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The Corrosion Coulometer – A New Corrosion Monitor for Steel Structures

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ADVANCED TECHNOLOGY FOR LARGE STRUCTURAL SYSTEMS

Lehigh University

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by

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ABSTRACT

A new type of corrosion monitor (corrosion coulometer) has been developed for use on steel structures. It is designed to incorporate corrosion products and air borne contaminants into the system in order to simulate actual conditions in a structure. It operates as a galvanic cell when wet and uses a microcoulometer to store the electrical output, although instantaneous voltages and/or currents may also be monitored. Evaluation in the laboratory by monitoring successive wet/dry cycles and exposure on the roof of a building at Lehigh University for 20 weeks showed excellent correlations with corrosion of adjacent steel panels. It was estimated that the cell should have a lifetime of at least four years.

I. Introduction

An observation frequently made concerning corrosion of steel structures is that the most serious attack on the steel is in areas where there is an accumulation of debris and corrosion products [1]. In the case of weathering steels, there can also be severe pitting underneath [2]. This problem has been studied in automobile bodies, where debris and road dirt can collect in crevices, wheel wells and other entrapment areas. The accumulation is referred to as "poultice" and can result in severe corrosion of the auto body, although the chemistry occurring in the poultice is complex and varies with geographic location and whether the material is continually wet or has wet/dry cycles [3].

No similar work has been reported for larger steel structures, but there is no doubt that the same effects should occur. The effects of ionic contaminants, particularly chlorides, on the "critical humidity" necessary for rusting to occur have been well documented [4,5]. In addition, chlorides accelerate corrosion. Any debris on the steel that holds moisture exacerbates the effect of ionic contaminants.

Despite the known influence of debris accumulation on corrosion, the corrosion monitors that have been described do not include provisions for this effect. There are devices that measure polarization curves [6], impedance [7,8], or time of wetness [9,10], but these do not include the effect of poultice on the output. A related investigation was carried out by Agarwala [11] who compared the output of several galvanic cells in laboratory-simulated environments and concluded that the copper/steel probe was the most responsive (compared to copper/aluminum and steel/aluminum). The primary interest in Agarwala's work, however, was in monitoring marine corrosion, so no attempt was made to accumulate debris to simulate what might occur on a bridge structure.

In order to take into account the effect of debris accumulation, it was apparent that a new type of cell would have to be designed, built and tested for use on steel structures exposed to atmospheric corrosion environments, such as airborne contaminants, road dirt and miscellaneous debris. This report summarizes the successful accomplishment of this effort.

II. Design and Construction of Corrosion Monitor

The intent of the design of the corrosion monitor was to have a system that would incorporate corrosion products and collect airborne contaminants over a long period of time and would record the amount of corrosion occurring during that time. The simplest way of doing the latter is by means of an electrical signal and a convenient way of generating such a signal is with a galvanic cell. Thus, a cell was designed that incorporated these features.

The cell is shown in Figure 1. A standard 1 3/4" diameter copper end cap (obtained from a plumbing supply house) formed the basic container and one electrode. The height of the cap was cut down to 5/8" and the inside of the cap cleaned by abrading with steel wool or fine SiC paper. Several 3/16" holes were drilled in the bottom for drainage and a piece of filter paper (Whatman #4) was cut to fit the inside bottom. On top of this was placed a single layer of solid glass beads 3 mm in diameter. An "O" ring, 3/32" thick and 1 5/8" outside diameter was put on the inside bottom of the cap to keep the beads away from the inner perimeter so that better contact was made between the screen and the glass beads; without this "O" ring, the split tubing around the screen would rest on the beads and the screen would be held away from the beads.

A piece of 14 × 14 mesh screen, either carbon or stainless steel, was cut into a 1½" diameter circle for the other electrode. This screen was put on top of, and in contact with, the glass beads, after a piece of tygon tubing,

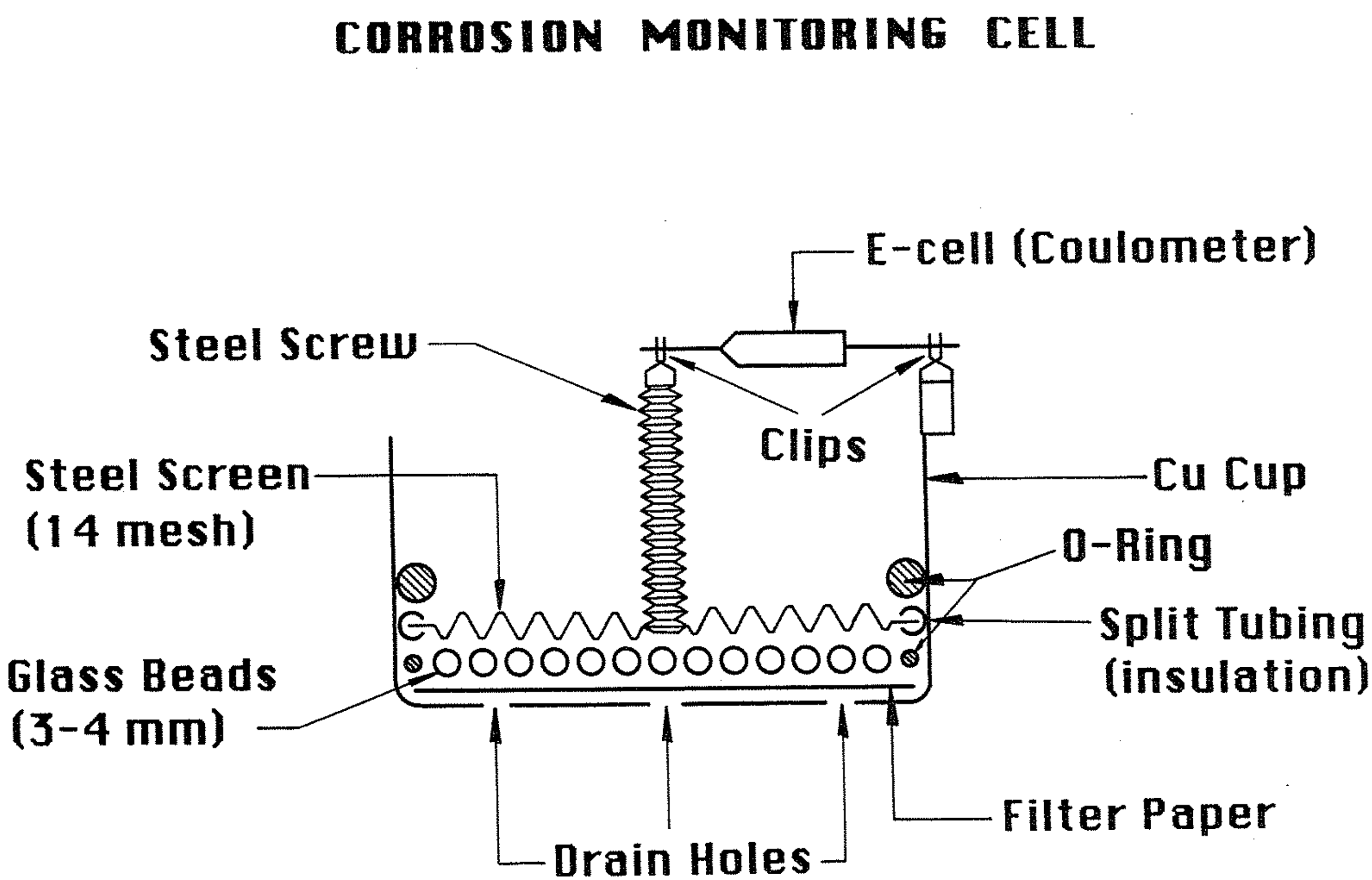

Figure 1. Corrosion Monitoring Cell

1/8" outside diameter and 1/32" wall thickness, was slit and put around the perimeter of the screen so that it would not contact the copper cup. Another "O" ring, this one 1/8" thick and 1-11/16" outside diameter was forced into the cup (1-5/8" inner diameter) to hold all the components together in the cell, so it could be used in any position.

To make electrical connection to the screen, a machine screw (either cold rolled or stainless steel) is put through the screen and into the threaded end of a Mueller alligator clip. A copper Mueller clip is fastened to the edge of the cup with a copper screw. With these two connections, it is possible to measure the potential and currents developed when the cell is wet. In order to monitor the electrical output of the cell continuously, a microcoulometer was clipped to the two electrodes and used to measure the total output of the cell during wet/dry cycles. The one chosen is called an E-cell* which operates on the principle of plating silver on a gold electrode to accumulate quantitatively the number of coulombs (current × time) generated by the cell. The cell is then "read" and "cleared" for the next cycle by a controlled deplating to measure the amount of accumulated charge in microcoulombs. The coulometric data are a convenient way to measure the total output of the cell. When used in this way, the cell is referred to as a "corrosion coulometer".

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*Series 560, Pacific Electron Corporation, Sterling Heights, MI 48077.

III. Laboratory Studies

A. Experimental. When the cell is saturated with water and is generating a potential because of the galvanic cell operating, the output can be read in either of two ways: (1) as an instantaneous current (or potential); or (2) as a summation of the total charge generated, using a micro-coulometer as discussed in the previous section. The cell was initially operated in the laboratory by filling it completely with water (or a solution) and then periodically recording both the current and potential as it dried at room temperature. These are referred to as wet/dry cycles. The total charge generated was also determined, using the coulometer. By weighing the cell periodically, the percent saturation with the solution can be calculated, knowing the original (after saturation) and final (dry) weights.

Three solutions were used for this study: (1) deionized water; (2) water adjusted to a pH of 4.5 with sulfuric acid ($3\times10^{-5}M\ H_2SO_4$) to simulate acid rain; and (3) a 1 ppm NaCl solution to simulate salt contamination on a structure such as a bridge.

After the initial filling and draining of each cell, current and potential readings were made and are referred to as initial readings. The cells were then allowed to dry at room temperature for 40 to 50 hours. The micro-coulometers were read, the cells resaturated, and the procedure repeated.

The rust was removed from the carbon steel screens by treating with 10% H_2SO_4 containing 2% Rodine 95* at 75°C for 2-3 minutes, or until all visible corrosion product is removed. This solution has a minimal attack on unoxidized steel, so the weight loss after treatment represents the amount of steel rusted.

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*Amchem Products, Inc., Ambler, PA.

B. Results

1. Current/Potential Data

When the cells are saturated with solution, there is an immediate onset of a potential due to the galvanic cell action between the cup and the iron screen. Current and potential readings* were made periodically as the cell began to dry out. Figure 2 is a typical plot of the two measurements as a function of the percent saturation for a cell saturated with DI water. The current shows a continuous decline from about 50 μA at 100% saturation (initial condition) to 0 μA when the cell is completely dry. The voltage, as would be expected, stays at about 500 mV until 80% of the water has evaporated and then rapidly drops to 0 mV. Since the current was the measurement of primary interest, only these values will be shown in subsequent plots.

Figure 3 shows the current versus saturation plots for the initial wet/dry cycle for the three solutions evaluated. Interestingly (and surprisingly) the DI water had the highest initial current, with the NaCl solution next lower, and the acidified water the lowest. At about 40% saturation the curves all come together.

2. Initial Currents

The initial currents, measured right after saturation, were determined for each wet/dry cycle and are shown in Figure 4 for the cells with steel screens for each of the three solutions. The DI water shows the most rapid dropoff in values, with the pH 4.5 and NaCl solutions behaving similarly. This decrease of current is due to the build-up of corrosion products (rust) on the screens which act as an insulator for the anodic part of the galvanic cell. The higher current values for these solutions are due to their higher

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*Readings were made with a Beckman Tech 300 Digital Multimeter.

