

# Evaluation of Corrosion Prevention Methods for Aboveground Storage Tank Bottoms

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*An investigation was conducted to determine the effectiveness of various corrosion protection methods for aboveground storage tanks with secondary containment designs. Small-scale test tanks simulating the environment and geometry of an inner section of a double-bottom storage tank were exposed with and without cathodic protection (CP). Results showed that, when measured reference potentials and CP current suggest corrosion has been arrested, CP may not completely protect against corrosion.*

Cathodic protection (CP) is commonly used to mitigate corrosion on the bottoms of aboveground storage tanks. To protect the environment from leaks due to through-floor corrosion, new tanks and refurbishment of old tanks are often designed with double-bottoms. The sides and bottom of the inner annulus typically are lined with high-density polyethylene for additional leak protection. The best method of protecting the exposed steel of the upper bottom from corrosion within the annulus is not clear. Several recommendations have recently been published suggesting that impressed current (IC) is a reliable method for long-term protection of floors in double-bottom tanks.<sup>1-4</sup> Few if any corrosion tests have been conducted to simulate the

closed system of a double-bottom storage tank.

## Experimental

Small-scale test tanks simulating the environment and geometry of an inner section of a double-bottom storage tank were constructed and exposed for 101 days. Each plastic tank simulated the high-density polyethylene (HDPE) liner and was filled with six inches of backfill and three anodes positioned 25 mm (1 in.) above the tank bottom on 200-mm (8-in.) centers. A base case, sacrificial anode, and impressed current case were run for both pea gravel and sand backfill. The sacrificial anode tests had 9.5 by 19 by 292 mm (3/8 by 3/4 by 11-1/2 in.) magnesium ribbon anodes and the impressed current tests used 6.4 by 0.6

by 292 mm (1/4 by 0.025 by 11-1/2 in.) titanium anodes. Although the two base cases had buried anodes, none were connected. Two additional pea gravel tests with nitrogen purge and vapor phase inhibitor were run for comparison. The nitrogen-treated tank was continuously purged under slight positive pressure with nitrogen bubbled through water at a rate of 0.12 L/min (0.26 ft<sup>3</sup>/h) in order to avoid drying out the pea gravel. The vapor phase inhibited pea gravel was treated 2.5 cm (1 in.) below the surface with 90 g/m<sup>3</sup> (8.4 g/ft<sup>3</sup>) of inhibitor, per the manufacturer's recommendation. Hereafter the tests will be referred to as Sand (sand base case), PG (pea gravel base case), PG/N<sub>2</sub> (pea gravel with nitrogen purge), PG/VPI (pea gravel with vapor phase inhibitor), PG/Mg (pea gravel with magnesium anodes), Sand/Mg (sand with magnesium anodes), PG/IC (pea gravel with impressed current) and Sand/IC (sand with impressed current).

Rain water was sprinkled over the backfill to simulate a one-inch rainfall during tank construction.



After compacting and leveling, a 16-gauge (1.54 mm [0.060 in.]) carbon steel test panel was placed over the backfill. The internal side of each test panel was sand blasted. The plates were weighted down with steel blocks and sealed with caulking. The center of each panel was equipped with a sealed fitting for Calomel half-cell (mercury-mercurous chloride) potential measurements. Copper-copper sulfate ( $\text{Cu}/\text{CuSO}_4$ ) reference cells were buried one inch below the center of each steel panel. An illustration of the test tank design is given in Figure 1.

