



UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

FEB 08 1984

MEMORANDUM FOR: Everett A. Wick
Engineering Branch
Division of Waste Management, NMSS

WM Record File
109.1

WM Project 1
Docket No. _____
PDR
LPDR _____

FROM: Michael B. McNeil
Waste Management Branch
Division of Health, Siting, and
Waste Management, RES

Distribution:
EW

(Return to WM, 623-SS) 15

SUBJECT: USE OF POLARIZATION RESISTANCE MEASUREMENTS TO PREDICT
UNIFORM CORROSION OF BURIED STEEL OBJECTS

The attached paper proposes a way of using short-term polarization resistance measurements to predict average uniform corrosion rates of pipelines.

It appears to me that the approach has merit and that the same type of argument could be used for HLW containers. Hence, DOE could use this technique to bound uniform corrosion rates for HLW containers by the following reasoning: a DOE contractor could perform the appropriate tests at the maximum temperature expected and with the maximum gamma flux expected and then use the results to project long-term uniform corrosion rates.

This approach would introduce two uncertainties. First, there is the question of whether the worst case is the highest temperature and the highest radiation flux. Normally, uniform corrosion rates rise with temperature and with flux, but I can think of two effects which might make a difference: a) increasing T could lead to increased concentration of some species such as SiO_4^- which might lower uniform corrosion rates; and b) increasing T might lower the redox potentiation by accelerating reactions associated with consumption of radiolysis products.

If you believe that DOE might be taking such an approach, it might be worthwhile to consider asking a TA contractor to consider the consequences.

Incidentally, this approach is probably not suitable for monitoring buried containers during site operation, because of probable drift in the calibration of equipment buried with the containers.

WM DOCKET CENTER
FEB -9 AM 11:33

Michael

Michael B. McNeil
Waste Management Branch
Division of Health, Siting, and
Waste Management, RES

Determination of Underground Corrosion Rates from Polarization Resistance Measurements*

KOMEI KASAHARA* and FUMIO KAJIYAMA

Abstract

An improved technique for measuring polarization resistance, involving the use of two different frequencies of complete reverse square wave polarizing current, was applied to 40 varieties of soil corrosion systems. Results of polarization resistance monitoring over a 308 day period were directly correlated to the weight loss measurements which were taken using identical probes. This experimentally verified the applicability of the technique to underground corrosion monitoring.

Introduction

The corrosion of buried steel pipes has been, and may continue to be, a serious engineering problem and hence a matter of primary concern for those corrosion engineers engaged in the related industries. Corrosion of buried steel pipes is primarily governed both by soil corrosivity and by outside electrochemical forces such as stray current from DC sources or localized corrosion cells. Of the various factors associated with soil corrosivity is available. Penhale,³ who determined significant, such as low soil resistivity, less noble corrosion potential, high soluble salts content, low permeability, etc.^{1,2} No one, however, can predict the extent of corrosion even when complete information about those factors associated with soil corrosivity are available. Penhale,³ who determined the correlation coefficients among various soil properties and actual corrosion rates, concluded that corrosion rates could never accurately be predicted from the chemical and physical properties of the soil. Therefore, a direct determination of corrosion by means of weight loss measurements for each steel and soil combination has at present been considered to provide a better and more direct indication of the soil corrosivity. However, this most basic and traditional physical measurement of weight loss has inherently been accompanied by several difficulties. It is very time consuming and the results obtained are not always fully reliable unless multiple specimens can be evaluated. In order to overcome such difficulties, electrochemical methods such as polarization resistance techniques have recently been developed to instantaneously appraise the corrosivity. While the application of this polarization resistance technique has so far been restricted to relatively limited electrochemical systems such as steel in homogeneous electrolytes,⁴ it was applied in the present study to the inhomogeneous soil corrosion system, wherein galvanostatic polarizing steps were applied externally to the steel electrodes alternately toward anodic and cathodic directions at both

high and low frequencies. The resultant potential variations were read off either an oscilloscope or a strip chart recorder as peak-to-peak variations. The net polarization resistance was then obtained by subtracting the effect of the capacitance component involved in the corroding electrode circuit, as well as of IR component due to the passage of the polarizing current across the soil.