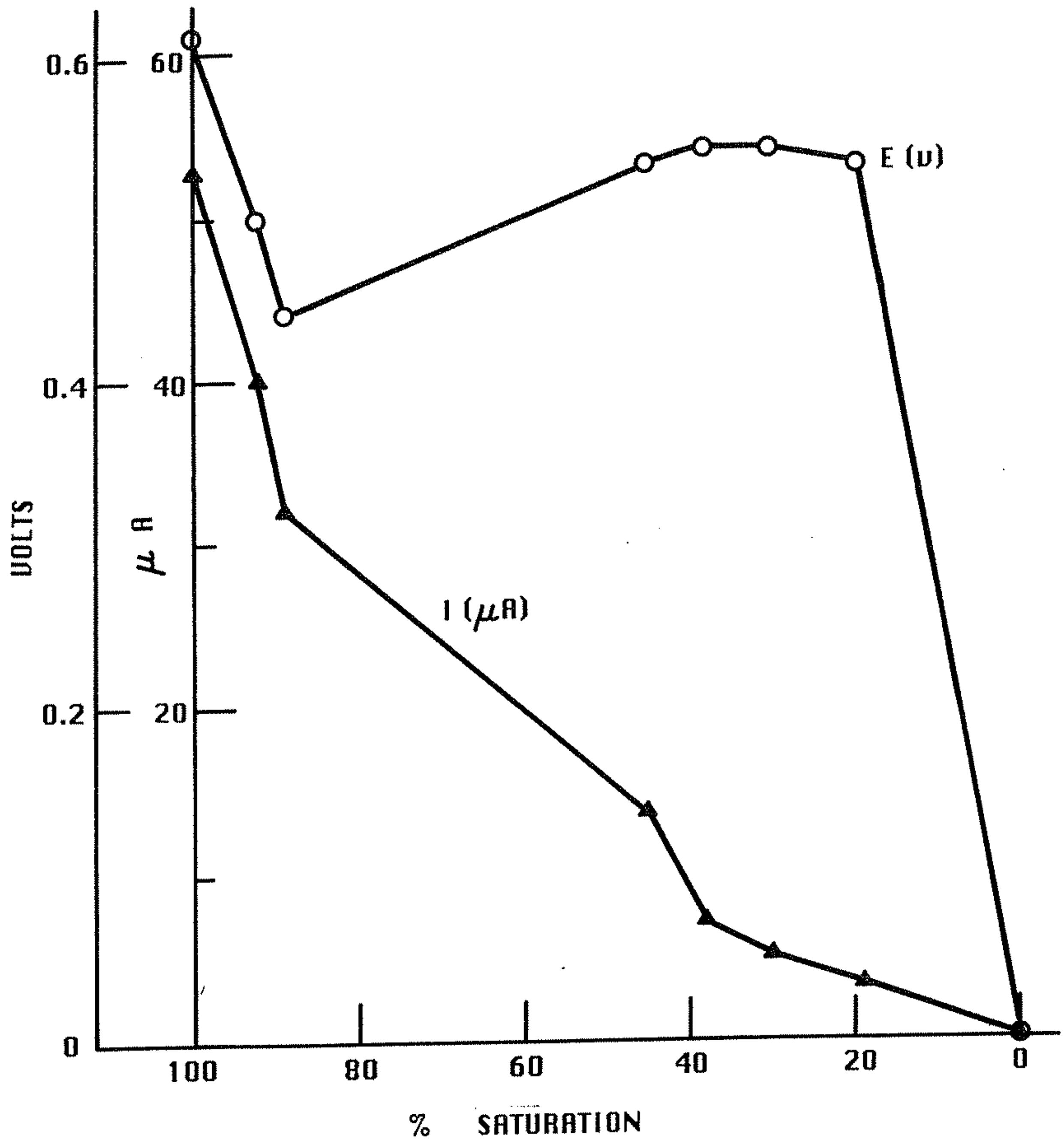

Figure 2. Drying Curve for DI Water in Cell

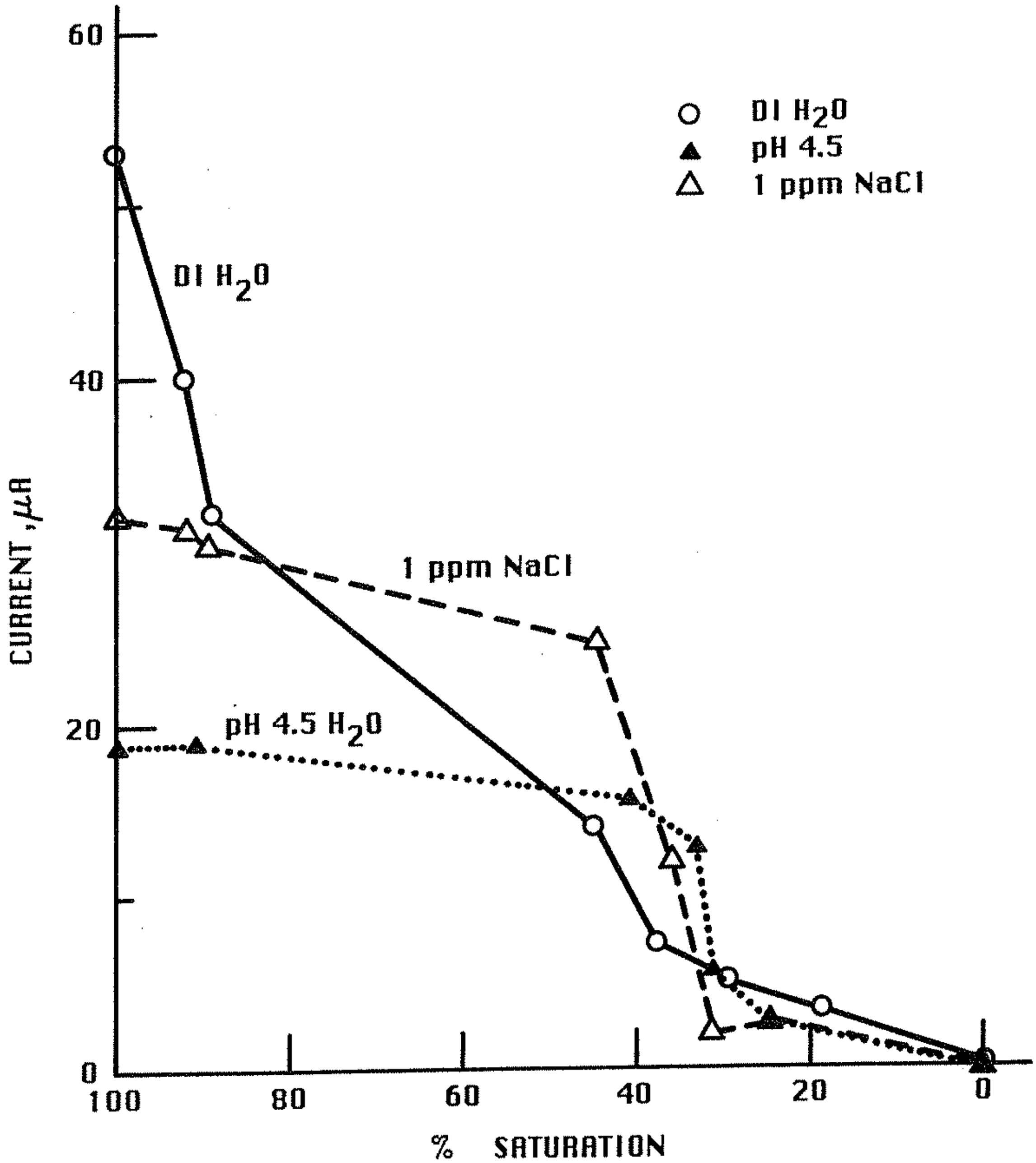

Figure 3. Drying Curves for Solutions on First Cycle

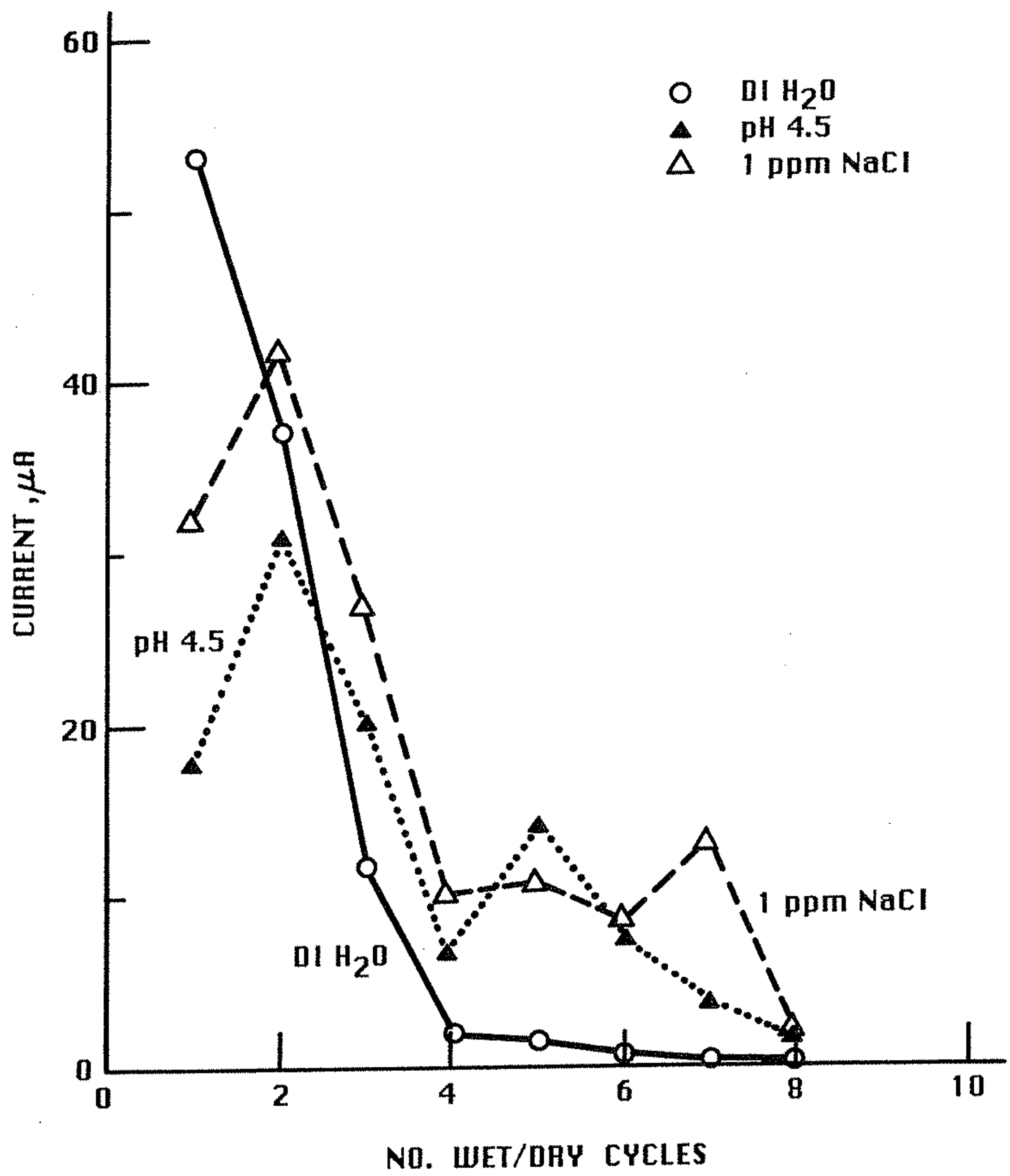

Figure 4. Initial Currents with Carbon Steel Screens

conductivity.

