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Measurement of the Instantaneous Corrosion Rate By Means of Polarization Data★

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Abstract

The use of polarization data in the measurement of instantaneous corrosion rates is described. Steel and cast iron specimens were tested in 3000 ohm-cm waters; potentials were measured by a multicombination meter.

Potential-time studies were made on all specimens in order to determine any relationship which such studies might have to the corrosion rate. It was found that a limited empirical quantitative relationship exists between the polarization slope, $\Delta E/\Delta I$, at low current density and the corrosion rate as measured by weight loss. Such a relationship will permit a rapid empirical determination of the corrosion rates of metal specimens while they are immersed in a fresh-water environment.

The effect of pH on the corrosion rate of mild steel is considered briefly. 2.3.5

Introduction

THERE HAS BEEN considerable attention focused lately upon the need for reducing the degree of corrosion taking place in water distribution lines. The annual expenditures for power costs, necessitated by loss in carrying capacity, as well as for cleaning and replacement as a result of tuberculation within the lines is on occasion exorbitant. In order to decrease the corrosion of pipe lines, the fundamental corrosion factors are being studied, the water characteristics are being investigated and inhibitors are being evaluated so that corrective measures may be taken.

One of the initial objectives[1] of this study was to determine an adequate measure at a particular time of the corrosion rate in "fresh water" mineralization which would be applicable both as a laboratory and field measurement. For this purpose, preliminary studies were made on changes in specimen potentials resulting during corrosion (potential-time studies), and changes on specimen potentials caused by externally applied current (polarization studies).

Apparatus and Testing Equipment

The apparatus used in these studies was the same as that described by other investigators.[2,3] This apparatus supplied a constant velocity-total immersion testing of the specimens. The specimens tested were principally $1^{1}/_{2}$ x 3 inch sections of 0.01 inch "black plate" steel free from mill scale. Machined cast iron specimens also were tested. All specimens had holes drilled near the top edge to facilitate connection of an electrical test lead.

Cleaning of the specimens prior to use involved the following procedure:

1. Degreasing in carbon tetrachloride
2. Preliminary acid cleaning in a 5 percent solution of HC1 and HNO_3 for two minutes
3. Acid cleaning in concentrated HC1 for one minute
4. Neutralizing in 1-N Na_2CO_3 solution for one-half minute
5. Rinsing in distilled water for one minute
6. Rinsing in acetone.

The specimens were then dried and stored in a vacuum dessicator for a minimum of 48 hours. Immediately prior to use, the specimens were attached to the electrical test leads which also served as specimen holders, and the electrical contacts and the edges of the specimens were coated with paraffin wax. The velocity of motion furnished by the apparatus was 0.085 and 0.14 foot per second. All tests were conducted at room temperature. . . .

The total dissolved solids content and quality of the waters were varied over a considerable range but essentially most of those studied were with waters similar in anion content and in total dissolved solids

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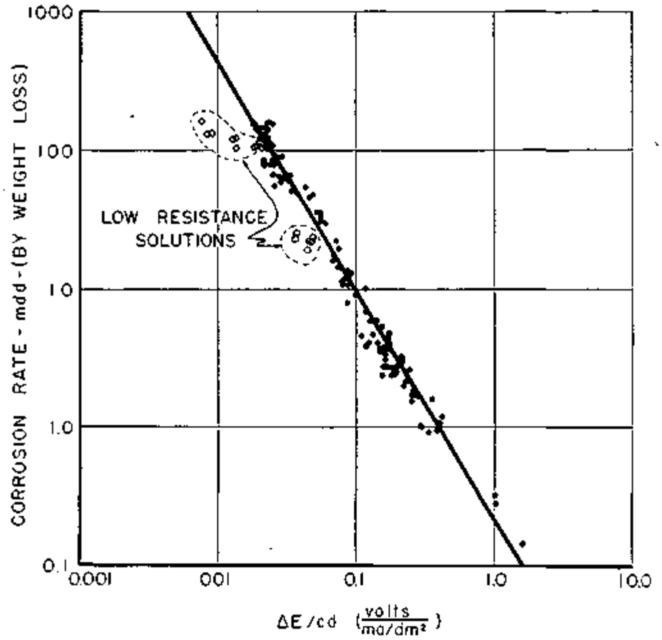
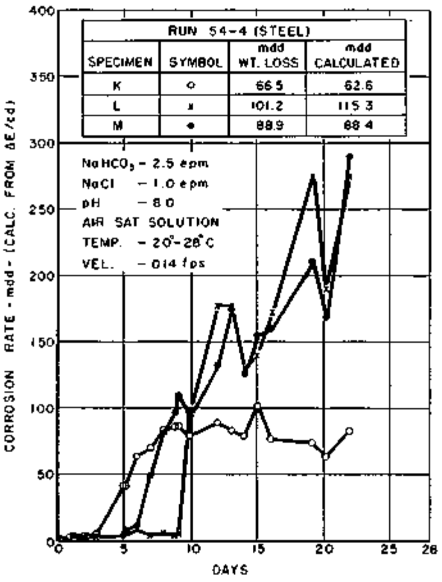


