Measurement of the Corrosion Rate of Iron by Polarization Techniques

W. J. Schwerdtfeger

Corrosion-rate-measuring techniques previously shown to be applicable to low-carbon steel exposed to corrosive soils are also shown to apply to low- and medium-carbon steels in a sodium chloride solution having a concentration of 2,000 parts per million. Unlike the work previously reported, IR drops, attributable to polarizing currents, are included in the potential measurements.

It is shown how corrosion-rate measurements can be made automatically by using a synchronously driven voltage divider and a two-pen electronic recorder.

The polarizing characteristics of high-silicon cast iron when exposed to a 2,000-parts-per-million sodium chloride solution were also studied. It is shown that the corrosion rate becomes relatively low as the corrosion reaction changes from cathodic to anodic control.

1. Introduction

Iron and steel are the most commonly used structural materials and under certain conditions of exposure are very susceptible to severe damage by corrosion. In the laboratory, the extent of corrosion is usually expressed in such terms as "weight loss" or "pit depth," whereas, in the case of permanent field structures, visual inspection is probably the chief way of evaluating damage.

When the degree of corrosion is based on weight loss, the test specimens must be exposed sufficiently long to render the cleaning errors negligible in comparison with the actual weight losses. Also, in order to study the effect of exposure time on the rate of corrosion of a given material, removals of similar specimens at several intervals must be resorted to. Under these conditions, the results depend on the uniformity of the electrolyte. If the electrolyte is a soil, the corrosion rates of similar specimens may differ unless the degree of aeration around each is the same.

On permanent field structures, corrosion products must be removed in order to estimate the extent of corrosion damage. After inspection, unless preventive measures are taken, corrosion will be resumed, temporarily at least, at an accelerated rate.

The foregoing encourages the search for any method of measuring corrosion rate in which the disadvantages discussed above might be overcome. Previous work has shown that the corrosion rates on small low-carbon steel specimens exposed to soils in the laboratory can be measured electrically by the analysis of polarization curves [1].[1] During that investigation, weighed steel disks (exposed area—2.4 in.²) were exposed to 6 soils for a period of 2 months. Cathodic and anodic polarization curves were obtained on the specimens at periodic intervals, followed by cleaning and reweighing. On the average, the calculated weight losses based on the electrolytic measurements and Faraday's law were within 4 percent of the measured weight losses. In each of the 6 soils, it was observed that a relatively constant ratio existed between the calculated corrosion current and a value of current, designated I_p, ob-

tained from a break (change-in-slope) in the cathodic-polarization curve. As the corrosion process was cathodically controlled, the use of cathodic polarization, exclusively, in measuring corrosion rate appeared to be justifiable. The simplified approach was suggested by Pearson [2] and by Holler [3]. During that investigation [1] this was tried, using one soil, and found to be satisfactory.

Up to the present time, corrosion-rate measurements, based on cathodic and anodic polarization cruves, have been made with null or current-interruption circuits [1, 2, 3, 4, 5]. Although such circuits are necessary when accurate potential readings are desired, their use is not always necessary for observing breaks in polarization curves. The purpose of this investigation is to show, at least for the conditions of the experiments, that substantially all corrosion can be evaluated by using somewhat more simple electrical measuring techniques than usually employed, in which the IR drops are included in the potential measurements. The use of cathodic-polarization measurements, exclusively, is evaluated by measuring the effects of heat treatment and carbon content on the corrosion rate of carbon steel. The adaptability of a duplex electronic recorder for use in studying polarization characteristics and measuring rates of corrosion is also illustrated and discussed.

2. Theoretical Considerations

The hypothetical polarizing characteristics of a galvanic couple exposed to an aqueous medium of negligible resistance are shown graphically in figure 1. Part A shows the polarization of the anode and cathode of the couple and part B represents the effect of external current on the couple.

The symbols used in this paper are identified and defined as follows:

E_a = open-circuit potential of the anode.
E_c = open-circuit potential of the cathode.
E_g = potential of the couple.
i_0 = local action or corrosion current.
I_p = external cathodic current applied to the couple when the anode current (local-action current) becomes zero. This is the minimum current required for cathodic protection.