Figure 5 is a plot of the initial currents for the two cells with the stainless steel screens. The values are about 1/50 of those for the carbon steel screens and show a much more erratic behavior, some of which may be due to the low current values which are near the limits of measurement of the meter (0.1 μA).

3. Coulometer Readings

The E-cells were read after every two cycles. Figure 6 is a plot of the current passed (in coulombs) for the carbon steel screens for each of the three solutions. All three show similar behavior—a decreasing charge passed up to eight wet/dry cycles and then an increase in the tenth cycle. Figure 7 shows the same values for the cells with the stainless steel screens. The values are about 1/20 of those for the carbon steel screens.

4. Corrosion of Screens

At the end of ten wet/dry cycles the screens were stripped to remove all of the rust and the weight loss determined to assess the amount of corrosion that had occurred. Table 1 shows these values. The weight loss is about the same for all the solutions at about 6%, with the DI water having the most corrosion, the 1 ppm NaCl next and the pH 4.5 the least. Extrapolating from these values, the screens should last for at least 160 wet/dry cycles before they completely corrode away. The actual lifetime is probably considerably longer than this, because the data presented suggest that the corrosion rate slows as the amount of corrosion product increases.

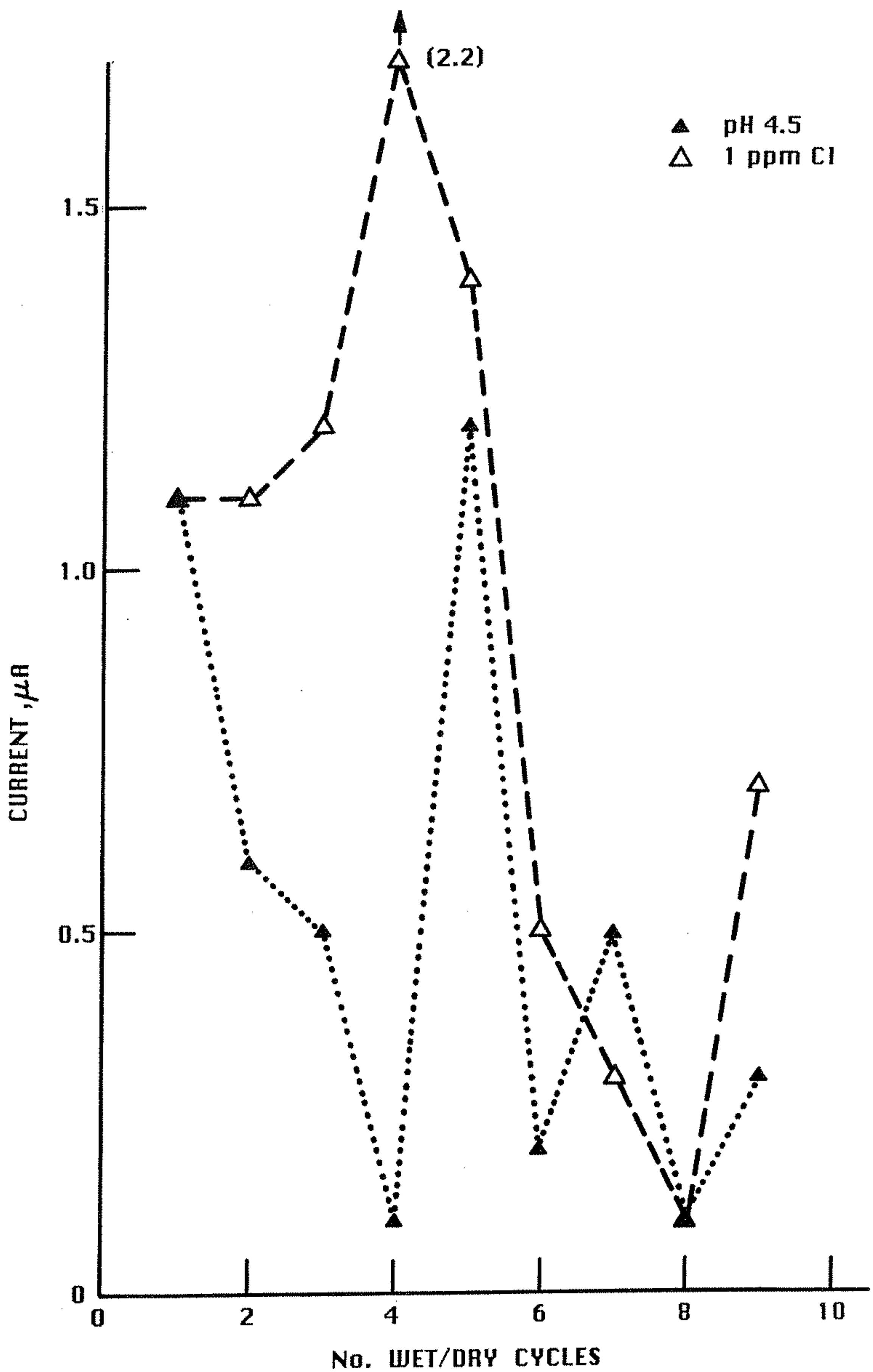

Figure 5. Initial Currents with Stainless Steel Screens

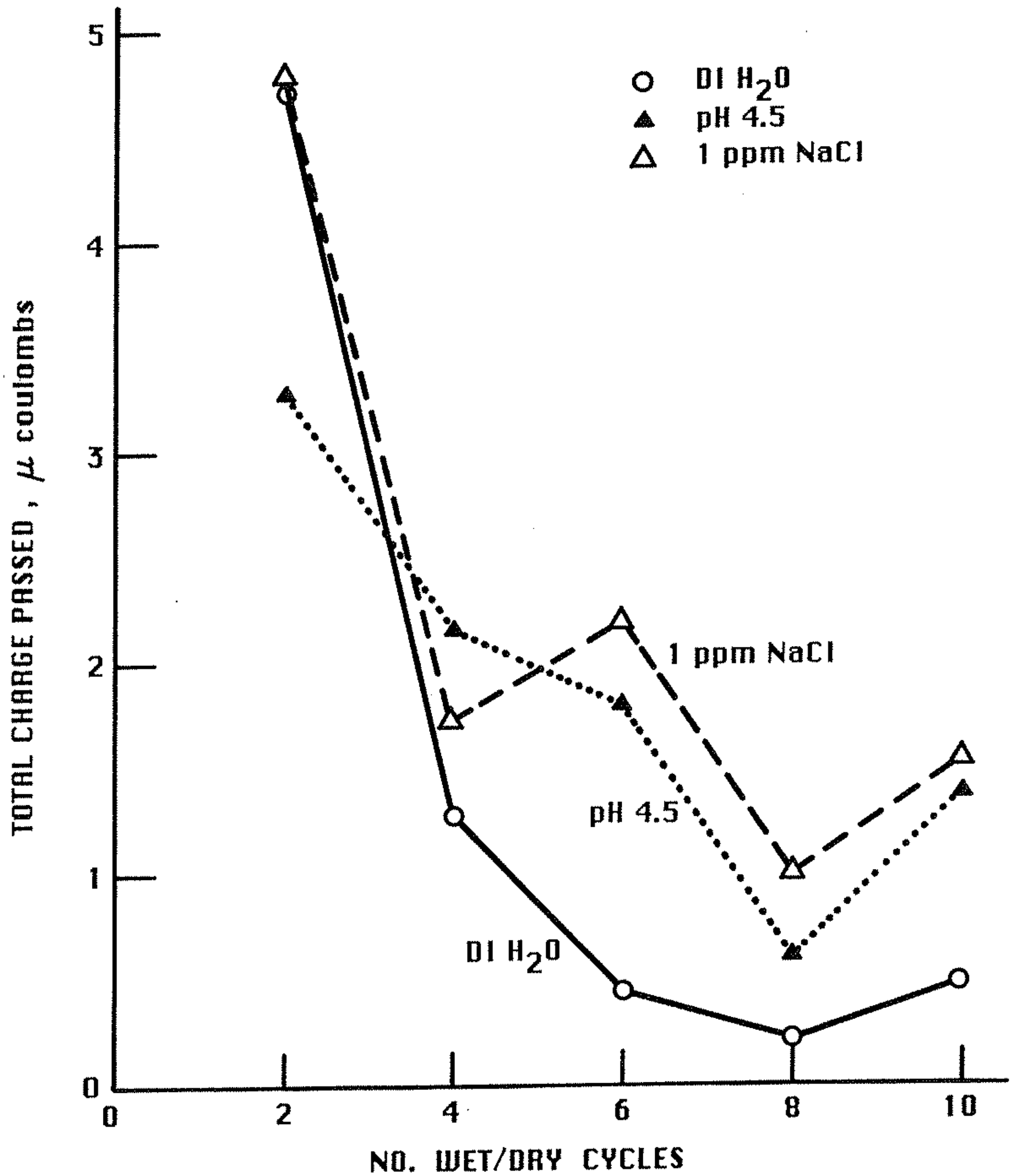

Figure 6. Coulometer Readings with Carbon Steel Screens

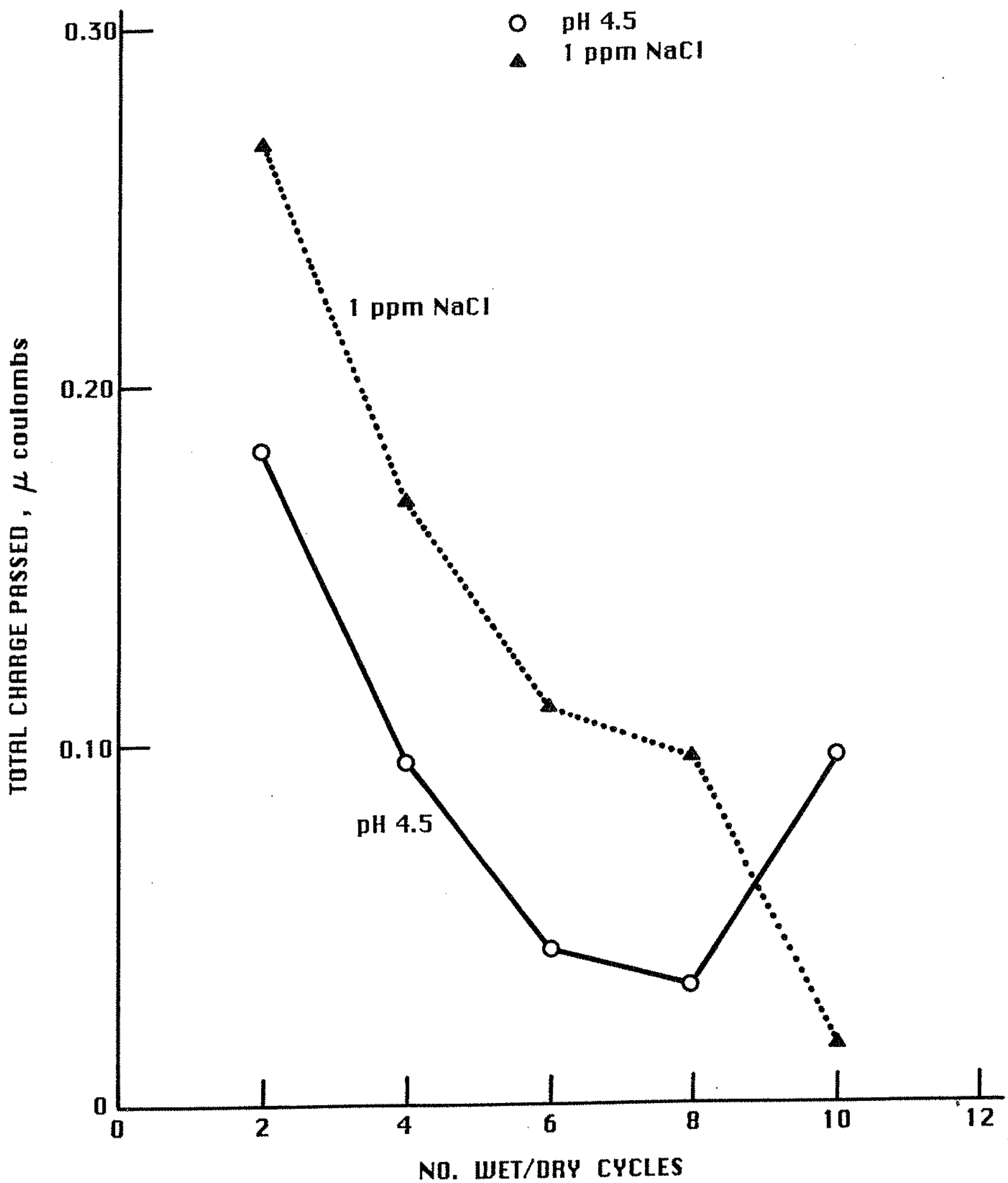

Figure 7. Coulometer Readings with Stainless Steel Screens

Table 1

Weight Loss of Screens after Ten Cycles

Solution Used in Cell	Wt. Loss, mg.	% Weight Loss
DI H_2O	418	6.7
pH 4.5	336	5.6
1 ppm NaCl	399	6.4

C. Laboratory Study Summary and Conclusions

1. The corrosion coulometer cell with a carbon steel screen generates about 0.6 volt when wet with DI water and an initial current (short circuit) of about 50 microamps. The cell completely dries out and the voltage and current drop to zero in 40-50 hours in a laboratory atmosphere.

2. When 3×10^{-5}M H_2SO_4 (to simulate acid rain at pH 4.5) is used in the cell, the initial current is about 20 μamps in the cell.

3. When the cells are successively saturated with the solutions and allowed to dry, the initial currents decrease with each successive wet/dry cycle over a period of eight cycles.

4. When the total charge generated is measured with a coulometer, the values decrease up to eight wet/dry cycles, but then show an increase at the ninth and tenth cycles.

5. When a stainless steel screen is used in the cell, the currents and charge generated are over an order of magnitude less than with the iron screens, but show generally similar behavior on drying.

6. This laboratory evaluation has shown that the corrosion coulometer cell responds to the presence of water or dilute acid/salt solutions to generate currents which can be monitored. The output of the cell can also be determined by measuring the total charge generated with a coulometer.

IV. Field Exposure

A. Experimental