Basic Concept

The polarization resistance technique, which was first described by Wagner and Traud,⁵ and subsequently improved by Stern and Geary,⁶ is based on the relation:

$$I = I_{\text{corr}} \left[\exp \frac{2.303(E - E_{\text{corr}})}{B_a} - \exp \frac{-2.303(E - E_{\text{corr}})}{B_c} \right] \quad (1)$$

where I and E are current and potential, I_{corr} and E_{corr} are corrosion current and corrosion potential, and B_a and B_c are anodic and cathodic Tafel slopes, respectively. This relationship provides the polarization to a potential E from the rest potential (i.e., corrosion potential, E_{corr}) by an externally applied current I . Relating the slope of the E - I curve at the point of zero current, a first differentiation of Equation (1) yields:

$$\left(\frac{d\Delta E}{dt} \right)_{I \rightarrow 0} = R_p = \frac{B_a B_c}{2.303(B_a + B_c) I_{\text{corr}}} = \frac{K}{I_{\text{corr}}} \quad (2)$$

where R_p is polarization resistance and

$$\Delta E = E - E_{\text{corr}}$$

$$K = \frac{B_a B_c}{2.303(B_a + B_c)}$$

*Submitted for publication May, 1982; revised December, 1982.

*Tokyo Gas Company, Research and Development Institute, Tokyo, Japan.

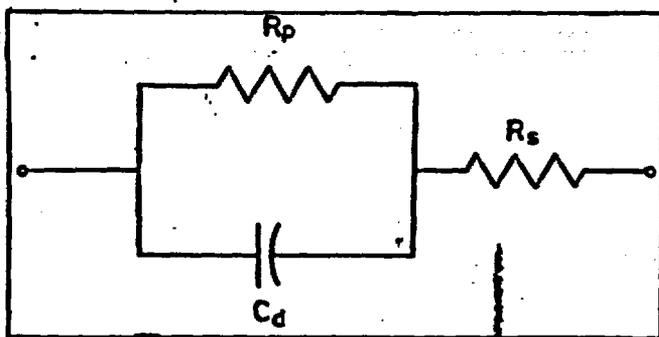


FIGURE 1 — Equivalent circuit of a corroding electrode/electrolyte interface during application of a galvanostatic step, where R_p , C_d , and R_s are the Faradaic resistance or polarization resistance, double layer capacitance, and electrolyte resistance, respectively.

To determine the derivative $(d\Delta E/dt)|_{t=0}$, a galvanostatic step can externally be applied to the corroding electrode, and the resultant potential variation can be measured as a function of time. However, an externally applied single current step must introduce several difficulties in the potential measurements as follows:

1. It causes a modification of the concentration ratios of the anode and cathode couple, which in turn results in the variation of the mixed potential introducing a large error in the measured $E - E_{\text{corr}}$ value.

2. It gives rise to changes in the surface conditions, that is, the corroding electrode surface becomes covered by corrosion product layers which results in a very large electrode capacity to cause a transient on the potential variation, therefore introducing a significant difficulty in pinpointing the time when the steady states are attained.

3. It gives rise to a large IR drop due to the passage of current through the high resistance of the electrolyte introducing a large error into the measured potential value, E . To avoid these difficulties, an alternative technique can be used in which a galvanostatic square wave current is applied alternately toward anodic and cathodic directions at a definite frequency. To describe the concept of this technique, an equivalent circuit of corroding electrode/electrolyte interface is used as shown in Figure 1. In such a C-R parallel circuit, the overvoltage, $\Delta E = E - E_{\text{corr}}$, of the corroding electrode which is produced by a single galvanostatic polarizing current step I can be expressed as follows:

$$I = C_d \frac{d\Delta E}{dt} + I_{\text{corr}} \left[\exp \frac{2.303\Delta E}{B_a} - \exp \frac{-2.303\Delta E}{B_c} \right] \quad (3)$$

For a sufficiently small overvoltage, as within 10 to 20 mV of the corrosion potential, Equation (3) may be reduced to

$$I = C_d \frac{d\Delta E}{dt} + \frac{\Delta E}{R_p} \quad (4)$$

Here, if galvanostatic steps are alternately applied to anodic and cathodic directions at a frequency of f (sec^{-1}), Equation (4) can be modified as:⁷

$$\Delta E = IR_p \tanh \left(\frac{1}{4R_p C_d} \cdot \frac{1}{f} \right) \quad (5)$$

Then the actually observed potential variation as a function of frequency, that is, $\Delta E(f)$, when completely reverse cyclic galvanostatic current steps are applied can be written as