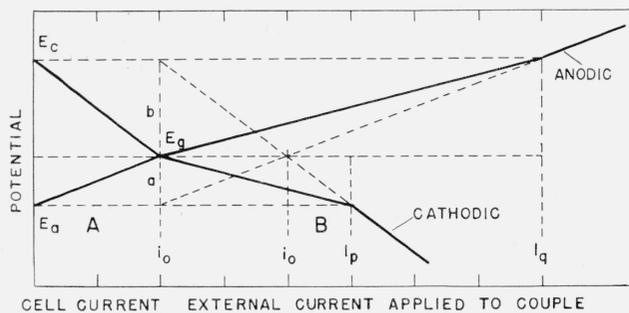[1] Figures in brackets indicate the literature references at the end of this paper.

FIGURE 1. *Hypothetical polarization of a galvanic couple in an electrolyte of high conductivity.*

I_q = external anodic current applied to the couple when the cathode current (local-action current) becomes zero.

a = change (ΔE_g) in the potential of the couple from the value at zero applied current to the value at I_p.

b = change (ΔE_g) in the potential of the couple from the value at zero applied current to the value at I_q.

With reference to figure 1, it has been shown previously [1] that

$$\frac{a}{b} = \frac{I_p}{I_q} \qquad (1)$$

and

$$i_0 = \frac{b}{a+b} I_p = \frac{I_q}{I_p + I_q} I_p. \qquad (2)$$

The ratio a/b might be regarded as a measure for expressing the type of polarization control. Complete cathodic control is approached as the current I_q becomes large as compared with the current I_p. Under such conditions, on the basis of eq (2), i_0 is substantially equal to I_p.

It can be seen (fig. 1) that as the ratio a/b becomes smaller the change-in-slope of the curve at I_q becomes increasingly difficult to observe. Fortunately, the change-in-slope at the current I_p is relatively easy to observe in many cathodically controlled reactions, where it is also more significant than I_q. Such happens to be the case with low-alloy ferrous materials exposed to soils and solutions.

It has been shown that, for steel exposed to soils, the cathodic-protection current, I_p, bears a nearly linear relationship to the corrosion current, i_0, and as a consequence the rate of corrosion can be estimated from cathodic-polarization curves [1]. Based on eq (2), it is interesting to note that a variation in the ratio I_p/I_q from 0.1 to 0.25, for a given value of I_p, results in a change in the corrosion current of only about 11 percent. Thus, it is desirable to establish the ratio empirically and to base corrosion-rate calculations on the cathodic-polarization curves, exclusively, whenever possible, as some degree of error is possible even when estimating I_p from the polarization curve. Evans [6] has pointed out that, in the absence of passivity, cathodic polarization bears a greater influence on corrosion rate than does anodic polarization.

In obtaining polarization curves by ordinary potential measurements between a reference electrode and the specimen during passage of the polarizing current, the *IR* drop in the corroding medium is included in the measurements. However, whether measuring this potential, or the potential, free of *IR* drop (as in fig. 1), obtainable by special methods of measurement, there will occur a break in the potential-current curve at I_p or I_q as dependent on the type of polarization being employed. Thus, in corrosion-rate studies, potential measurements including *IR* drops are satisfactory.

Although most corrosion reactions are said to be cathodically controlled, the polarization method of measuring corrosion rate also applies to reactions that are anodically controlled. In reactions under anodic control the current I_q (eq 2) becomes the more significant as it is then smaller than I_p. Also, the slope (a/i_0) of the anodic-polarization curve beyond the current I_q will be steeper than the slope (b/i_0) of the cathodic-polarization curve beyond the current I_p. This follows from eq (1), which could be written,

$$\frac{I_p}{I_q} = \frac{a/i_0}{b/i_0}, \qquad (3)$$

and will be shown later to apply to experimental data on high-silicon cast iron.

3. Experimental Procedure

All the electrical measurements to be described later were made on ferrous specimens exposed to a solution containing 0.2 percent (2,000 ppm) of sodium chloride in tap water, which varied in temperature between 20° and 27° C. Based on data in the Corrosion Handbook [7], this solution is almost as corrosive to iron as one containing 3 percent of sodium chloride. Thus, sizable weight losses could be expected in a reasonable length of time, and yet the concentration was low enough to provide *IR* drops of sufficient magnitude to affect the potential readings and thus permit study of the usefulness of the proposed method. The electrolyte was contained by an open cylindrical wooden vat (fig. 2) having an inside diameter of about 66 in. and was maintained to a depth of about 18 in. The arrangement of supporting bars, shown fastened across the top of the vat, was used for mounting and positioning of the specimens and a half-cell probe. Auxiliary anodes are shown mounted on the inner wall of the vat. The solution was renewed between the individual tests described in the experimental results.