In order to test the cell under more realistic conditions, several corrosion coulometer cells were assembled and placed on the roof of a building at Lehigh University along with a rain gage and a commercial corrosion monitor that works on the principle of expansion of stacked disks as crevice corrosion occurs. Steel panels, in several configurations, were also exposed at the same time and used to determine the extent of actual corrosion. One purpose of this exposure was to determine the relationships between the two monitoring techniques (corrosion coulometer and crevice/expansion technique), rainfall and the extent of corrosion of the steel panels. All the devices were kept on the roof for 20 weeks, from March 14 to August 3, 1988.

Two corrosion coulometers with carbon steel screens and one with a stainless steel screen were mounted on a lucite board so that they could drain freely through the holes in the bottom of the cell after being wet by rain. The E-cell coulometers were kept on the cells during the test, but were removed and read periodically.

Around the cells on the lucite board were mounted 1½" square steel coupons (Q/R panels) in three positions: vertical, horizontal and a 45 degree angle. When the E-cells were removed for reading, the oxide was stripped off the panels and a weight loss determined in order to evaluate the amount of corrosion occurring during the same time period. The stripped panels were returned to the board for further exposure. A photograph of this setup is shown in Figure 8.

The commercial corrosion monitor used was an ECM (Environmental Corrosion Monitor) from Cormon, Ltd., Lansing, West Sussex, England. This piece of equipment consists of a stack of cold-rolled steel washers around a non-corrodable central core. The expansion of the stack of washers, as rust

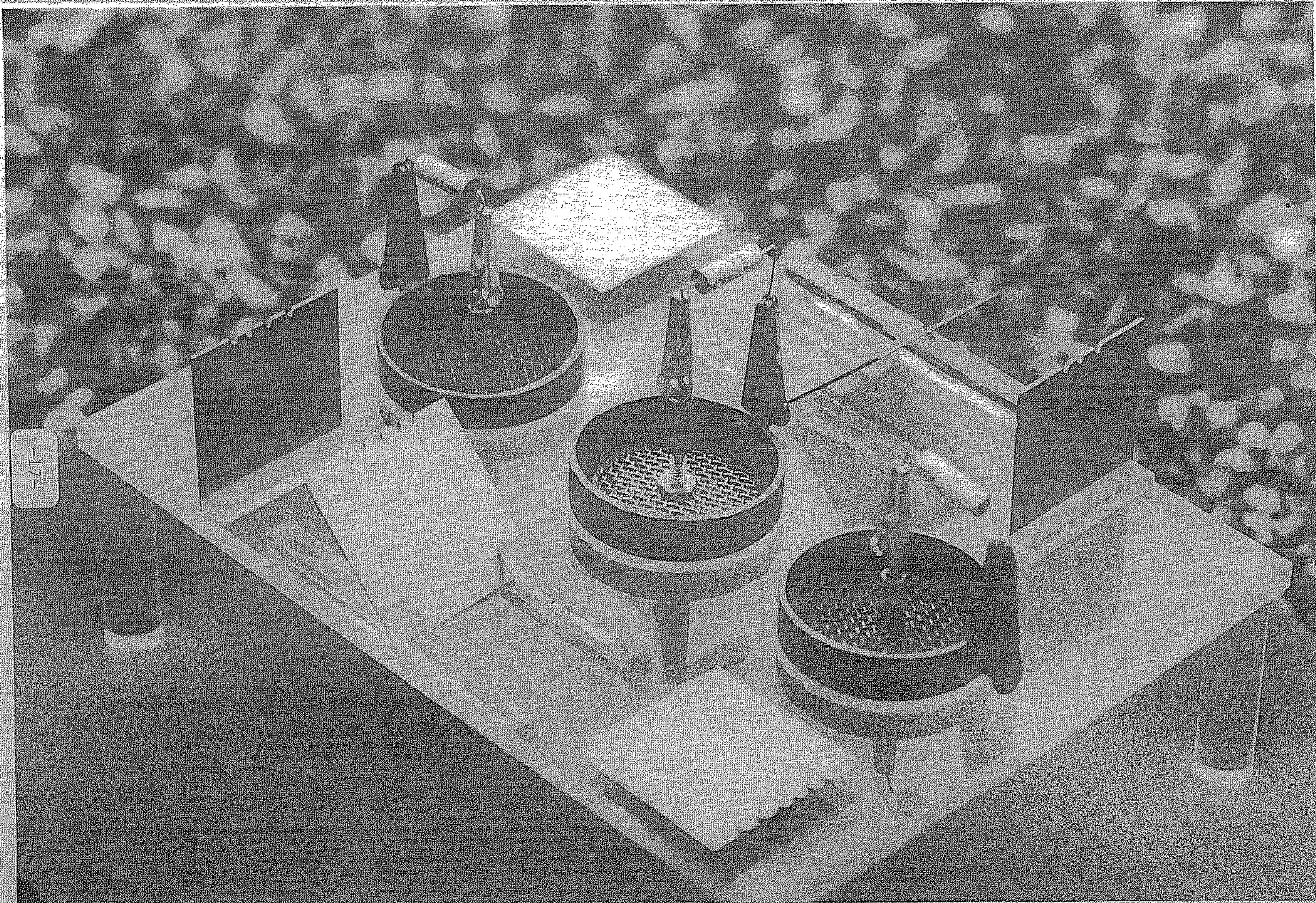

Figure 8. Corrosion Coulometer and Steel Panel Exposure Setup on Roof

builds up between the washers, is measured with a displacement gage. This "jacking" rate has been shown to correlate with corrosion on a group of transmission towers in England [12].

A rain gage that could record 0.01 inch of rain was placed on the roof near the ECM and corrosion coulometers. Readings were made at approximately one-week intervals. The rain gage was emptied and the E-cells read and cleared every time, but the ECM was allowed to accumulate readings.

B. Results

Figure 9 is a plot of the weight losses (after oxide removal) of the duplicate steel panels mounted with the corrosion coulometers on the roof of Sinclair Laboratory. As expected, the vertically mounted panels showed less corrosion than the horizontal panels, with good agreement between duplicate panels. The horizontal panels showed more variability.

The average values for weight loss for the three duplicate panels are shown in Figure 10, along with the cumulative rainfall for the same period. The panel angled at a 45° showed a very similar corrosion rate to the vertical panel. The rainfall curve followed the horizontal panel corrosion quite closely for the first ten weeks, but during a relatively dry spell the corrosion continued at approximately the same rate.

The ECM readings (jacking rate) with exposure time are shown in Figure 11, along with the cumulative rainfall. The relationship between the two appears to be very good.

Figure 12 shows the E-cell (coulometer) readings for the two cells that were exposed on the roof. Although there is some variation between the two, particularly after the tenth week, the amount is not large and the trend is similar. The average value of the two cells with carbon steel screens is shown in Figure 13, along with the cumulative rainfall. Figure 14 is the same