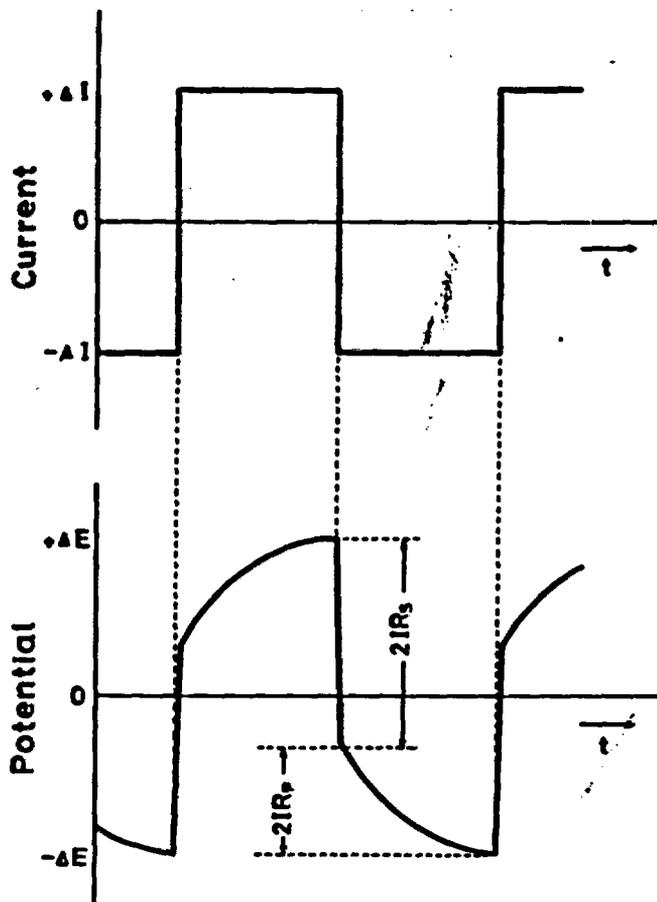


FIGURE 2 — Schematic representation of a typically observable potential response to completely reverse galvanostatic steps.

$$\begin{aligned} \Delta E(f) &= IR_s + \Delta E \\ &= IR_s + IR_p \tanh \left(\frac{1}{4R_p C_d} \cdot \frac{1}{f} \right) \end{aligned} \quad (6)$$

Here, if frequency f approaches zero, Equation (6) reduces to

$$\Delta E(f) = IR_s \quad (7)$$

whereas at stationary state (i.e., $f = \infty$ or $1/f \gg R_p C_d$), Equation (6) reduces to

$$\Delta E(f) = IR_s + IR_p \quad (8)$$

Then polarization resistance R_p can be determined as a difference between Equations (7) and (8). To facilitate the understanding of such a concept, a typical potential variation with time when galvanostatic steps are applied alternately toward anodic and cathodic directions is shown schematically in Figure 2. In order to avoid errors introduced by the potential shift which is attributable to the transient effect caused by electrode capacity, actual measurements can be taken by means of peak-to-peak readings, wherein at a high frequency of pulses, only $2IR_s$ can be read off depending on Equation (7); whereas at a sufficiently low frequency of pulses, $2(IR_s + IR_p)$ can be read off according to Equation (8). In other words, effects of corrosion product layers can be minimized by applying alternate galvanostatic steps, while the effect of potential shift, which is primarily due to the time required to achieve the stationary state in galvanostatic polarization measurements, can be reduced by a peak-to-peak reading.

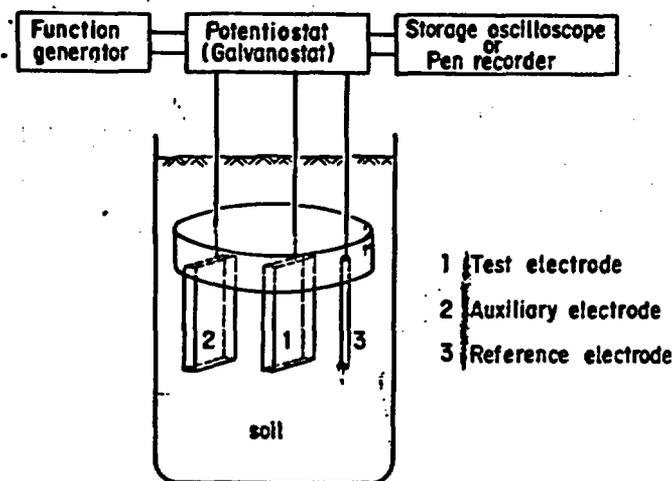


FIGURE 3 — Schematic wiring diagram of the test apparatus.