## Results

### Visual Appearance

Upon removing the steel panels, it was observed that all internal plate surfaces were wet with moisture condensation over the entire surface. The test panels were immediately dried and photographed (Figure 2). A surprisingly small amount of corrosion appeared on the PG test. There were large areas on the steel plates that showed an uncorroded bright metal finish. In those cases, most of the corrosion occurred between the pieces of gravel and the steel at the point of contact. There was a dark grey discoloration of the steel surface on both the PG/ $\text{N}_2$  and PG/VPI tests and no gravel adhered to either surface. The most extensive and uniform corrosion appeared in the Sand test. It showed a 15 percent coverage of light general corrosion. The PG/Mg test exhibited a dark grey discoloration on the surface with very little if any red rust. The Sand/Mg test exhibited zones of concentrated corrosion adjacent to large areas of bare steel with no noticeable

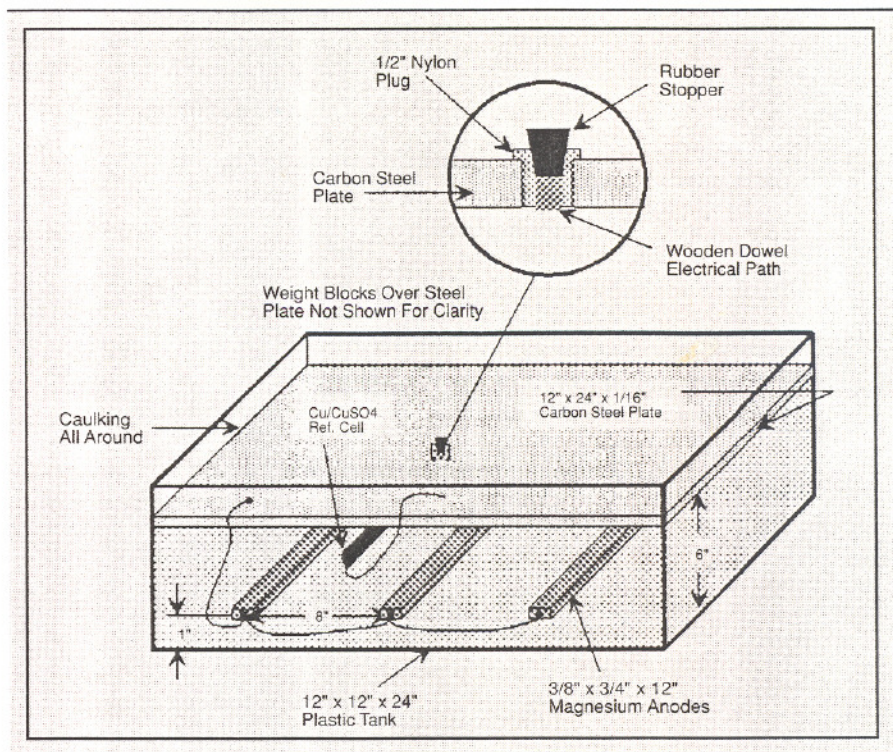


FIGURE 1  
Test tank design

corrosion. Some of the most corroded areas were immediately next to areas where the plate had intimate contact with the sand.

The impressed current tests showed very aggressive corrosion. The PG/IC test corroded the most under the contacting pieces of gravel. The Sand/IC test corroded most in areas not in contact with the backfill. The corrosion morphology was similar to, but more severe than, the Sand/Mg test. Tubercle formation (oxygen concentration cells) occurred at areas around the perimeter where the steel appeared not to have complete contact with the backfill. The formation mechanism of these was proposed by Riggs, Sudbury, and Hutchinson at Conoco Production Research Division and published by Fontana and Greene.<sup>5</sup> A more detailed description of tubercle morphology and chemical reactions was given by Herro.<sup>6</sup>

### Pitting and Weight Loss

At the end of the test period, each panel was cleaned with a solution of inhibited 15% hydrochloric acid. Weight loss and pitting measurements were made in accordance with NACE Standard RP0775-91.<sup>7</sup> For all tests, the weight loss was too

small to give a significant general corrosion rate. Pitting ranged from a low of 1.8 mpy (46  $\mu\text{m}/\text{y}$ ) for PG/Mg to 27.1 mpy (688  $\mu\text{m}/\text{y}$ ) for Sand. There was very little pitting under the points of gravel contact on both the PG/ $\text{N}_2$  and PG/VPI tests. A bar chart comparison of the pitting rates is given in Figure 3. An important finding illustrated in this graph is that impressed current does not appear to be effective in reducing pitting corrosion. Pitting on the impressed current tests was higher than any of the tests employing corrosion protection. Pitting was found where backfill contacted with the steel plate for the IC test with pea gravel and away from the contact points in the IC test with sand backfill.