Except for one tubular-steel specimen, all steel specimens were of rod material. Specific dimensions are given in the section on experimental results. The ends of the rods and edges of the tubing were rounded and all burrs removed so as to avoid weight-loss errors and accelerated corrosion at the edges. This was followed by degreasing with carbon tetrachloride. The aluminum- and silicon-killed steel specimens were immersed in a 5-percent sulfuric acid solution for 2 hr, with intermittent scrubbing to remove loosened mill scale, followed by immersion
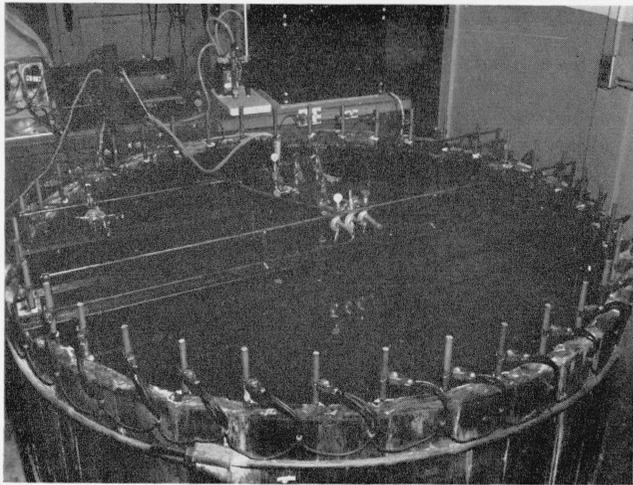
FIGURE 2. *View of the experimental arrangement.*

in a 10-percent calcium hydroxide solution for 15 min and finally washing the specimens in running hot water. All specimens were then steel-wire brushed so as to produce a bright surface and weighed to the nearest 5 mg. The high-silicon cast-iron specimen, although wire brushed, was exposed without weighing, in anticipation of negligible corrosion. Having a rough surface, a cleaning error could easily exceed the actual weight loss due to corrosion.

All specimens were protected against corrosion at the water line by covering a 3-in. intermediate section with plastic electrical tape (half-lapped). The unexposed portion of the specimen (bare surface above the tape) was covered with a film of oil in order to prevent atmospheric corrosion, the portion on the other side of the tape being exposed to the electrolyte. The rod specimens were each fitted with a perforated rubber stopper over which a clamp was fitted for holding the specimen in a vertical position during exposure.

Polarization data were obtained on a given set of specimens at fairly regular intervals during the exposure periods, which ranged from 14 to 45 days. After the exposure of the specimens, the tape was removed and the corrosion products loosened and removed by cathodically cleaning the specimens in the test electrolyte for a period of 2 to 3 hr at a current density of about 1 amp/ft.² Following this, the specimens were lightly brushed under running hot water with a steel wire brush and then, when dry, more vigorously with a brass wire brush. The specimens were then reweighed in order to measure the actual weight losses attributable to corrosion.

All potential measurements were made with reference to a saturated calomel half-cell, which was bridged to the electrolyte by a flexible plastic tube filled with a saturated potassium chloride-agar mixture. When measurements were to be made, the agar bridge was slipped into a sleeve made of insulating material mounted vertically inside of the wooden vat and also symmetrically with respect to the set of specimens under exposure. The end of the flexible tube just protruded from the lower end of the sleeve. The end of the flexible tube was in a horizontal plane through the centers of the exposed lengths of the specimens and off to the side a distance not less than one-quarter of the length of an exposed section. In the beginning, when the recorder was not used, potentials were measured with a high-resistance voltmeter (200,000 ohms/v) and the polarizing current, supplied through graphite anodes, was adjusted manually. The polarization data were obtained by increasing the current in equal increments of 2-min duration. Later, when using the recorder, polarizing current was applied by linearly increasing the applied voltage by means of a synchronously driven voltage divider. Metal anodes were used when measurements were made with the recorder in order to eliminate the polarization difficulties present with the graphite anodes.

4. Experimental Results

4.1. Evaluation of i_0/I_p for Carbon Steel

In order to find the relationship between the polarizing currents I_p and I_q pertaining to carbon steel exposed to the 0.2-percent sodium chloride solution, and consequently the evaluation of i_0/I_p, a 3/16-in.-diameter cold-rolled specimen was exposed for 29 days.

In addition to the preparatory procedure outlined in section 3, the exposed tip of the specimen was coated by dipping the rod into molten bitumen, leaving 12 in. for exposure to the electrolyte.