Figure 1—Empirical relation between initial slope of polarization curve (resistance) and corrosion rate determined by weight loss.



RUN 54-4 (STEEL)			
SPECIMEN	SYMBOL	mdd WT. LOSS	mdd CALCULATED
K	○	66.5	62.6
L	x	101.2	115.3
M	●	88.9	68.4

Figure 2—Corrosion rate variation with time for Run 54-4.

to Great Lakes water. The usual specific resistance of the water was about 3,000 ohm-cm. The salts consisted primarily of $NaHCO_3$ and NaCl. The pH of the solutions were usually 7.0 and 8.0, maintained by carbon dioxide. In one study the pH was varied from 6.0 to 8.5. Constant dissolved oxygen was maintained by continuous diffusion with air. Each jar with three metal specimens in each was maintained at 18 liters of solution by a constant level apparatus.

Potentials were measured by a multicombination meter (W. C. Miller, Model B-3). Applied current was measured by the ammeter portion of a Weston Circuit Tester Model No. 785 having ranges of 0-50 microamps, and 0-1 milliamp. Current was supplied by a Type C dry cell battery, and was regulated by a variable resistance in the external circuit.

A saturated calomel reference electrode for measuring the potentials was fastened to the side of the test jars approximately three to six inches from the specimens. A double-faced platinum electrode was used for application of current to the specimen. This electrode was fastened by a clip to the specimen holder so that each face of the platinum electrode was approximately one-half inch away from the surface of the specimen.

Preliminary Electrical Measurements

The potential-time studies confirmed observations by others[4] that a particular specimen potential was not related in any way to the corrosion rate.

Complete polarization studies were made in order to calculate corrosion rates from the initial "breaks" in the polarization curves according to the work of Pearson,[5] Schwerdtfeger and McDorman[6] and others. This type of study was abandoned for several reasons: (1) the "breaks" in the polarization curves were not sharp enough to allow sufficient accuracy in the calculation of corrosion rates, (2) the collection of data was very time consuming, and (3) the applied current, especially in high amounts, often increased the subsequent rate of corrosion.

Polarization At Low Applied Current

One characteristic of the polarization studies was that polarization potential appeared to be a straight line function of the applied cathodic and anodic currents at low current density. It had been noted that the slope of this line, ΔE/Δl, was higher for a specimen having a low corrosion rate than for one having a high corrosion rate. Simmons[7] corroborated this observation in a study on evaluation of inhibitors. His experiments indicated that there may be a quantitative relationship between the ΔE/Δl slope and the weight loss tests.

Such a measure of the corrosion rate was desirable, since it would require only small amounts of applied current and would therefore probably not affect the local cell polarization equilibrium and could be determined in a relatively short period of time.

Results of the ΔE/Δl Slope Determination

To establish the anticipated relationship between ΔE/Δl and the corrosion rate calculated from weight loss data, several measures of ΔE/Δl were made on each specimen, each day that it was exposed to the corrosion environment. To place each determination on an equivalent basis, the ΔE/Δl was converted to ΔE/c.d. (the change in potential per unit applied current density). In order to relate the weight loss corrosion rate to ΔE/c.d. (volts/ma/dm^2), a time average value of ΔE/c.d. was calculated. This resulted in an apparent logarithmic relation as shown in Figure 1.