### Internal Gas Atmosphere

The gas chromatographic samples, taken at the end of the test period and prior to removal of the panels, revealed significant variations in the nitrogen and oxygen content compared to air. The PG test showed that the composition of the atmosphere within the tank annulus remained the same as air. This is consistent with the corrosion appearance since very little uniform corrosion took place to consume the oxy-

### TEST TYPE KEY

Sand base case = sand  
 Pea gravel base case = PG  
 Pea gravel with nitrogen purge = PG/ $\text{N}_2$   
 Pea gravel with vapor phase inhibitor = PG/VPI  
 Pea gravel with magnesium anodes = PG/Mg  
 Sand with magnesium anodes = Sand/Mg  
 Pea gravel with impressed current = PG/IC  
 Sand with impressed current = Sand/IC



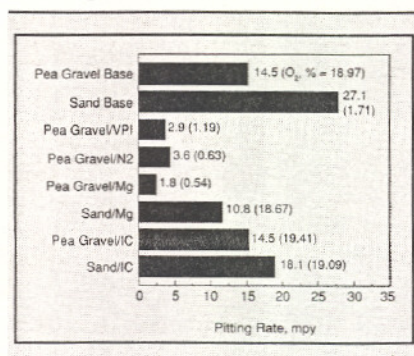
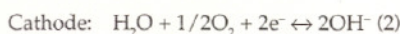
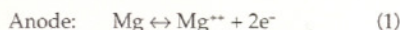
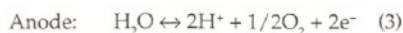


FIGURE 3  
Maximum pitting rate.

gen. The heavier corrosion of the Sand test was accompanied by a reduction of oxygen to 1.71 mol%. The low corrosion rate, potentials, and current density of the PG/Mg test corresponded to the greatest reduction of the oxygen of all tests at 0.54 mol%. This oxygen reduction reaction, which occurs at the cathode, is given as follows for a magnesium sacrificial anode system:



The oxygen levels from Sand/Mg were much higher than expected and did support more corrosion than the pea gravel with magnesium anodes. A leak in the test tank seal is a possible explanation. Gas analysis of the internal atmosphere for impressed current tests gave the most telling results. The oxygen content for both at the end of the test was 19%, essentially the same level as for air. Since oxygen is produced at the anode and consumed at the cathode, there is no reduction in oxygen concentration. The following chemical reactions for a titanium anode impressed current system account for this condition:



### Bacteria and Chlorides

The total aerobic bacterial population count was measured on all backfills and rain water at both the beginning and end of the experiment. These were typical of normal rain water, sand, and gravel. The sulfate-reducing bacteria detection

system used at the end of the test showed insignificant levels of sulfate-reducing bacteria. Ion chromatographic analyses of backfill samples detected no significant levels of chlorides. All samples were below the 17.8 ppm (micrograms per gram of sample) measured for the rain water.

### Backfill pH

With the exception of one test, the soil pH ranged from 6.4 to 7.7. The backfill of the Sand/Mg had a pH = 8.8. Litmus paper was used to check the pH of what appeared to be hydroxide deposits on the steel plate where it was in contact with the sand. Values as high as pH = 9.5 were obtained. The rain water pH was 7.1.

### Backfill Resistivity

Soil resistivity was compared using the four-electrode and an AC impedance method at 2 kHz. The resistivity of sand was the same for both the AC impedance and four-electrode method at 29,350 ohm-cm. The test was repeated for pea gravel where resistivity values based on the AC impedance meter were four times higher than for the four-electrode method. They were 105,210 and 23,740 ohm-cm, respectively. It is believed that the point contact effect of gravel at the end plate surfaces is dominating over the bulk soil resistance. This suggests that, for double-bottom tank designs similar to these with gravel backfill, the true circuit resistance of the CP system may be much higher than implied by bulk gravel resistivity measurements using the four-electrode method.