Experimental Procedures

In the present study, a three electrode polarization resistance system was employed which involved a function generator, galvanostat, storage oscilloscope, and a strip chart recorder, as schematically represented in the wiring diagram, Figure 3. The 3-electrode probe used in the study was a triangular spaced type in which two mild steel plates 30 mm long \times 20 mm wide \times 8 mm thick were used as test and auxiliary electrodes, and a steel rod of the same steel 30 mm long \times 10 mm diameter was used as a reference electrode. The steel electrodes were assembled together at a distance of 10 mm from each other by means of epoxy resin. To simplify the corrosion system, an exposed surface of 6 cm² was obtained for both test and auxiliary electrodes by applying waterproof paint leaving two surfaces opposite to each other. Each exposed surface was slightly abraded with 2/0 emery paper followed by degreasing with acetone. The probe thus prepared was then installed in a soil box of 700 \times 700 \times 500 mm long at a depth of 100 mm, wired into the electric circuit as shown in Figure 3, and then allowed to corrode under freely aerated conditions. The soils used in the study totalled 40, ranging from sand to clay with decreasing order of particle size. Among those 40 soils, 8 were identified as sand, 4 as sandy loam, 15 as silt loam, 7 as clay, 3 as silt, and the remaining 3 as organic soils. Polarization resistance measurements were taken for a 308 day period by applying galvanostatic anodic and cathodic polarizing current steps alternately in the test auxiliary electrode circuit at the frequencies of 0.03 Hz and 1 kHz, and measuring the resultant change in the test electrode potential relating to the reference electrode. The applied current density was chosen to be small enough to keep the potential shift within ± 10 mV of the corrosion potential. The corrosion potential was also measured throughout the test period by installing a Cu-CuSO₄ reference electrode in the immediate vicinity of the test electrode. Moisture content of soils was controlled by an intermittent addition of water. Upon conclusion of the tests, 308 days after the tests were started, every probe was removed from each respective soil box, followed by cleaning and weight loss determinations. The results of weight loss determinations, ΔW , were then correlated to the polarization resistance measurements by means of the relationship:

$$\int_0^t \frac{1}{R_p} dt = K \frac{nF}{M} \Delta W$$

where, n is the valency, M the atomic weight, F the Faraday constant, and K the proportionality constant, as defined in Equation (2).

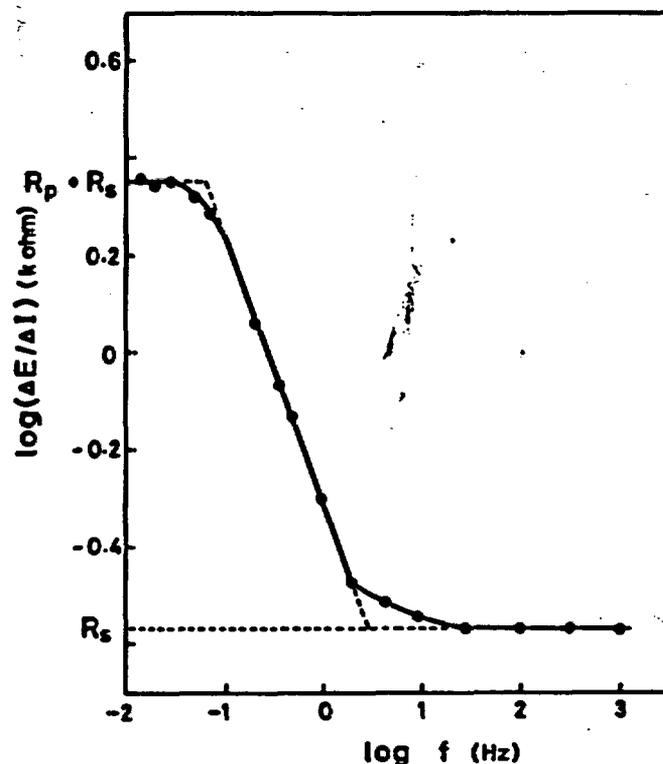


FIGURE 4 — Typical frequency dependence of the amplitude of potential change when the completely reverse galvanostatic steps were applied.

Results and Discussion

Determination of Optimum Measuring Conditions

As mentioned in the basic concept, the present polarization resistance method was characterized by the galvanostatic polarization in which completely reverse square wave current steps were applied both at high cycles to obtain an electrolyte resistance R_s , and at low cycles to obtain a total resistance, $R_s + R_p$. To determine the optimum conditions, the frequency dependence of potential change was first studied as shown in Figure 4. As evident in the figure, there appeared two plateaus on the $\log R - \log f$ diagram, that is, in the frequency ranges of $\log f < -1.5$ (i.e., $f < 0.032$) and $\log f > 1.5$ (i.e., $f > 32$). Depending on the results obtained herein, those frequencies of applying current to obtain $R_s + R_p$ and R_p were fixed as a rule as 0.03 and 1000 Hz, respectively. Although the measuring conditions were fixed as mentioned above, the response of potential to the applied current steps was checked prior to every measurement to make sure of the validity of the method.