Using this relationship, values were then obtained for the instantaneous corrosion rates. These instantaneous corrosion rates were then time-averaged to calculate an average corrosion rate for the period from which a value of ΔE/c.d. was obtained from the line in Figure 1. These corrected average values of ΔE/c.d. were then plotted against the weight loss

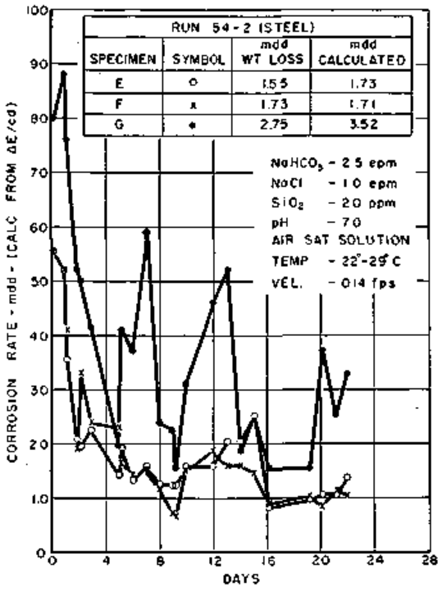


Figure 3—Corrosion rate variation with time for Run 54-2.

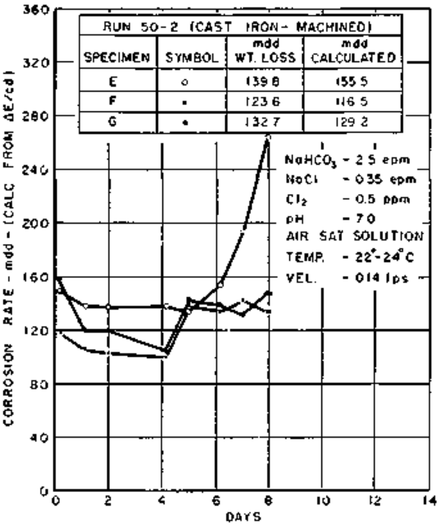


Figure 4—Corrosion rate variation with time for Run 50-2.

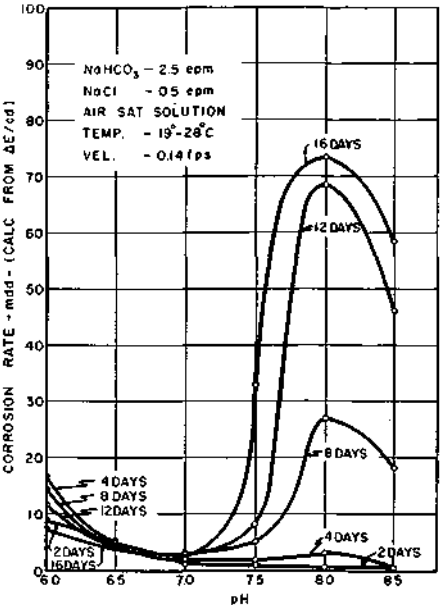


Figure 5—Effect of pH on corrosion rate.

corrosion rate. The points shown in Figure 1 relate to all such values as determined to date.

Figures 2-4 show actual tests on the instantaneous corrosion rate (mdd) versus the time exposed.

Figure 2 shows the typical results of specimens that have an initial resistance to corrosion that eventually breaks down with time of exposure to allow high rates of corrosion. The corrosion rate usually increased very sharply at the breakdown of the initial resistance to corrosion.

Figure 3 shows the instantaneous corrosion rates of specimens in a less aggressive environment. All three specimens indicate continually changing corrosion systems. Specimen G shows a greater variability with sharp increases and decreases in the corrosion rate.

Figure 4 shows the results with three machined cast iron specimens. With these specimens and with steel specimens in some environments there was little initial resistance to corrosion and the corrosion rate was high immediately.