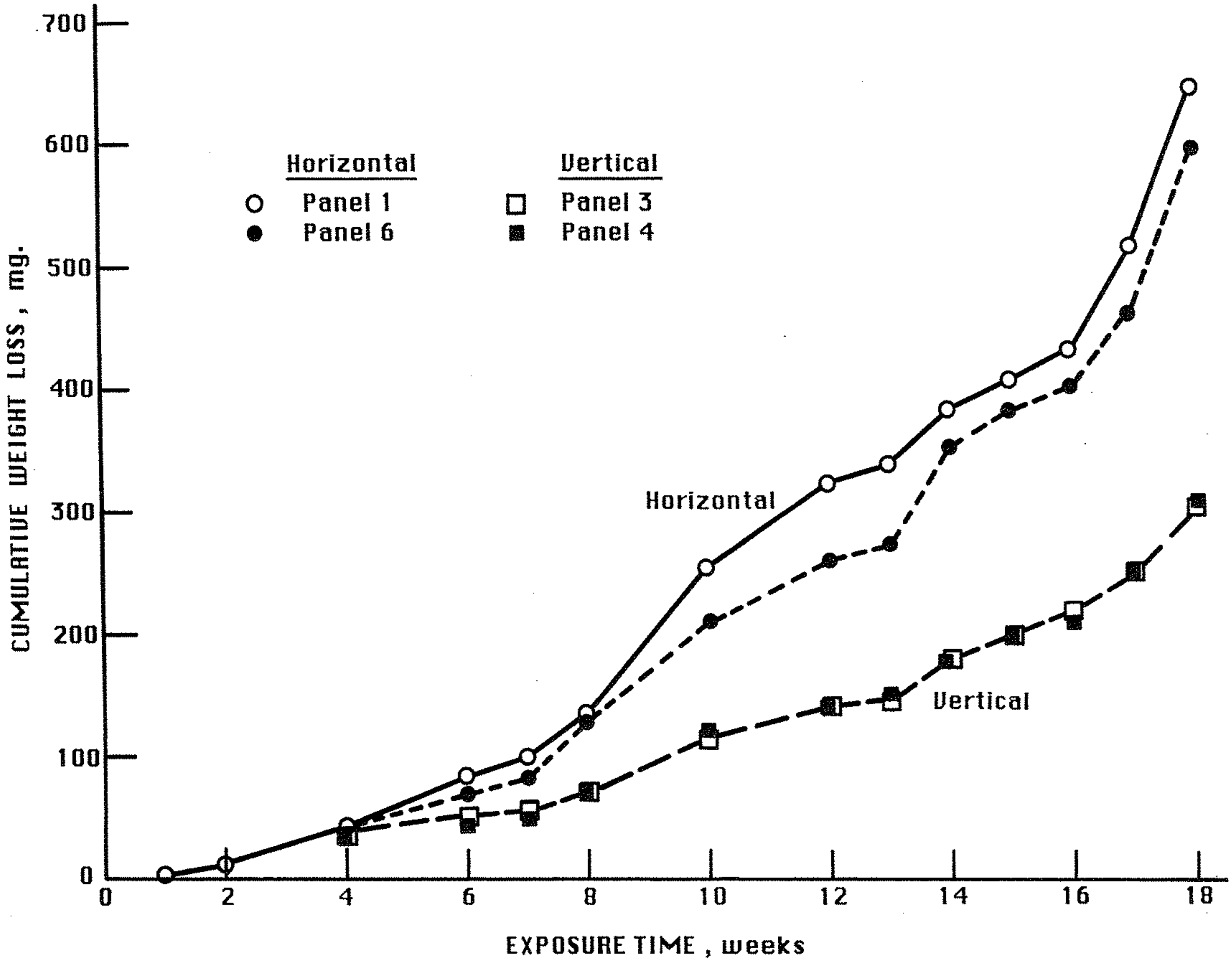

Figure 9. Cumulative Weight Loss of Steel Panels on Roof (Individual Values)

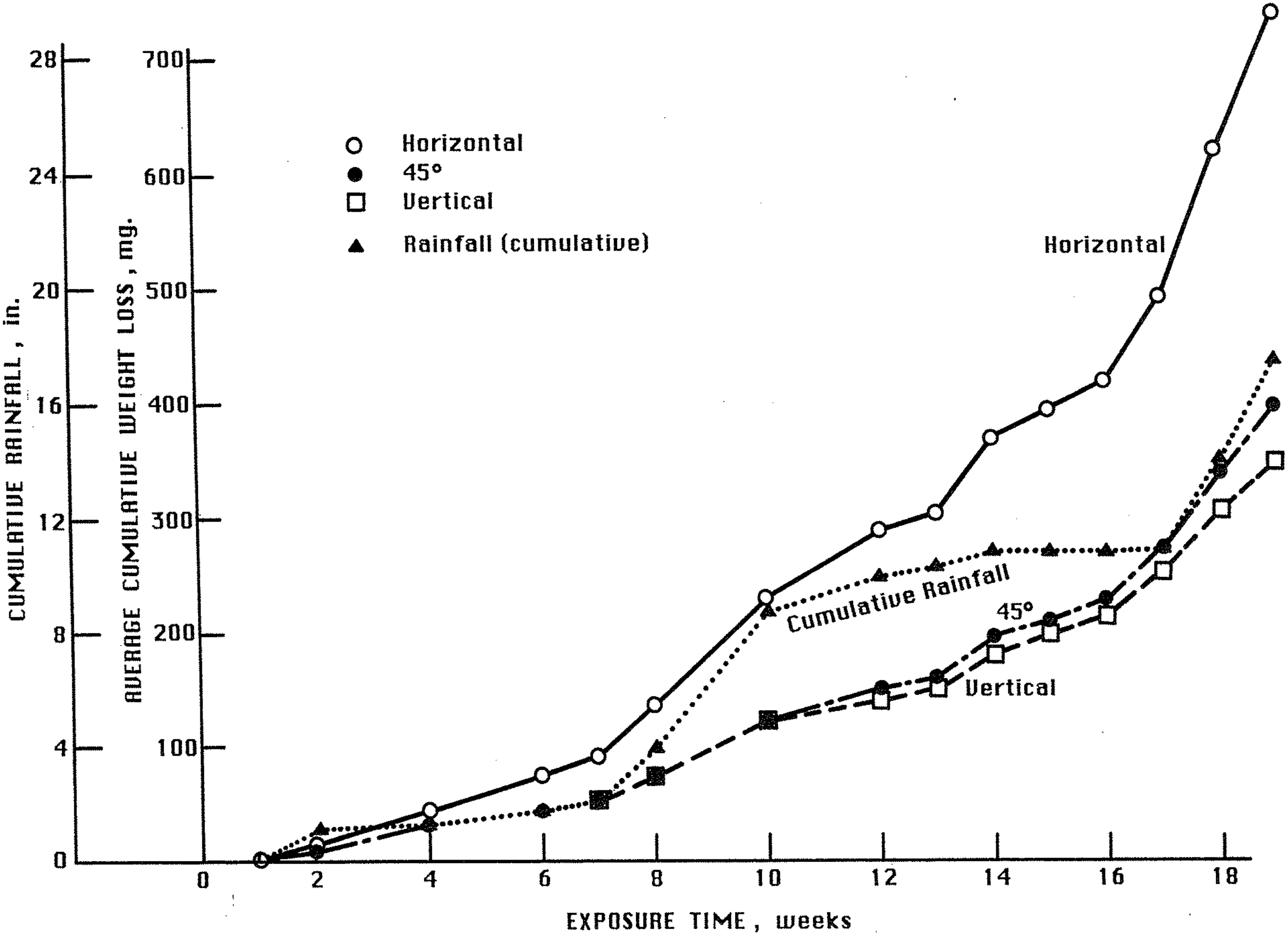

Figure 10. Cumulative Weight Loss of Steel Panels on Roof (Average Values) and Cumulative Rainfall

