

Results and Discussion

$CuSO_4$ LEACHING TEST

Figure 6 summarizes the results of the $CuSO_4$ leaching test for each cell type. The membrane/unbagged cell showed a steady decline in potential throughout the test. The remaining cells were relatively stable after 3,000 h of testing, though some of the cells indicate a potential significantly different from the standard.

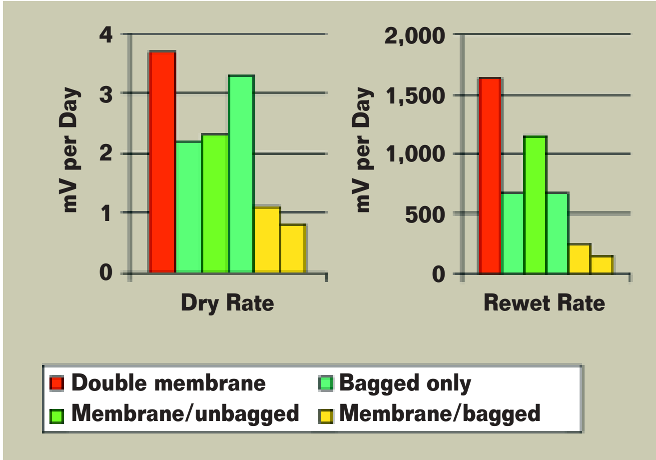
NaCl LEACHING TEST

Figure 7 summarizes the results of the NaCl leaching test for each of the cell types. There are two cells that are performing well to date. Four cells have shown signs of substantial chloride intrusion.

CELL DRYING TEST

Figure 8 shows the results of the cell drying test. As one might suspect, the cells that rewet quickly also dry out quickly. The backfill in the bagged cells slows rewetting and drying rates. The double-membrane cell has the slowest drying rate as well as the slowest rewetting rate.

FIGURE 8



Cell drying and rewetting rates for various cells.

Conclusions

- The development of standardized test criteria would allow an end user to compare the performance of reference cells. This will be the primary purpose of NACE Technical Exchange Group 102.
- Any testing that intends to represent "real-world" cell performance should consider the effects of the backfill.
- Further laboratory testing under "realistic" conditions and field testing are necessary to validate the test procedures.

References

1. F.J. Ansuini, J.R. Dimond, MP 33, 11 (1994).
2. R.J. Lopez, et al., MP 37, 5 (1998).
3. H.H. Uhlig, Corrosion Handbook (New York, NY: John Wiley & Sons, 1948), p. 931.

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