The data obtained as a result of cathodically and anodically polarizing the specimen are tabulated in table 1. Typical polarization curves from which the values of I_p and I_q were obtained are shown in figure 3. The weight loss of the rod during the exposure period, not stated in the table, was 345 mg. By Faraday's law, 30 mg was removed electrolytically during the 8 anodic polarization runs, each of which was 45 min in duration at an average current of 5 ma. The total calculated weight loss of 313 mg (283 mg during exposure plus 30 mg during anodic polarization runs) differs by about 9 percent from the measured weight loss of 345 mg. The estimated effect of the cathodic runs on weight-loss reduction is less than 1 percent and is therefore neglected. Aside from the possible errors attributable to the interpretation of the polarization curves (fig. 3), the degree of variation between the calculated and measured weight losses also depends on the margin of error in assuming linear changes in corrosion rate between successive measurements (table 1).

It will be noted (table 1) that the values of I_p/I_q lie within a range that corresponds to only a relatively small variation of i_0/I_p. In fact, in view of the reasoning already presented in section 2, the use of the expression $i_0 = 0.9\ I_p$ would appear to be justifiable. Accordingly, therefore, a considerably larger specimen was prepared for exposure in order to further test the i_0/I_p ratio. The specimen was a 3.25-in. o. d. cold-drawn steel tube with 9.25 in. of its outer length exposed to the salt solution. The exposed lower end of the tube was fitted with a rubber

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TABLE 1. *Relationship between the corrosion current and cathodic protection current for carbon steel exposed to a 0.2-percent sodium chloride solution*

Exposure time	Polarizing current at break in curve		Corrosion current,[a] i_0	Weight loss calculated[b]	Ratio $\frac{I_p}{I_q}$	Ratio $\frac{i_0}{I_p}$
	Cathodic, I_p	Anodic, I_q				
Days	*ma*	*ma*	*ma*	*mg*		
4	0.34	3.0	0.31	31	0.11	0.91
5	.34	3.0	.31	8	.11	.91
6	.50	4.0	.44	9	.12	.88
7	.51	4.0	.45	11	.13	.88
13	.33	3.8	.30	56	.09	.91
18	.29	3.2	.27	36	.09	.93
22	.66	5.0	.58	43	.13	.88
29	.50	4.1	.45	89	.12	.90
				[c] 283	[d] .11	[d] .90

[b] $i_0 = I_p I_q / (I_p + I_q)$, eq (2).
[b] Weight loss (grams) $= K t i_0$, where $K = 2.8938 \times 10^{-4}$ g/coulomb and i_0 is the average current (amp) for the period, t, in seconds, between successive readings during exposure. For the periods before the initial and following the final polarization runs, the values of i_0 for the initial and final runs, respectively, were taken as average.
[c] Total value attributed to normal corrosion.
[d] Average value.

stopper and sealed around the edge with molten asphalt in order to confine the corrosion to the external surface of the tube. This end rested on an inverted glass beaker, centrally positioned in the wooden vat. The tube was held in a vertical position and protected against corrosion at the electrolyte line and above as previously described.

Cathodic- and anodic-polarization curves were obtained on the specimen. The I_p/I_q ratio was found to be approximately the same as that observed with the 3/16-in. rod and therefore the weight-loss calcula-

FIGURE 3. *Polarization curves of a steel specimen exposed to a 0.2-percent sodium chloride solution.*

TABLE 2. *Corrosion rate on a 3¼-in.-diameter steel tube, as calculated from cathodic-polarization curves only, when exposed to a 0.2-percent sodium chloride solution*

Exposure time	Polarizing current at break in curve, I_p	Corrosion current,[b] i_0	Weight loss, calculated[c]
Days	*ma*	*ma*	*mg*
[a] 0	2.4	2.2	------
2	3.6	3.2	135
6	3.1	2.8	300
8	4.4	4.0	170
10	3.2	2.9	175
13	2.9	2.6	202
15	2.8	2.5	125
17	3.6	3.2	145
20	2.5	2.2	202
22	2.4	2.2	110
24	2.5	2.2	110
27	3.2	2.9	188
29	2.9	2.6	140
30	------	------	65
			[d] 2,067

[a] After 4 hr of exposure.
[b] $i_0 = 0.9 I_p$ (see footnote d, table 1).
[c] See footnote b of table 1.
[d] Total value attributed to normal corrosion.

tions are based on $i_0 = 0.9 I_p$ (table 2). During the running of the 13 anodic polarization curves, it was estimated that an additional 98 mg of iron went into solution; the effect of the cathodic runs on weight loss was neglected, it being less than 1 percent. The tube lost 2,245 mg during the 30-day exposure period. Based on this measured total value, the calculated weight loss of 2,165 mg (2,067 mg during exposure plus 98 mg during anodic-polarization runs) differed by 3.6 percent.