That the corrosion rate is not a smoothly changing function for a particular specimen is indicated by the rather sharp increases and decreases in the corrosion rates. Since this occurs, a continuous measurement of the instantaneous corrosion rate would be required in order to determine a more exacting relationship between the instantaneous rate as measured by the slope of ΔE/c.d. and the rate as measured by weight loss. The intermittant measurements of ΔE/c.d. which were made therefore did not include many other variations in the corrosion rates between measurements. This in part accounts for the deviations from the line shown in Figure 1. The results tend to deviate by an average error of about 20 percent.

Another primary source of error results from the specific resistances of the various solutions. These do not significantly affect ΔE/Δl for specimens having low corrosion rates since the local cell resistances are large in comparison to the solution resistances. However, when the local cell resistances are very low as would be the case with a specimen having a high corrosion rate, the effect of the solution resistance may be a significant portion of the ΔE/Δl readings. This is demonstrated in Figure 1 by the points outlined in the dashed-lined sections which represent specimens immersed in solutions of lower resistance (350-850 ohm-cm). The fact that most of the solutions under test have similar ionic strength, 3000 ohm-cm, reduces much of the possible deviation. If greater accuracy were required the effect of solution resistance could possibly be determined. The accuracy at lower corrosion rates is limited by instrument sensitivity.

The potential lag behind the application of current was another possible source of error. To avoid this, the potential was considered stable after the potential reading had been constant for two minutes. The time for the potential to reach a steady state after each increment of applied current, varied from a few seconds for specimens with high corrosion rates to about 15 minutes for specimens with very low corrosion rates.

Application of the ΔE/Δl Determination of Corrosion Rates

Effect of pH on the Corrosion Rate of Mild Steel

Using the ΔE/Δl determination, the effect of pH on the corrosion rate of mild steel was studied at room temperature in aerated water containing 2.5 epm $NaHCO_3$ and 0.5 epm NaCl. The pH (6.0 to 8.5) was controlled by the continuous addition of CO_2. Measurements of ΔE/ΔI were made each day to follow the course of the corrosion process. Figure 5 shows the results of this study, the calculated corrosion rate being plotted against pH with a series of curves for 2, 4, 8, 12 and 16 days of immersion at 0.14 foot per second. With the passage of time a maximum corrosion rate appears to be established at a pH of 8.0. However, since the corrosion rates of the steel specimens are still increasing at pH values of 7.5 and 8.5, the maximum corrosion rate could be somewhere between these pH values and not necessarily at pH 8.0.

Luce and Fontana[8] indicated a similar peak of corrosion rate at pH 8.0 in their study of the effect of pH on erosion-corrosion of mild steel in "distilled water" using circular rotating discs at high velocity. The reluctance of the specimens at pH 8.5 to start corroding indicates that at higher pH values there may be little corrosion. There appears to be a tendency for the corrosion rate at pH above 8.5 to approach a minimum.

The rates at pH 6.5 and 7.0 are fairly constant. At a pH of 6.0, the corrosion rate reached a peak value of 16.8 mdd after 4 days, but decreased to 7.3 mdd at 16 days.

The average corrosion rates as determined by weight loss for the 17.2 days of immersion were: pH 6.0—10.0 mdd; pH 6.5—5.0 mdd; pH 7.0—2.6 mdd; pH 7.5—11.9 mdd; pH 8.0—49.9 mdd; pH 85—34.1 mdd.

In review of these data, the quality of water must be stressed. Considering the chloride-bicarbonate ratio, these results are in agreement with previous studies[1,3] which also show that higher chloride-bicarbonate ratios result in higher corrosion rates at pH 7. At lower chloride-bicarbonate ratios, equal or lower rates might be expected at pH 8 and 8.5. Thus the relation of pH to corrosion rate depends on the mineral composition of the environment.

Summary

A limited empirical quantitative relationship has been shown to exist between the polarization slope, $\Delta E/\Delta I$, at low current density and the corrosion rate as measured by weight loss. Such a relationship permits a rapid empirical determination of the corrosion rates and changes in the corrosion rates of metal specimens while they are immersed in a "fresh water" environment. The measurement of $\Delta E/\Delta I$ is an important aid in the study of the effect of changes in the corrosion environment, such as in the evaluation of the effectiveness of inhibitors.

Acknowledgment

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