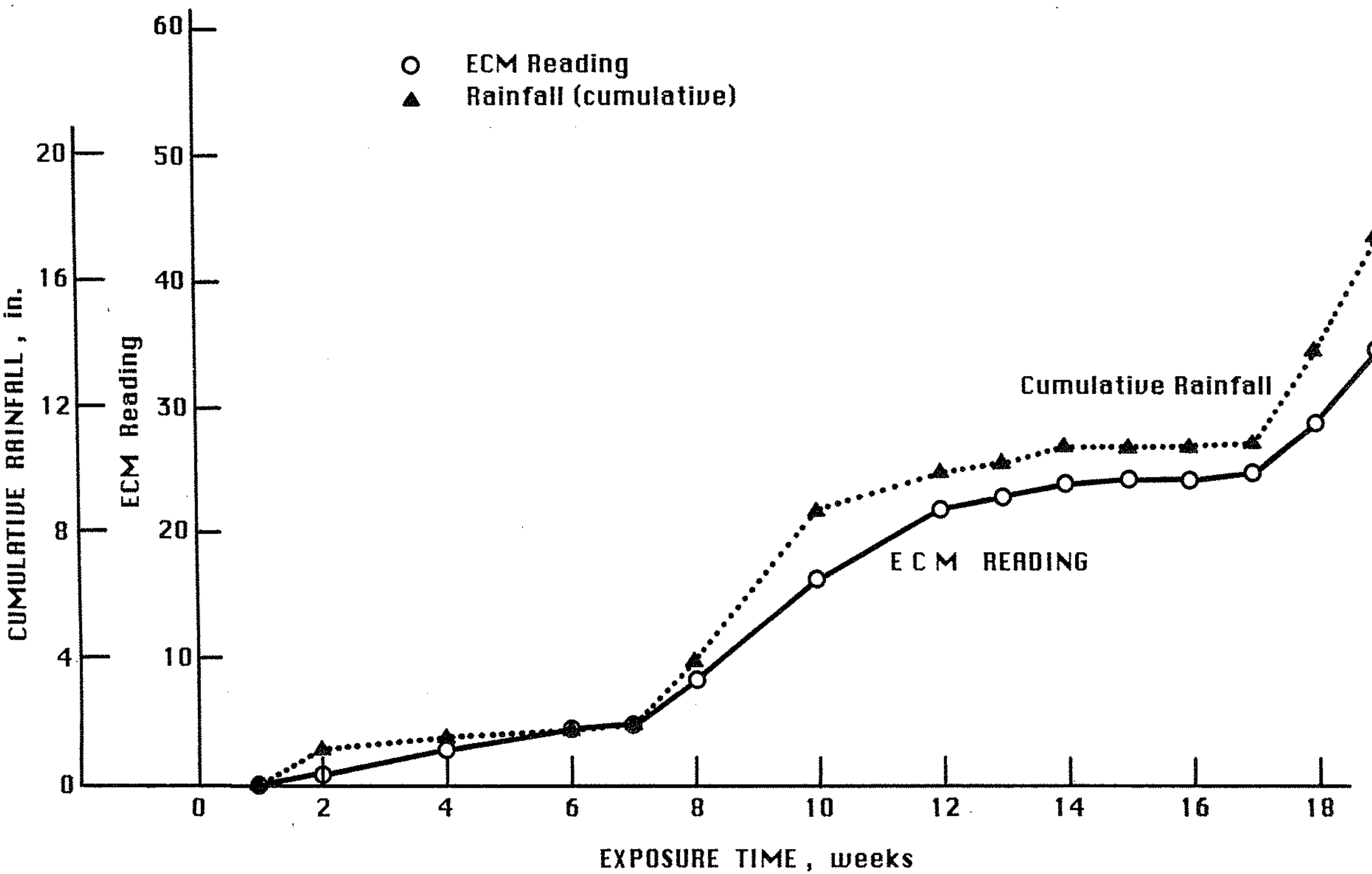

Figure 11. ECM Reading on Roof and Cumulative Rainfall

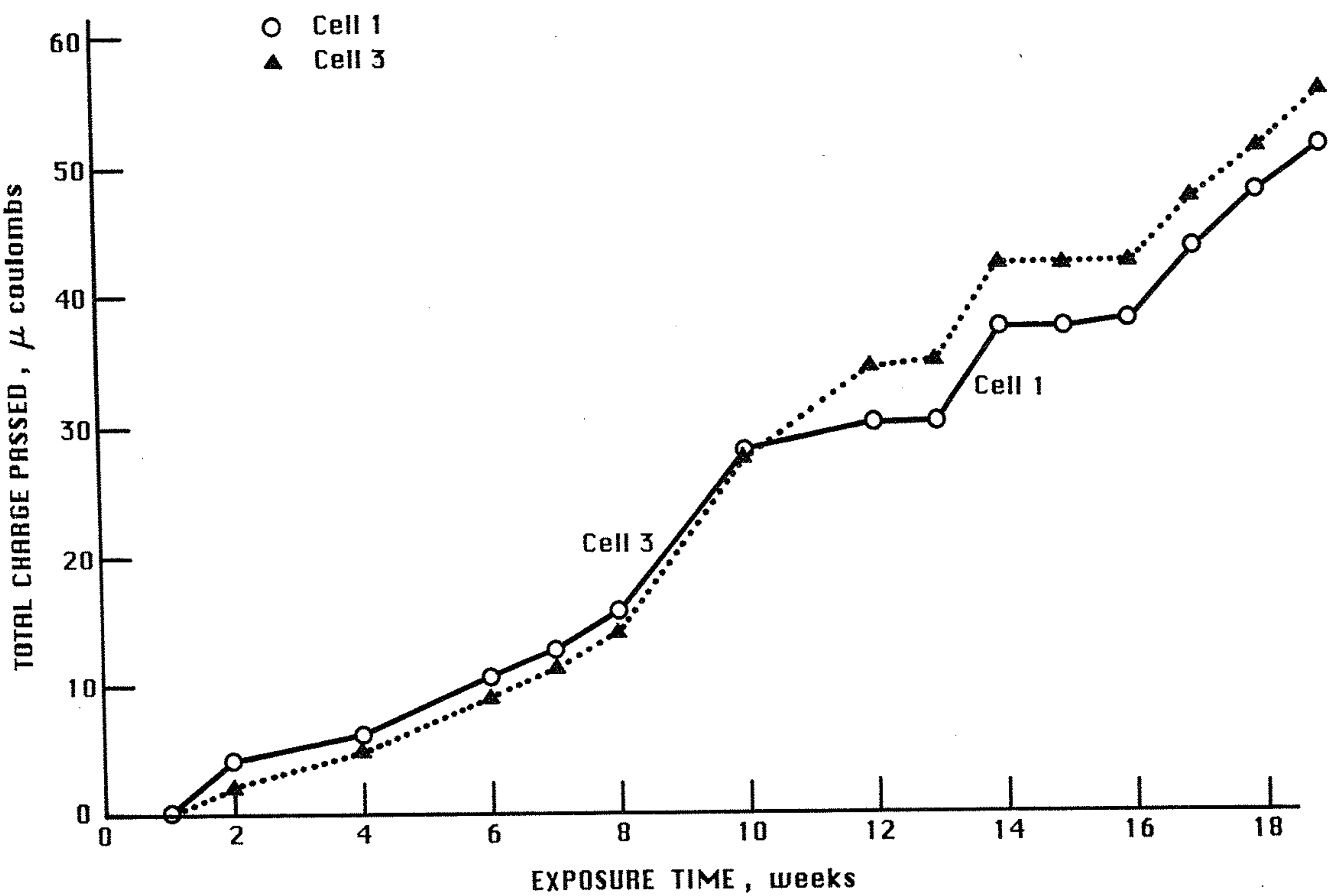

Figure 12. Coulometer Readings for Individual Cells

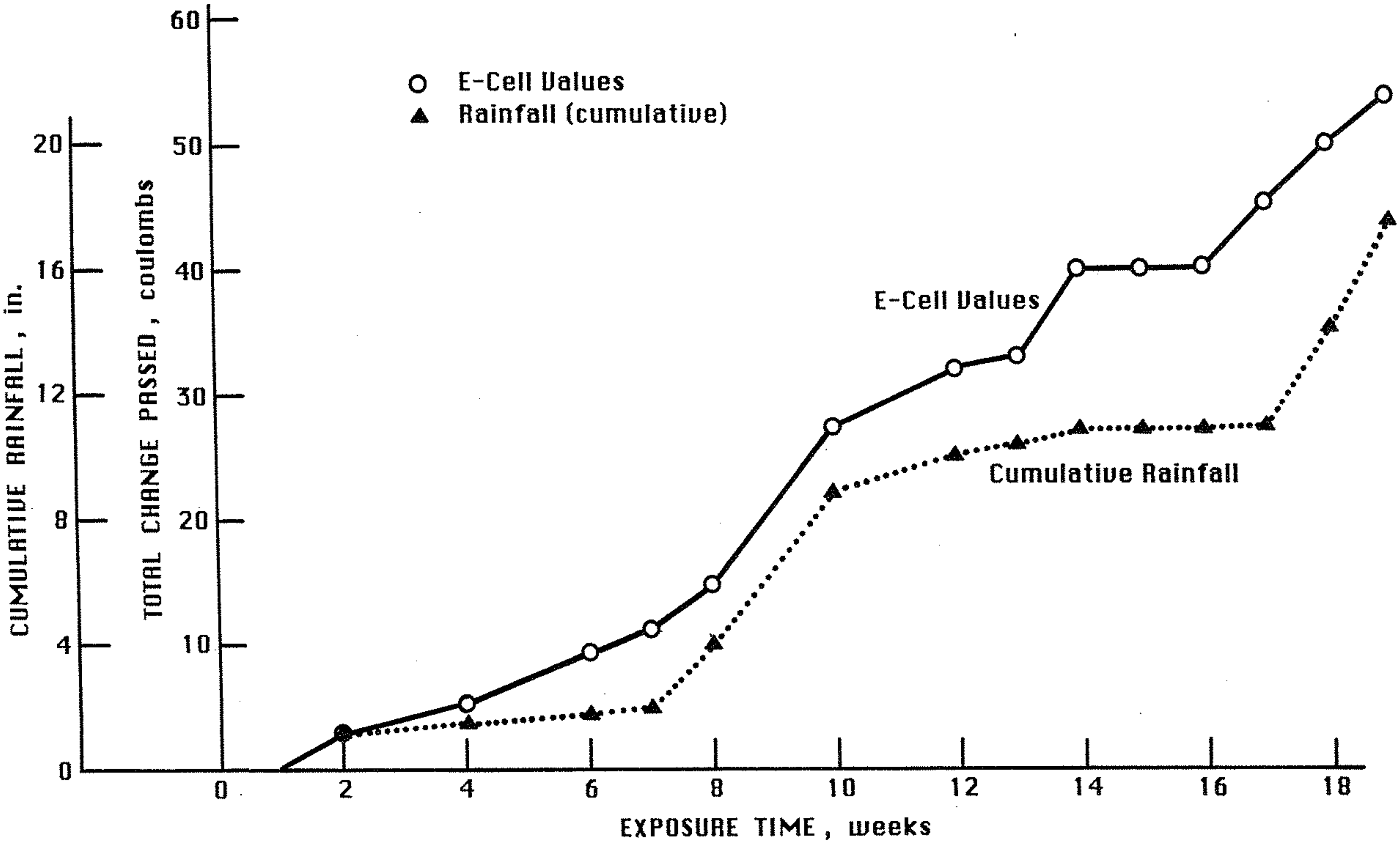

Figure 13. Coulometer Readings of Cells (Average) with Carbon Steel Screens Exposed on Roof

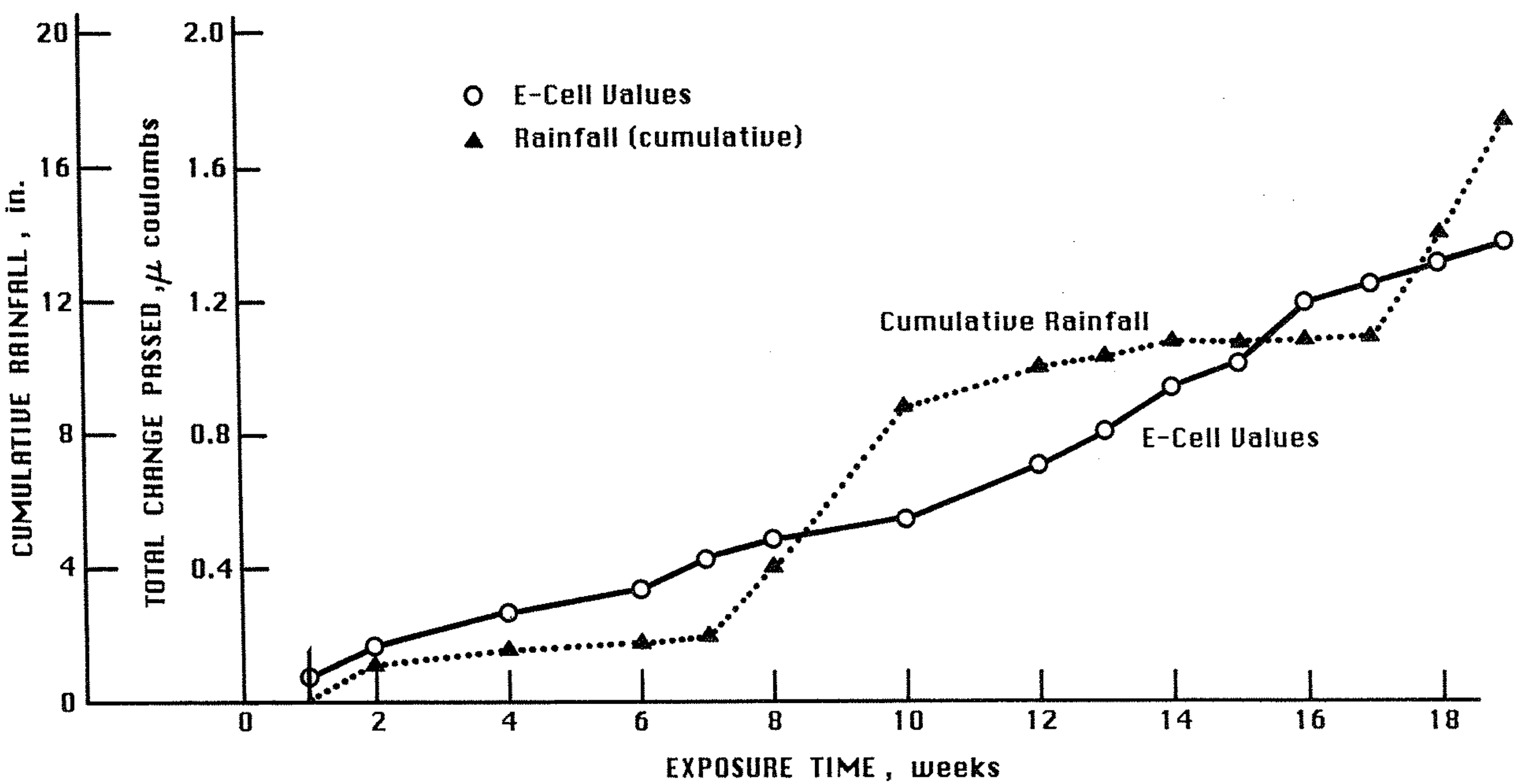

Figure 14. Coulometer Readings of Cells (Average) with Stainless Steel Screens Exposed on Roof

plot for the cells with stainless screens.

Since the primary purpose of this study was to develop and evaluate corrosion monitors, plots were developed to relate the three measurements made (rainfall, ECM/jacking and corrosion coulometer readings) to corrosion as measured by weight loss of the steel panels, all exposed on the roof. These relationships are shown in Figures 15-18, where the measurement is plotted against the cumulative weight loss of the horizontal panels. These panels were chosen because they represent a more severe corrosion situation (as reflected in the rates shown in Figure 10) than the vertical or angled panels. In order to quantify the relationships, a correlation coefficient was calculated for the data in each plot and is shown on the plot.

Figure 15 shows the correlation between rainfall and weight loss with a correlation coefficient of 0.97. The ECM readings are shown in Figure 16. The correlation is good up until the last point, which shows an anomalous amount of jacking. This latter point is primarily responsible for the lowering of the coefficient to 0.93. The coulometer readings are plotted in Figure 17. At about half of the weight loss (corresponding to about 10 weeks' exposure) there is a distinct change in slope, with a very strong linear relationship (correlation coefficient of 0.99 above, and 1.00 below the midpoint) for each segment. Figure 18 shows the relationship for the corrosion cell with the stainless steel screen. The absolute values of charge passed are more than three orders of magnitude smaller than with the carbon steel screens, but the overall correlation is very good, with a correlation coefficient of 0.98.