4.2. Comparison of Aluminum- and Silicon-Killed Low-Carbon Steels—Normal and Heat-Treated

It has been shown that cathodid-polarization curves are useful alone as a means for measuring the corrosion rate of carbon steels. This section will be devoted to further study of the sensitivity and practicability of this method.

The specimens were prepared as discussed in section 3 and were cut from ½-in. rod with 12 in. of rod length exposed to the corrodent. Four specimens were simultaneously exposed to the 0.2-percent salt solution for a period of 14 days. Two of the specimens were of aluminum-killed steel, one being heated to 1,650° F and water-quenched before exposure. The other two specimens were of silicon-killed steel, one being similarly heat-treated.

The data (table 3) indicate that the corrosion rates of the two steels are approximately alike. However, water-quenching appears to have increased the corrosion rates by about 10 percent, on the basis of both the calculated and the actual weight losses. The agreement between the calculated and actual weight losses is remarkably good. As the polarization curves were obtained on the 4 rods within a period of 3 hr, the average values of I_p (table 3) are probably just as valid as the calculated weight losses for comparing the relative rates of corrosion.
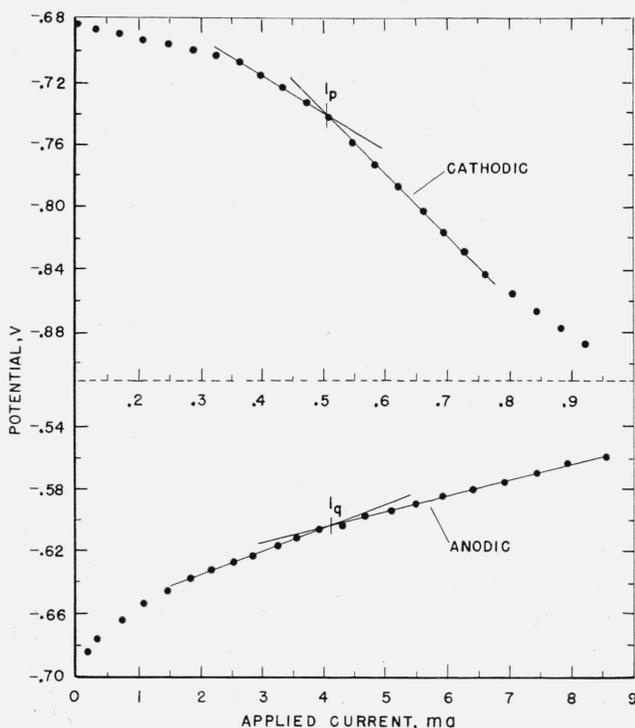
TABLE 3. *Comparative corrosion rates of aluminum- and silicon-killed steels—effects of water-quenching*

Exposure time	Polarizing current at break in curve, I_p	Weight loss	
		Calculated [d]	As weighed
Aluminum-killed, no heat treatment [a]			
Days	ma	mg	mg
4	1.60	144	------
7	1.16	93	------
10	0.66	61	------
12	.68	30	------
14	------	30	------
	[c] 1.02	[e] 358	365
Aluminum-killed, water-quenched [a]			
4	1.60	144	------
7	1.28	97	------
10	1.00	77	------
12	0.86	42	------
14	------	39	------
	[c] 1.18	[e] 399	400
Silicon-killed, no heat treatment [b]			
4	1.70	153	------
7	0.92	88	------
10	.68	54	------
12	.78	33	------
14	------	35	------
	[c] 1.02	[e] 363	360
Silicon-killed, water-quenched [b]			
4	1.82	164	------
7	0.94	93	------
10	.97	64	------
12	.78	39	------
14	------	35	------
	[c] 1.12	[e] 395	390

[a] Composition of steel in percent: 0.20 C, 0.53 Mn, 0.016 P, 0.027 S, 0.03 Si.
[b] Composition of steel in percent: 0.19 C, 0.42 Mn, 0.015 P, 0.025 S, 0.14 Si.
[c] Average value.
[d] $i_0 = 0.9I_p$ (see footnotes b and d, table 1).
[e] Total value.