### Corrosion Potentials

Corrosion potentials for the PG test did not change much throughout the test and were similar to freely corroding steel (approximately -700 mV) based on the Cu/CuSO<sub>4</sub> reference. There was a substantial negative shift of the Sand potentials within one week. This is possibly due to the consumption and lowering of oxygen levels within the tank during initial corrosion. A sudden upward shift in the Cu/CuSO<sub>4</sub> measurements occurred after about 40 days. The cause is not clear, but at the end of the test, the reference cell

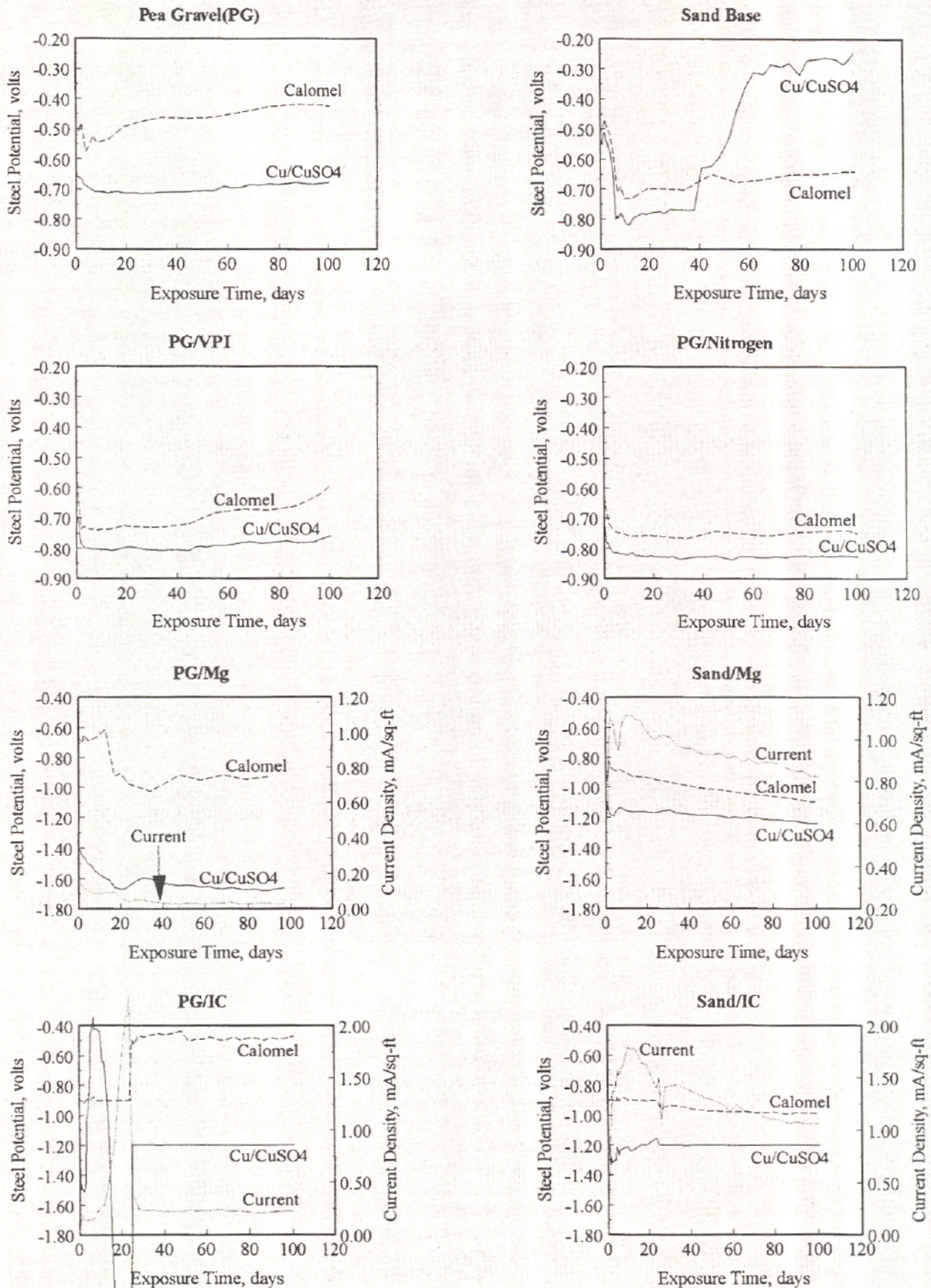
had a black scale completely covering the porous plug. The steel corrosion potentials of PG/Mg, as measured by both reference cells, were below -900 mV. Corrosion potentials and current measurements are illustrated in Figure 4.