At the end of 20 weeks one of the two carbon steel screens was removed and the oxide stripped to determine the amount of corrosion that had occurred. There was a loss of 604 mg or about 10% of the total weight of the screen. Extrapolating to the point of complete corrosion of the screen, this results in a figure of 200 weeks or about 4 years for the lifetime of the present

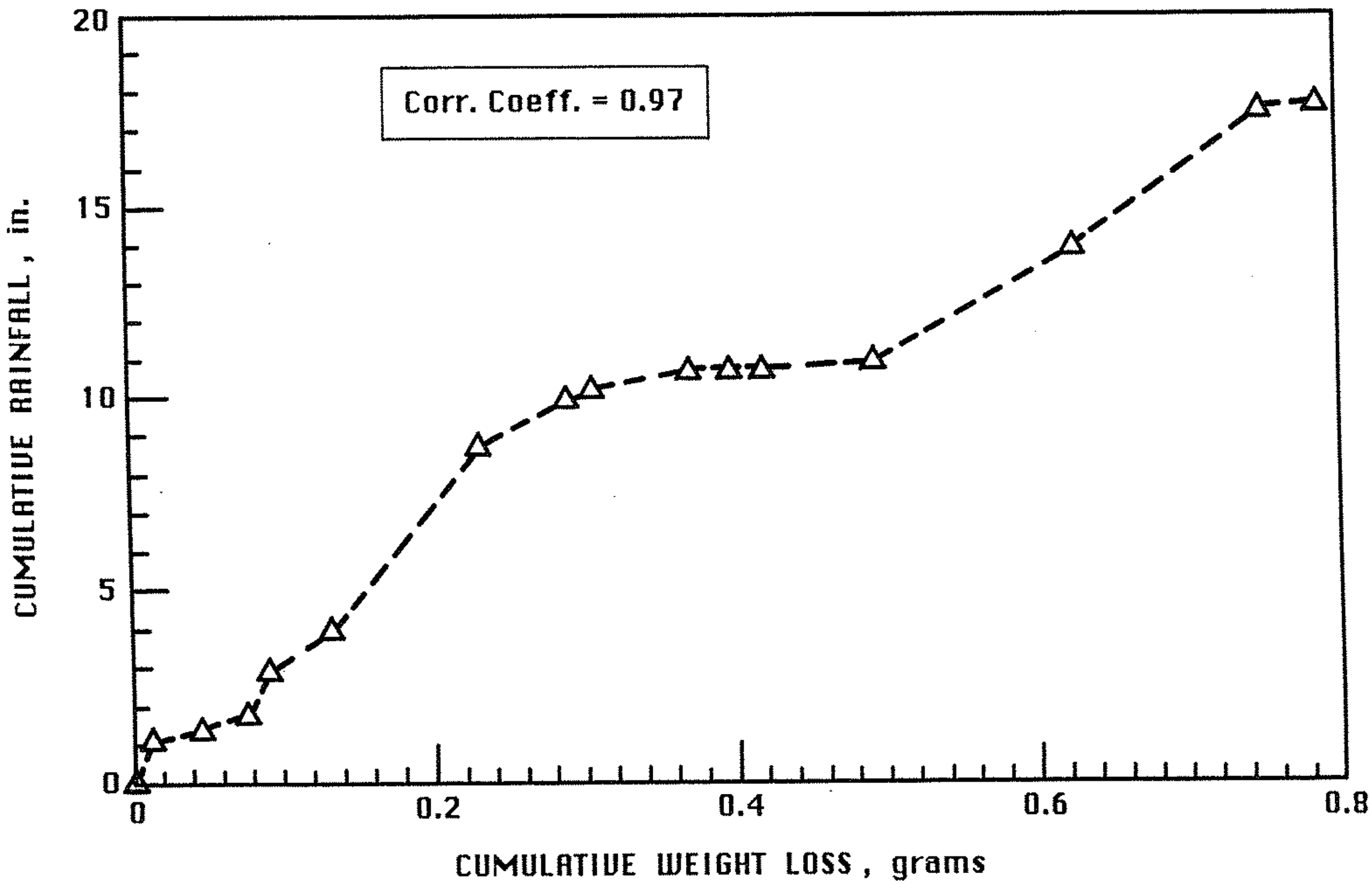

Figure 15. Weight Loss of Horizontal Panels and Rainfall

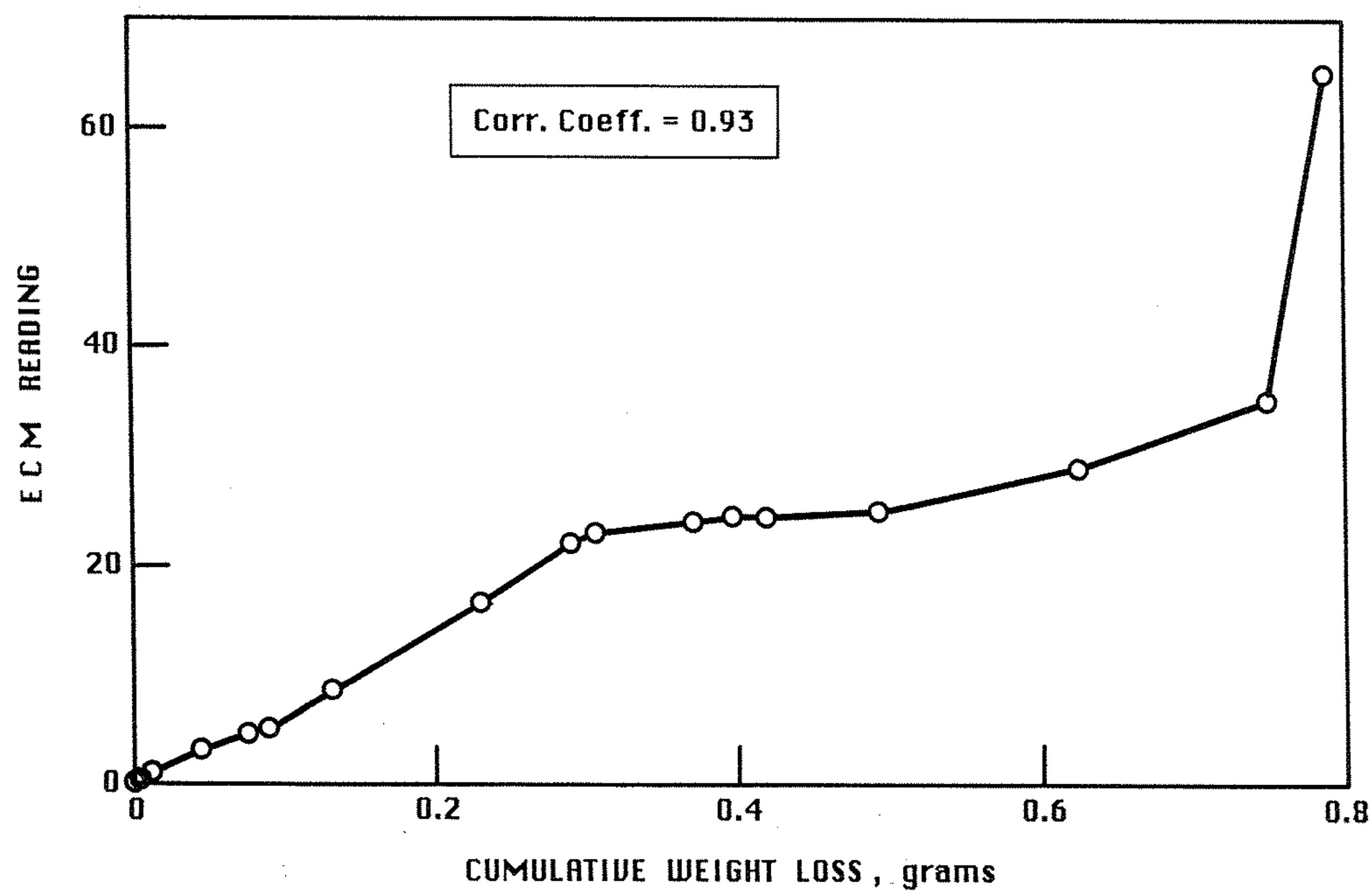

Figure 16. Weight Loss of Horizontal Panels and ECM Readings

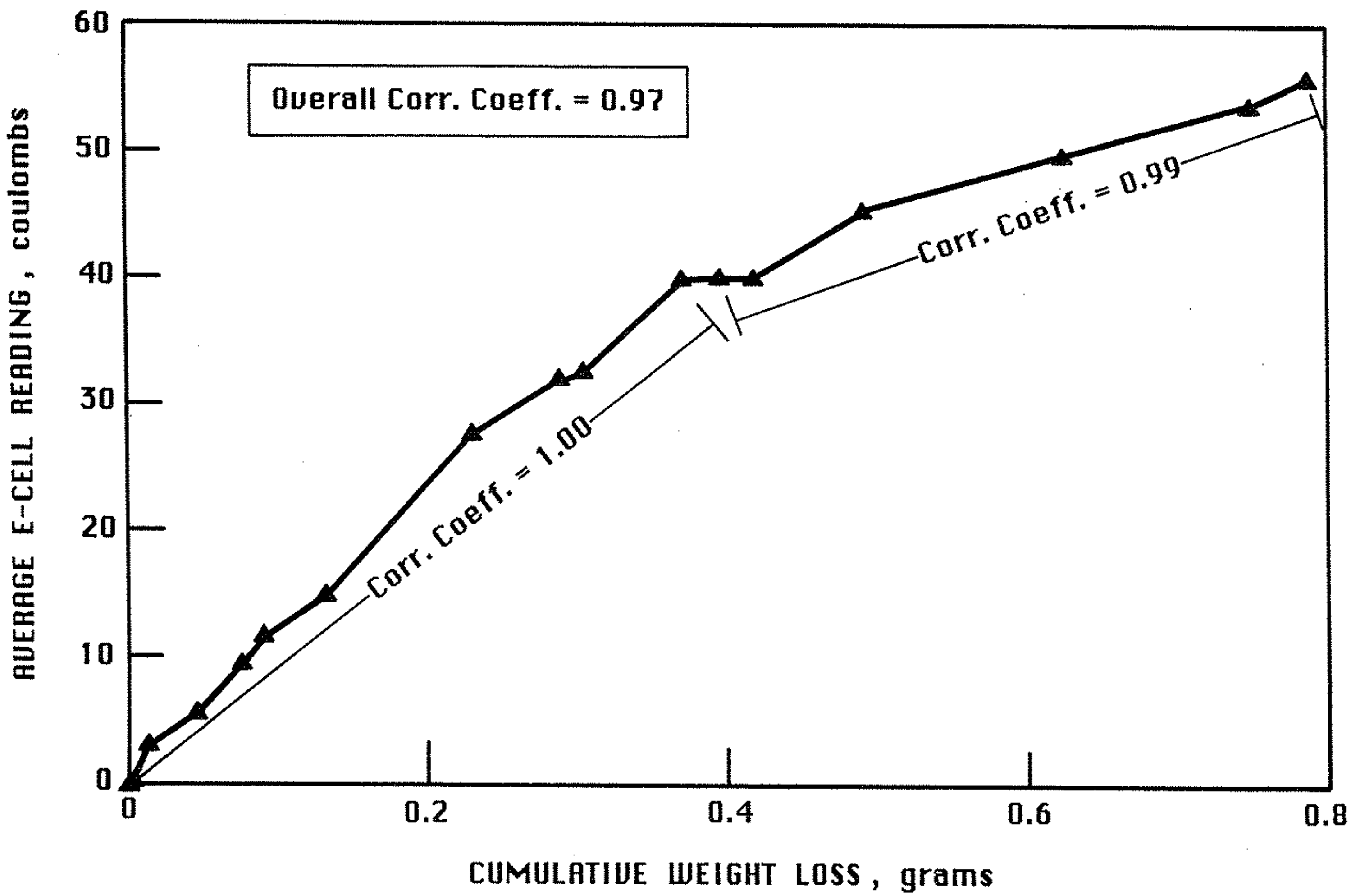

Figure 17. Weight Loss of Horizontal Panels and Coulometer Readings with Carbon Steel Screens.