Variation with Time of Polarization Resistance

In the present study, polarization resistance as well as corrosion potential measurements were taken at regular intervals over a 308 day period. Figure 5 shows typical plots of $(1/R_p)$ and corrosion potential versus time for those two probes exposed to clay and sand which were two extremes of corrosion potential. During the test period, the corrosion potential changed with a continuously decreasing rate from -0.82 to -0.795 V vs Cu-CuSO₄ in clay, and from -0.57 to -0.38 V in sand. On the other hand, time variations of polarization resistance were quite different in that $(1/R_p)$ changed from 0 to 40×10^{-4} (ohm-cm²)⁻¹ in clay with a continuously decreasing rate taking some 200 days to attain the stationary state, while in sand it decreased from 0.6×10^{-4} to 0.2×10^{-4} and the time required to attain the stationary state was as short as 60 days which was much shorter than that in clay. Such tendencies were commonly observed throughout the present study.

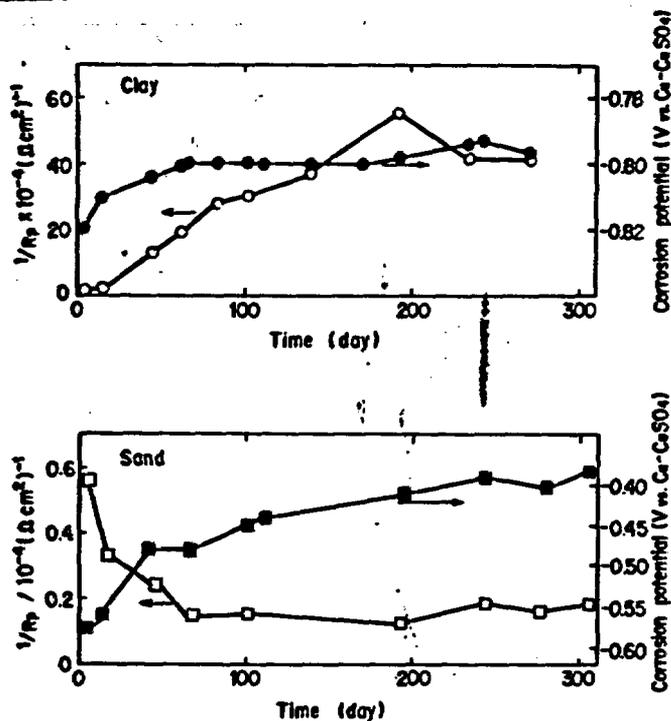
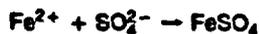


FIGURE 5 — Typical plots of $1/R_p$ and corrosion potential versus time observed over a 308 day period in clay and sand.

That is, in those soils characterized by a relatively low noble corrosion potential, such as clay, organic soil, etc., a significant decrease in polarization resistance (therefore increase in corrosion rate) was noticed with a slight shift of corrosion potential toward the noble potential direction, while in those more noble corrosion potentials such as sand, corrosion rates were more than two orders of magnitude lower as compared with those in clay, and they showed slight decrease with time accompanied by a significant shift of corrosion potential toward the noble direction.

Those factors most responsible for such behavior of polarization resistance and corrosion potential are thought to be permeability as well as the soluble salt content of the soil. That is, in soils with low noble corrosion potentials such as clay, initial corrosion rates were relatively slow due to the low permeability, as evident in Figure 5. However, once the corrosion reaction initiated, corrosion rates began to increase due to several factors which were associated with higher soluble salt content. Those included: (1) the poor protective action which was played by corrosion product layers due to the film breakdown by anions such as Cl^- , SO_4^{2-} , etc., and (2) the acceleration of corrosion reactions by dilute acids such as HCl or H_2SO_4 which were formed at the immediate vicinity of anodic sites under the pressure of soluble salts such as NaCl or $CaSO_4$. The corrosion reaction which was proposed by Larson,⁵ could proceed as follows:



On the other hand, in those soils characterized by higher permeability and low salt content, corroding electrode surfaces were soon covered by corrosion product layers owing to the sufficient amount of oxygen. The corrosion product layers thus formed remain protective films because of low salt content which might break down the films.