Compared to the base case, the Cu/CuSO<sub>4</sub> measurements of the vapor phase inhibitor and nitrogen tests produced corrosion potential shifts of -100 and -150 mV, respectively. This differential persisted throughout the experiment. An upward trend began to develop in the VPI potentials toward the end of the test. This suggests that some longer term testing might under simulated field conditions be needed to fully assess its long-term effectiveness.

Instant-off measurements revealed that the Cu/CuSO<sub>4</sub> values for all tests with CP were driven to extremely negative values from IR drop effects. A typical instant-off curve is shown in Figure 5, with the measured data for all tests reported in Table 1. In Pea Gravel, the effect of IR drop on reference potentials was negligible for calomel and over 500 mV for Cu/CuSO<sub>4</sub>. In sand, the calomel IR drop increased to just over 200 mV, and the Cu/CuSO<sub>4</sub> IR drop lowered by approximately 200 mV.

Initially the impressed current systems were set to produce a Calomel reference potential of -900 mV. After three days of exposure, Cu/CuSO<sub>4</sub> steel potential became increasingly positive for PG/IC. After seven days, the calomel began to sense a positive shift, which required a large increase in current to maintain -900 mV. This also drove the Cu/CuSO<sub>4</sub> value to extremely low values. Considering the possibility that the calomel may be reading a local aberration, the potential under control was shifted for both impressed current tests to the Cu/CuSO<sub>4</sub> reference cells. The controlling voltage was changed to -1200 mV, which was the stable Cu/CuSO<sub>4</sub> potential of the Sand/IC test and similar to the corrosion potentials of the Sand/Mg test. This resulted in far more protection than would typically be used in the field.<sup>8</sup> Unlike the PG/IC test, the reference cell corrosion potential of Sand/IC remained stable throughout the 101-day test.





**FIGURE 4**  
Corrosion potentials and electrical current test data.



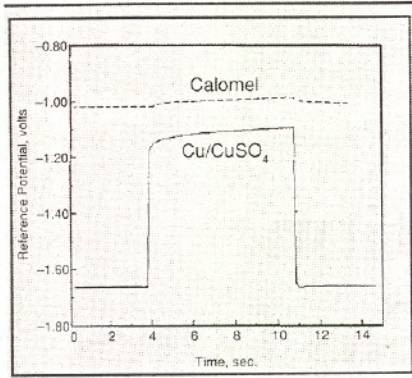


FIGURE 5

Instant-off curves for PG/Mg test.

That is, the current needed to maintain -900 mV while controlling off of the calomel reference did not drastically increase. Throughout the test, the current peaked at 0.166 mA/m<sup>2</sup> (1.78 mA/ft<sup>2</sup>) after 10 days, then decreased to 0.099 mA/m<sup>2</sup> (1.06 mA/ft<sup>2</sup>) at the end of the test. A current density greater than 0.093 mA/m<sup>2</sup> (1.0 mA/ft<sup>2</sup>) is within what is roughly considered adequate protection.<sup>9</sup> Based on visual examination and measured pitting rates, impressed current was clearly insufficient to prevent corrosion.