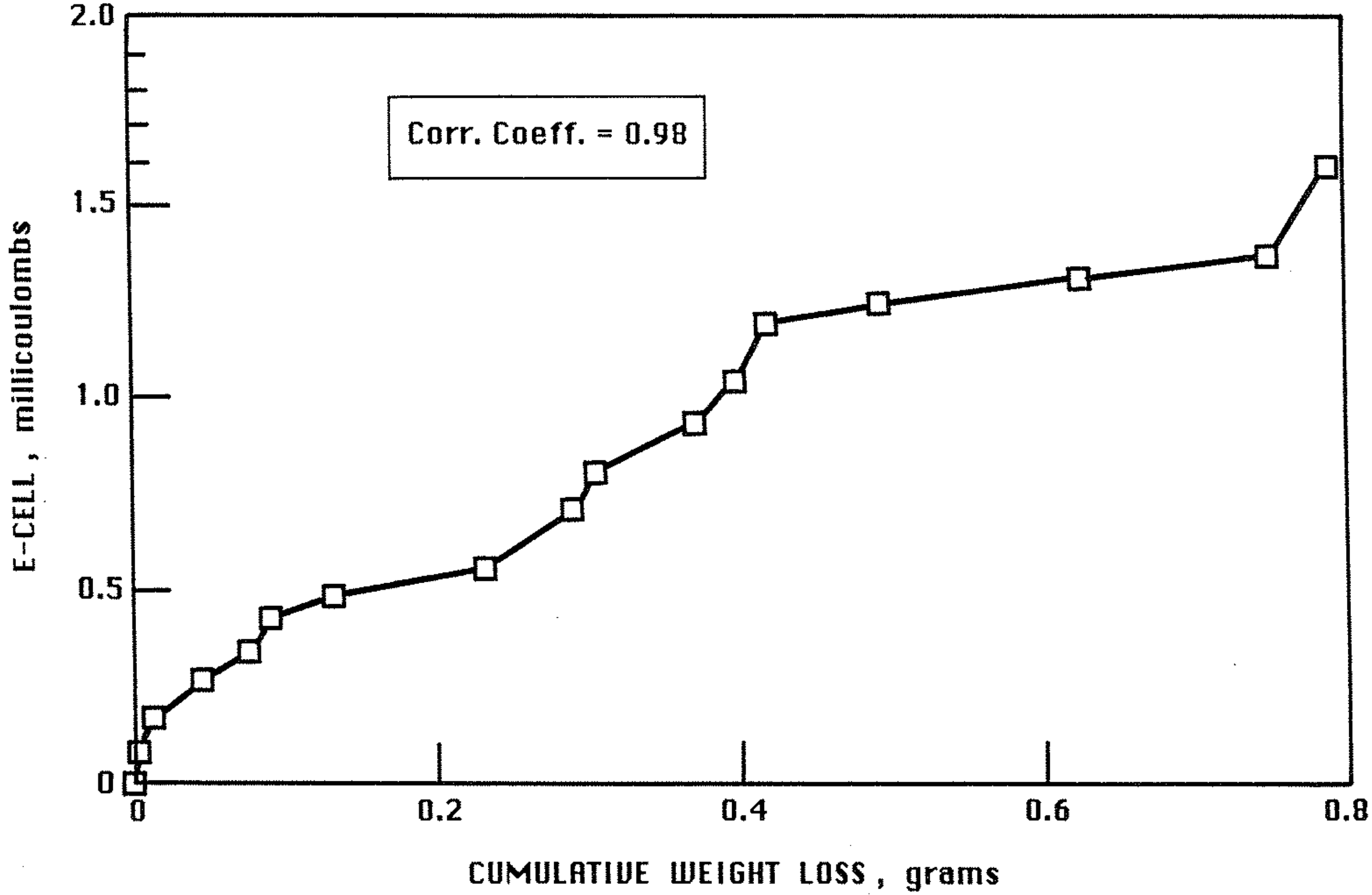

Figure 18. Weight Loss of Horizontal Panels and Coulometer Readings with Stainless Steel Screens

design of the cell. This time could be greatly extended by use of a stainless steel screen, which showed almost no evidence of corrosion after the roof exposure and showed a good correlation with the steel panel corrosion (Fig. 18).

C. <u>Field Exposure Summary and Conclusions</u>

1. Two corrosion coulometers with carbon steel screens and one with a stainless screen were exposed on the roof of Sinclair Laboratory for a 20-week period, along with a device for measuring the "jacking" effect of crevice corrosion (ECM), and a rain gage. Steel panels exposed in three different positions (horizontal, 45° and vertical) were placed nearby.

2. The reproducibility of corrosion of the steel panels was good, with the horizontal panels showing about double the corrosion of the vertical and angled panels after 20 weeks of exposure.

3. Correlations between the weight loss of the horizontal panels and parameter measurements showed the best correlation with the coulometer readings of the corrosion coulometer cells with carbon steel screens, if two different time periods were considered (correlation coefficients of 1.00 and 0.99). The next best correlation was with the corrosion coulometer cells with stainless steel screens (correlation coefficient of 0.98). The cumulative rainfall showed a coefficient of 0.97 and the ECM meter a value of 0.93. This latter value, however, was affected by an anomalously large increase in one ECM reading during the last week.

4. The carbon steel screens were found to corrode at a rate such that the lifetime of a cell should be about four years.

5. Thus, the corrosion coulometer has been shown to have a very good correlation with the rate of steel corrosion in a natural environment, so can be considered as a viable monitor for steel structure corrosion.

V. Recommendations for Future Work

A. Field Exposure on Steel Structures

The next logical step in continuing the monitor evaluation is to expose it to a variety of locations in an existing steel structure, for periods of a year or more. There is currently some knowledge of "critical areas" for corrosion in bridges, for example. Cells could be placed in these areas and the output compared with monitors put in areas known to be benign. There are also geographic locations, e.g. salts water environments, known to be particularly corrosive.

Although it might be possible to devise some laboratory testing to simulate and accelerate corrosive environments in structures, there is not any real certainty that actual conditions could be duplicated.

B. Remote Monitoring of Cell Output

In connection with further field exposure, some consideration should be given to devising techniques for remote monitoring the output of the cell. The coulometers used in the present study have the advantage of integrating the output current over a whole wet/dry cycle. It should be possible to devise a circuit where the cell could charge a capacitor or battery which periodically could be switched into a discharge mode to power a signal generator that could be monitored remotely. Such switching could be accomplished by simple (and inexpensive) radio control equipment.

Another possibility would be to make use of commercially available remote sensing units, such as the "d Link" system available form Harco Technologies Corporation. These use a remote terminal unit which takes a voltage input and transmits the signal via UHF or VHF radio to a master terminal unit which can then process the information in a variety of ways. These systems are relatively expensive, but are quite versatile.

C. Further Investigation of Jacking Meter

The ECM device showed a good correlation with corrosion, except for one reading at the end of the exposure. Since this works by the action of crevice corrosion, it duplicates some situations occurring on steel structures, e.g. in rivet or bolt weathering. There are a number of variations on this type of device that could be investigated, e.g. the use of pressure or linear transducers for measuring the output.

An advantage of this type of monitor is that a variety of alloys could be used to simulate corrosion of a particular material, e.g. weathering steel.

SUMMARY

A new type of corrosion monitor, called a corrosion coulometer, has been developed for use on steel structures. It consists of a copper cup with a layer of glass beads on the bottom and a circular steel screen resting on the beads. When saturated with water, the galvanic action between the cup and screen results in a potential being established. This output can be monitored as a voltage or current. As the cell dries out, the output decreases (especially the current) until it stops when the cell is completely dry. The total output of the cell can be stored in a micro-coulometer which can then be read at any time. As the steel screen rusts, corrosion product collects on the screen and on the glass beads and underlying filter paper to simulate debris accumulation. The cell can also collect airborne contaminants.

The corrosion coulometer was initially evaluated in the laboratory by monitoring ten successive wet/dry cycles. Both the initial current (short-circuit) generated by wetting, and the total charge passed (as measured by the micro-coulometer) decreased with successive cycles. When DI water was used, this decrease was slightly greater than when $3\times10^{-5}M$ H_2SO_4 (to simulate acid rain) and 1 ppm NaCl solution (to simulate salt contamination) were used.

Several cells were put on the roof of Sinclair Laboratory for 20 weeks, along with a rain gage and steel panels (to measure corrosion rates). The coulometer readings showed excellent correlation with weight loss of the steel panels. When a stainless steel screen was used in place of the iron screen, the correlation was not quite as good.

A commercial device for measuring the "jacking" effect of crevice corrosion was also exposed on the roof. The initial condition of this device with the steel panels was good but there was one anomalously large value at the end of the exposure which adversely affected the results.

The steel screens corroded at a rate that predicted a lifetime of at

least four years. An even longer life would be obtained with stainless steel screens. Thus, the corrosion coulometer is a viable corrosion monitor for use on steel structures.

ACKNOWLEDGEMENTS

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REFERENCES

1. J. S. Fisher, Private Communication.

2. A. Raman, in Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., 1988, pp. 16-29.

3. R. C. Turcotte, T. C. Comeau and R. Baboian, in Materials Degradation Caused by Acid Rain, ACS Sympos. Series 318, 1986, pp. 200-12.

4. K. A. Chandler, Brit. Corros. J., 1, 264-66 (1966).

5. P. R. Vassie, Brit. Corros. J., 22, 37-44 (1987).

6. J. A. Gonzalez, E. Otereo, C. Cabans and J. M. Bastidas, Brit. Corros. J., 19, 89-94 (1984).

7. S. Haruyama and T. Tsuru, in Electrical Corrosion Testing, ASTM STP 727, F. Mansfeld and U. Bertocci, Eds., 1981, pp. 167-86.

8. S. Ito et al., Nippon Steel Technical Report No. 32, January 1987.

9. F. Mansfeld et al., in Atmospheric Corrosion of Metals, S. W. Dean and E. C. Rhea, Eds., ASTM STP 767, 1982, pp. 309-38.

10. V. Kucera and J. Gullman in Electrochemical Corrosion Testing, F. Mansfeld and U. Bertocci, Eds., ASTM STP 727, 1981, pp. 238-55.

11. V. S. Agarwala, in Atmospheric Corrosion, W. H. Ailor, Ed., 1982, pp. 183-92.

12. M. I. Manning, A. G. Crouch and B. Lloyd, Document No. TPRD/L/CH from Enchance Co., Inc., Stafford, TX 77477 (1987).