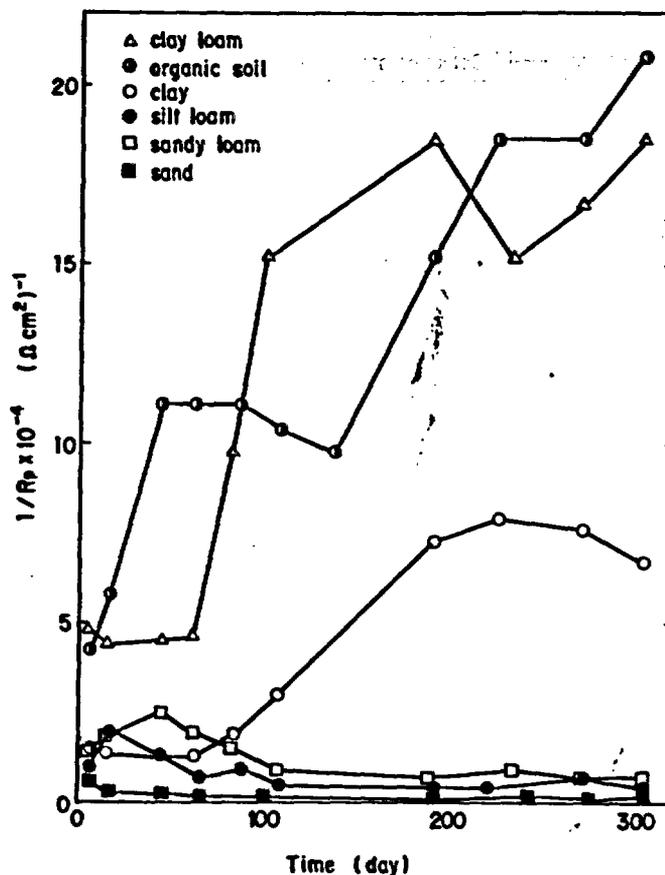


FIGURE 6 — Typical plots of $1/R_p$ versus time for six typical types of soils.

Thus, one of the significant findings of the present study was considered to be that polarization resistance was revealed to provide information about the mechanism of corrosion or the rate determining stages in the corrosion reaction, provided it was monitored with time.

Determination of Proportionality Constant K

As mentioned in the basic concept, the proportionality constant K in Equation (2) can in theory be calculated, provided both anodic and cathodic Tafel slopes are known. This has, however, been seldom successful, as indicated by Callow, et al.,⁴ because the theoretical linear relationship between potential and log current has seldom been obtained in the practical polarization measurements. Therefore, in the present study, K value was determined empirically from weight loss determinations.

Figure 6 shows typical plots of $(1/R_p)$ versus time for six types of soils. Graphic integration of such plots, obtained on each probe, was then compared, as shown in Figure 7, with the average corrosion current, i_{corr} , which was determined from actual weight loss measurements taken on each identical probe. Although whole data thus obtained were plotted together in the figure, no significant difference appeared among the six types of soil involved in the study. Despite the various differences in soil properties, the amount of scatter of the whole data was found to be much less than expected. In the figure, a trend line, which was determined by means of the least square fit method, was also shown and approximated as follows:

$$\log T_{corr} = 1.12 + \log (\overline{1/R_p}) \quad (9)$$

where T_{corr} and $\overline{R_p}$ stand for corrosion current (mA/cm^2) and polarization resistance ($ohm\text{-}cm^2$), respectively. This means that the well-known Stern and Geary's Equation (2) held true

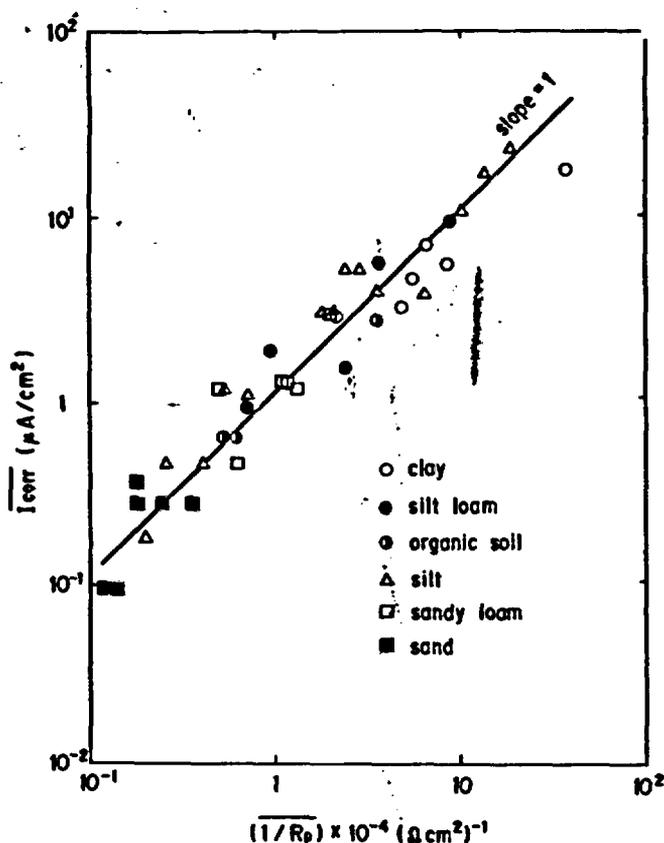


FIGURE 7 — Relationship between $1/R_p$, averaged over an extended period, and average corrosion current converted from actual weight loss measurements using Faraday's law.