### Conclusions

- The conditions within the sealed annulus of a double-bottom storage tank significantly change the corrosion behavior and must be simulated to properly evaluate the effectiveness of corrosion protection methods.
- Pitting was not totally mitigated by CP methods. Only in tests in which the oxygen levels were substantially reduced was pitting arrested. Oxygen that is generated by impressed current anode systems is retained within closed systems and supports continued corrosion.
- Systems with pea gravel backfill and magnesium anodes provided the best protection against pitting attack of those tested.
- Installation of impressed current CP designs should not be used in the annular space of double-bottom storage tanks.
- Nitrogen purge is effective in controlling corrosion in moisture-saturated conditions, and it is the only tested method that is easily renewable in the field.

TABLE 1

Instant-Off and IR Drop Voltages for Tests with CP

Test Type	IR Voltage Drop		Instant-Off Potential	
	Calomel	Cu/CuSO <sub>4</sub>	Calomel	Cu/CuSO <sub>4</sub>
PG/Mg	0.010	0.502	-1.009	-1.161
Sand/Mg	0.231	0.306	-0.796	-0.890
PG/IC	0.079	0.664	-0.397	-0.562
Sand/IC	0.200	0.354	-0.783	-0.859

- Vapor phase inhibitor is effective in controlling corrosion in moisture-saturated conditions.
- For double-bottom tank designs with gravel backfill, the true circuit resistance of the CP system may be four times higher than calculated when based on soil resistivity measurements using the four electrode method.

### References

1. D.H. Park, "Cathodic Protection of Aboveground Tank Bottoms with Secondary Containment Liners," *Materials Performance (MP)* 30, 4 (1991): pp. 22-25.
2. S.F. McJones, "Retrofitting Hot Service Storage Tanks with Double Bottoms and Improved Cathodic Protection," *MP* 31, 5 (1992): pp. 25-29.
3. D.H. Kroon, "Tank Bottom Cathodic Protection with Secondary Containment," *CORROSION/91* paper no. 579, (Houston, TX: NACE, 1991).
4. D.H. Kroon, "Cathodic Protection for Above Ground Tank Bottoms," *Pipe Line Industry*, 6 (1992): pp. 23-28.
5. M.G. Fontana, N.D. Greene, *Corrosion Engineering* (New York, NY: McGraw-Hill Inc., 1967), pp. 53-54.
6. H.M. Herro, "Tubercle Formation and Growth on Ferrous Alloys," *CORROSION/91* paper no. 84, (Houston, TX: NACE, 1991).
7. NACE Standard RP0775-91, "Preparation and Installation of Corrosion Coupons and Interpretation of Test Data in Oilfield Operations," (Houston, TX: NACE, 1991).
8. NACE Standard RP0169-83, "Control of External Corrosion on Underground or Submerged Metallic Piping Systems," (Houston, TX: NACE, 1983).
9. A.W. Peabody, *NACE Basic Corrosion Course, Principles of Cathodic Protection*, (Houston, TX: NACE, 1970), pp. 16-21.

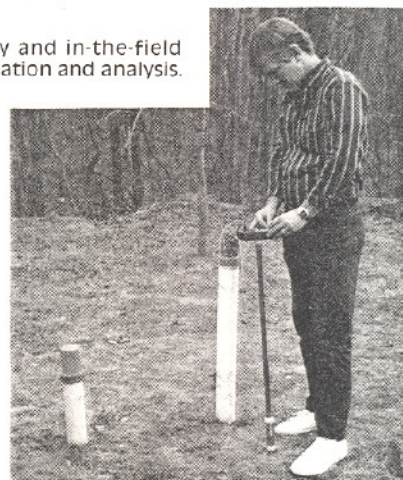
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