4.3. Corrosion-Rate Measurements, Using Automatic Equipment

These data were obtained by using a two-pen "continuous balance" electronic recorder. One of the pens recorded the potential of the corroding specimen as measured with a high-impedance circuit, and the other pen recorded the polarizing current to the specimen produced by a linearly increasing applied voltage. The applied voltage was taken from a 10-turn potentiometer (voltage divider) geared down to a speed of 0.2 rpm by a synchronous motor equipped with a gear train. Thus, the potential and the current were recorded simultaneously.

In addition to minimizing human error, the recorder offers other advantages over indicating instruments. For example, upon interruption of the applied voltage, the magnitude of IR drop included in the polarized potential can be estimated from the polarization decay curve following the removal of applied current.

a. Preliminary Measurements

The data were taken on the aluminum-killed non-heat-treated specimen previously discussed in section 4.2. A composite photograph (fig. 4) of a series of strip-chart records shows the effect on the corrosion rate of the specimen, as reflected by the cathodic-polarization curves, when air was forced into the electrolyte. Charts A and B were run on the fourth
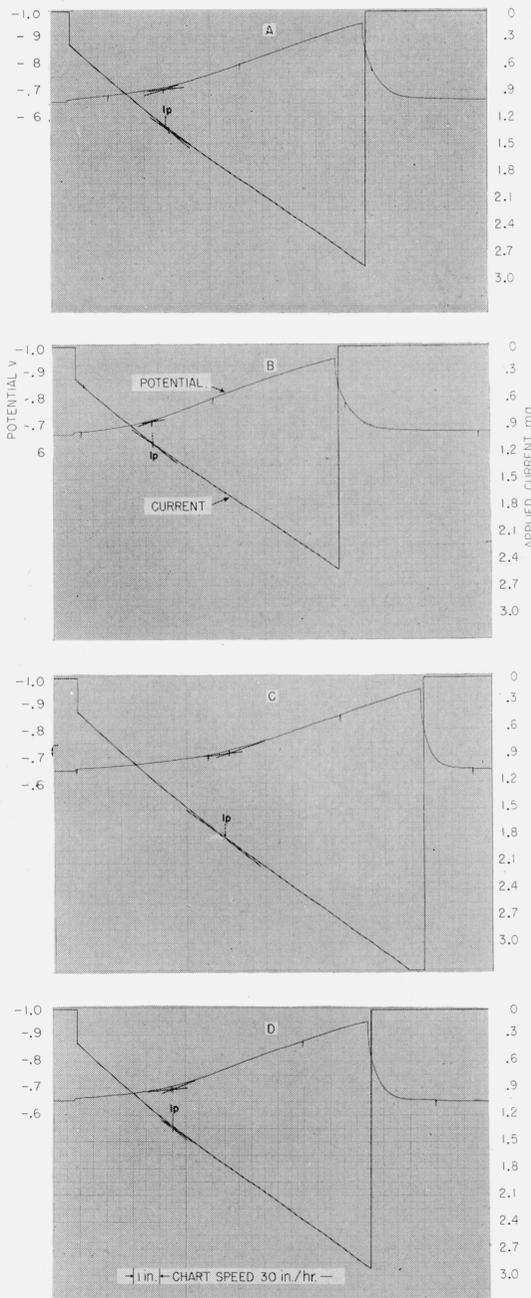

FIGURE 4. *Cathodic polarization of a steel specimen exposed to the 0.2-percent sodium chloride solution as recorded by the electronic recorder.*

A, 4 days after initial exposure, solution is still; B, 5 days after initial exposure solution is still; C, 7 days after initial exposure, air forced into the solution since B; D, 8 days after initial exposure, solution is still, air off since C.
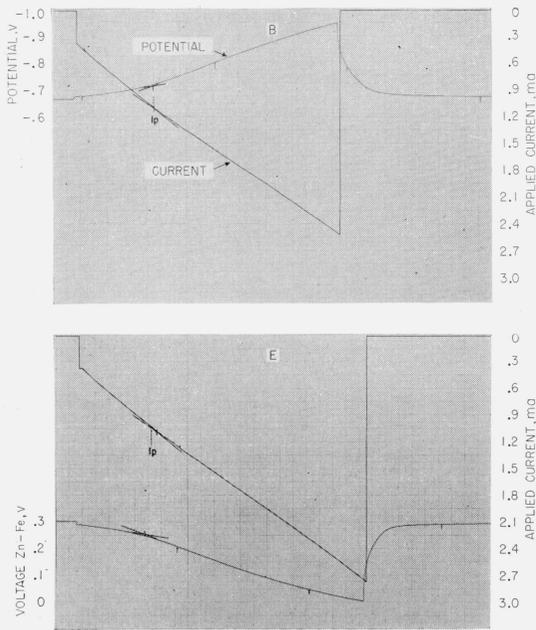
FIGURE 5. *Use of auxiliary anode (Zn) as a reference electrode (chart E).*