also in the soil corrosion systems irrespective of the types of soil. Then the proportionality constant K could be determined as 11.2 mV. This value fell within the range of 10 to 45 mV which was obtained by Callows, *et al.*,⁴ for mild steel exposed to acid-based environments. The corrosion current I_{corr} in Equation (9) could then be converted into a corrosion rate d (mm/y) using Faraday's law to obtain the corrosion rate directly from polarization resistance measurements R_p (ohm-cm²) as follows:

$$d = \frac{130}{R_p} \quad (10)$$

The most significant findings of the present polarization resistance study would include:

1. The confirmation that the polarization resistance method could be applied to the steel-soil corrosion systems.
2. The fact that corrosion current (*i.e.*, corrosion rate) and polarization resistance could be correlated by a singular relationship as represented in Equations (9) or (10), irrespective of types and chemical and physical properties of soils.

Determination of Corrosion Rates for Initial Polarization Resistance Measurements

Although the applicability for corrosion monitoring of the polarization resistance technique was confirmed and the validity of the new electrochemical method for determining polarization resistance was experimentally verified, the derived relationship between corrosion rate and polarization resistance was not always valid for *in situ* corrosion monitoring in the fields because it depends upon the use of polarization resistance averaged over extended periods. Hence, it was very time consuming, as it took some 50 to 200 days to attain the

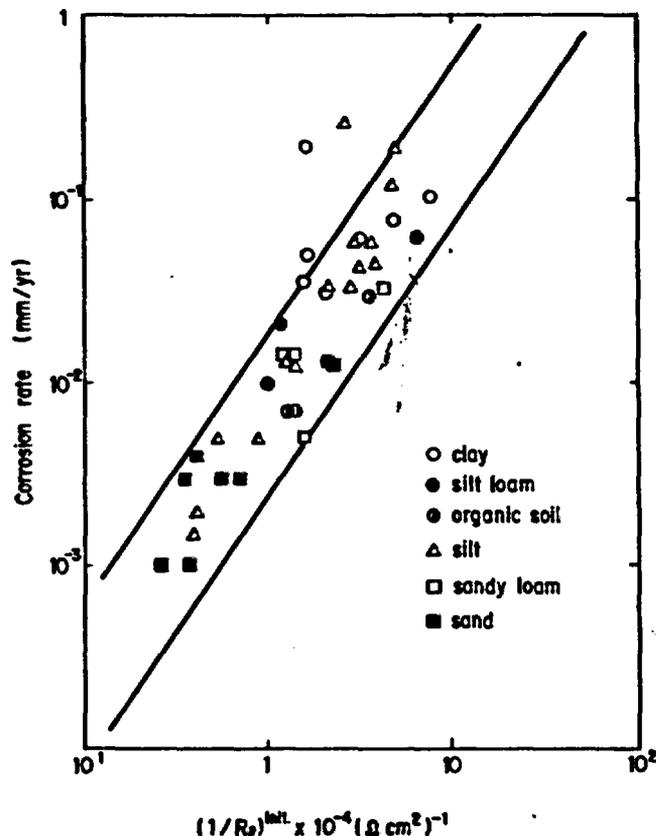


FIGURE 8 — Relationship between corrosion rate and initial polarization resistance measured immediately after the start of exposure of the probe to the soil.

stationary state. Here, if polarization resistance could be measured immediately after the start of exposure of the probe to the soil, the significance of the technique should be remarkably raised. Therefore, as shown in Figure 8, results of polarization resistance measurements which were taken immediately after the start of exposure of those probes to the soil were correlated to the actual weight loss determinations for identical probes after a 308 day period of exposure. Two solid lines in the figure correspond to the scatter band for the plots in Figure 7. As is evident in the figure, almost all data with only three exceptions fell within this scatter band. Those three data points which fell outside the scatter band were obtained in aggressive soils such as clay and silt. These soils had extremely negative corrosion potentials, -680 to -800 mV vs Cu-CuSO₄, and low resistivity, 1000 to 2000 ohm-cm. Thus, it was considered that polarization resistance which was measurable immediately after the set-up of probe in the field, R_p^{init} (ohm-cm²), could stand for corrosion rate estimation according to the relationship as follows:

$$d \text{ (mm/y)} = \frac{6310}{(R_p^{init})^{1.5}} \quad (11)$$

Conclusion

Results of polarization resistance measurements which were taken over a 308 day period on 3-electrode type probes exposed to 40 varieties of soil were correlated with those of the most basic physical measurements of metal loss taken on each identical probe. The results obtained are summarized as follows:

1. Polarization resistance in the soil (R_p ohm-cm²) could be determined with sufficient accuracy by means of the 3-electrode method and measuring the response of potential (ΔE mV) to the cyclic square wave current (ΔI mA/cm²) applied symmetrically toward anodic and cathodic directions at the

frequencies of 0.03 and 1000 Hz according to the following relationship:

$$R_p = \left(\frac{\Delta E}{\Delta I} \right)_{0.03\text{Hz}} - \left(\frac{\Delta E}{\Delta I} \right)_{1000\text{Hz}}$$

2. There existed a good linear relationship between average corrosion current (I_{CORR} mA/cm²) which was converted from actual metal loss using Faraday's law, and the reciprocal of the average polarization resistance (\bar{R}_p ohm-cm²). A resultant Stern and Geary's equation was determined as:

$$I_{\text{CORR}} = \frac{1.2}{\bar{R}_p}$$

3. Rates of general corrosion of steel in the soil could be determined according to either of the following relationships:

$$d = \frac{130}{\bar{R}_p} \text{ or } d = \frac{6310}{(R_p^{\text{init}})^{1.5}}$$

where d is general corrosion rate (mm/y), \bar{R}_p polarization resistance averaged over extended periods, and R_p^{init} polarization resistance measurable immediately after the start of exposure of the probe to the soil (ohm-cm²).

4. This method has been applied successfully in the field corrosion monitoring for evaluating the corrosivity of soils prior to the burial of new steel pipes.

Acknowledgments

The authors are extremely grateful to Mr. H. Kataoka, Director of Tokyo Gas Company Research and Development Institute, for his support and permission to publish this paper. Thanks are also due to Dr. Akinari Ro, Toho Technical Research Corp., for his cooperation in developing the Corrosion Monitor.

References

1. Romanoff, M., NBS Circular 579, National Bureau of Standards, U.S. Government Printing Office, Washington, D.C. (1957).
2. Kasahara, K., Adachi, H., and Kajiyama, F., Proceedings of 8th International Congress on Metallic Corrosion, Vol. 11, p. 1832-1837, DECHEMA, Frankfurt/Main (1981).
3. Penhale, H. R., New Zealand J. Sci., Vol. 14, p. 336-353 (1971).
4. Callow, L. M., Richardson, J. A., and Dawson, J. L., Br. Corros. J., Vol. 11, No. 3, p. 123-131 (1976).
5. Wagner, C. and Traud, W., Z. Electrochem., Vol. 44, p. 391 (1938).
6. Stern, M. and Geary, A. L., J. Electrochem. Soc., Vol. 104, p. 56 (1957).
7. Asakura, S., Mita, K., and Kato, K., Corrosion Engineering (in Japanese), Vol. 31, No. 1, p. 12-18 (1982).
8. Larson, T. E., PB-244723, National Technical Information Service, Springfield, Va. (1975).

Corrosion and Its Control: An Introduction to the Subject

by J. T. N. Atkinson and H. van Droffelaar



When the corrosion engineer needs to find the answer to the complex problems of corrosion, many times the answer lies in the basic understanding of the problem itself. **Corrosion and Its Control: An Introduction to the Subject**, is the source of that basic understanding. Atkinson and van Droffelaar have collaborated their expertise in the academic and practical aspects of corrosion engineering to write this comprehensive book on the subject of corrosion and its control. With understanding, recognition, and evaluation of the relevant factors, an engineer will have the basic knowledge to make the appropriate decisions and to create new solutions to corrosion problems.

Contents includes information on: electrochemical background and electrochemistry of corrosion cells, metallurgical aspects of corrosion, the corrosion product as a factor in corrosion control, synergistic modes of attack, control measures in modification of environment, protective coatings and design, economics, testing, detecting and monitoring corrosion, regulations and specifications, safety, engineering materials, stainless steels and failure analysis.

5 3/4 × 8 3/4" • hard cover • 202 pages • 101 figures • 26 tables • 42 references • NACE and ASTM Recommended Standards list • appendixes • subject index

Item #52010 \$20.00 NACE Member \$25.00 Nonmember

Available from:
NACE Publications Order Department
P.O. Box 218340, Houston, Texas 77218
713/492-0535

Note: All orders from Texas must include 5% sales tax. All orders from outside the USA must include \$3.00 for handling. All orders from Mexico and overseas must be prepaid. Proforma invoices will be sent for any orders which are not prepaid. Remittances from foreign countries must be by international money order or bank draft in USA funds. Shipping at any rate other than the most economical rate will be charged to the customer.