TABLE 4. *Corrosion rates of low- and medium-carbon steels based on strip-chart records—effect of heat-treating the medium carbon steel*

Exposure: 45 days in 0.2-percent sodium chloride solution.

Exposure time	Polarizing current, I_p (strip chart)			
	Low-carbon steel [c]	Medium-carbon steel [d]		
		No heat treatment	Heat-treated	
			Quenched [e]	Quenched and tempered [f]
Days	*ma*	*ma*	*ma*	*ma*
0	1.50	1.60	1.40	1.50
2	1.30	1.35	1.20	1.35
6	1.50	1.46	1.25	1.22
7	1.27	1.10	1.20	0.95
9	1.30	1.10	1.20	0.96
12	1.20	1.03	1.20	1.00
15	1.15	1.10	1.25	0.95
16	1.50	1.30	1.60	1.10
19	1.45	1.05	1.43	1.05
20	1.05	0.97	1.14	0.97
21	1.15	1.05	1.23	1.05
22	1.05	1.05	1.30	1.07
23	1.08	1.08	1.30	1.05
26	1.20	1.20	1.38	1.10
27	1.23	1.23	1.35	1.15
28	1.10	1.10	1.27	1.10
29	1.28	1.35	1.43	1.20
30	1.48	1.45	1.45	1.44
33	1.20	1.20	1.35	1.15
34	1.45	1.45	1.55	1.40
36	1.18	1.20	1.28	1.10
37	1.16	1.20	1.30	1.10
40	1.30	1.30	1.44	1.25
41	1.26	1.25	1.35	1.25
42	1.35	1.35	1.45	1.35
Avg I_p	1.27	1.22	1.33	1.15
Calculated weight loss [a] _____ mg__	1,286	1,235	1,347	1,164
Actual weight loss_____ mg__	1,300	1,285	1,285	1,225
Difference between actual and calculated weight loss [b] %__	−1.1	−3.9	4.8	−5.0

[a] $i_0 = 0.9\ I_p$ (see footnotes b and d, table 1).
[b] Based on the actual weight loss.
[c] Not over 0.15 C.
[d] 0.45 C.
[e] 1,650° F, then water-quenched.
[f] 1,650° F, then water-quenched, then tempered from 1,400° F.

and fifth days, respectively, of exposure. After recording chart B, air was introduced into the salt solution at an arbitrary rate, continuously for 2 days when the curves (chart C) were obtained. The aeration was then discontinued and the following day chart D was recorded.

It will be noted (fig. 4) that the breaks, I_p, are reflected by both the current and the potential curves. The aeration of the electrolyte caused the corrosion rate of the steel to be increased (chart C) by about 50 percent. This is shown by a reduction in the rate of corrosion (chart D) with the air off.

On charts A and D, the breaks I_p indicate approximately equal rates of corrosion and the respective changes in both the current and the potential-versus-time curves are almost identical.

The coincidence of the break in the current curve with that in the potential curve is due to the fact that the zinc, used as the auxiliary anode, did not polarize appreciably throughout the range of polarizing current. Such being the case, an anode might also be made to serve as a reference electrode. Figure 5 is composed of two curves obtained on this steel specimen; the first B, reproduced from figure 4, being obtained with the saturated calomel reference electrode, and the second, E, was obtained 6 days later, using the zinc anode as the reference. It will be observed that the break due to the polarization of the specimen is clearly shown by the voltage (Zn-Fe) curve and agrees fairly well with the break in the current curve.

b. Comparison of Low- and Medium-Carbon Steel and Effects of Heat-Treating the Medium-Carbon Steel

Four specimens were exposed to a 0.2-percent sodium chloride solution for 45 days. One specimen was of low-carbon steel (0.15 C) and the others were of medium-carbon steel (0.45 C). One of the medium-carbon specimens was in the hot-rolled condition (as received), one, water-quenched from 1,650° F., and the other, water-quenched from 1,650° F and tempered at 1,400° F. All were cut from ⅝-in.-diameter stock and 12 in. of length was exposed to the salt solution. The specimens were symmetrically positioned around the reference electrode, which was mounted in the center of the wooden tank.

Data obtained from the cathodic polarization curves and weight losses are shown in table 4. In order to check the i_0/I_p ratio, previously evaluated, anodic polarization curves, in addition to cathodic, were obtained on the 7th, 19th, 30th, and 42d days of exposure for each of the four specimens. The average i_0/I_p ratio, resulting from the 16 sets of

data, was again approximately 0.9, ranging from 0.88 to 0.92. The calculated weight losses (table 4) are based on the average values of I_p, as measurements were made frequently. The net effect of both cathodic and anodic polarization on the weight losses was estimated to be less than 1 percent and therefore is neglected.

The differences in the corrosion rates of the specimens, both actual and calculated, must be considered negligible with possibly the exception of the tempered specimen. These and previous measurements seem to indicate that variations in values of I_p as low as 10 percent can be considered as revealing significant differences in rates of corrosion when the control of the corrosion reaction is within the limits previously described.

c. Measurements on High-Silicon Cast Iron

High-silicon cast iron is known for its good corrosion resistance in many aqueous environments. The material is not machinable and comes fabricated only in the form of castings. Because of these characteristics, accurate corrosion weight-loss measurements cannot be made when high-silicon cast iron is exposed for relatively short periods of time, but the polarization technique of corrosion-rate measurement would appear to be particularly adaptable.

A specimen of high-silicon cast iron (Duriron), in the form of an anode ordinarily sold for use in cathodic protection, was exposed to a 0.2-percent sodium chloride solution for a period of 28 days, during which time the polarizing characteristics of the material were studied. The specimen had a diameter of 1 in., and 12 in. of its length was exposed to the electrolyte. Contrary to the behavior of carbon steel, the potential of the high-silicon cast iron started to change toward more cathodic values after having been exposed for 1 hr.

Cathodic and anodic polarization curves recorded during the first 14 days of exposure are shown in figure 6. The cathodic curve A was obtained after the specimen had been exposed for 3½ hr. Then, after a lapse of another 2 hr, allowed for the decay of the cathodic polarization, the anodic curve A was recorded. The break in the cathodic-potential curve, A, occurred at a current I_p of 1.8 ma, whereas no break appeared in the corresponding anodic-potential curve for the range of applied currents shown. This initial set of curves is typical of those for carbon steel in that the cathodic polarization is greater than the anodic polarization, and the magnitude of I_p is about what would be expected for the exposed area involved. There was visible evidence of a fairly high corrosion rate during the first 24 hr in the form of rust, which commenced to appear around the high-silicon cast iron a few hours after exposure. The action is considered normal for this material during the early stages of exposure. The change in potential toward more cathodic values continued and in 24 hr amounted to approximately 0.3 v, at which time the second pair of curves, B, was obtained. It will be observed that anodic polarization now occurs at a greater rate than on the previous day and that the corrosion reaction is now anodically controlled (table 5). Thus, the corrosion rate is now determined chiefly by the break in the anodic-potential curve as evaluated by the current I_q. The slope of the anodic-potential curve now becomes steeper at currents greater than I_q, whereas when the reaction was cathodically controlled (curves A) the slope of the cathodic potential curve became steeper at currents greater than I_p.

TABLE 5. *Polarization-curve data on high-silicon cast iron exposed to a 0.2-percent sodium chloride solution*

Exposure time	Curve (fig. 6)	Corrosion potential	Polarizing current		Slope [a]	
			cathodic, I_p	anodic, I_q	cathodic, b/i_0	anodic, a/i_0
Days		*v*	*ma*	*ma*	*mv/ma*	*mv/ma*
0.2	A	−0.530	1.80	>1.80	100	14
1	B	−.235	>0.40	0.40	80	480
5	C	−.075	.30	.05	117	700
14	D	−.060	.40	.05	115	960

[a] See the text.

The next set of polarization curves, C, were obtained after 5 days of exposure. It will be noted that the corrosion potential had changed still farther in the noble direction and that the corrosion rate as indicated by the current I_q is even smaller than previously. The final set of curves, D, shown in figure 6, were run on the 14th day of exposure. The corrosion potential is about the same as it was on the 5th day of exposure, as is the corrosion rate. Curves, not shown, were again obtained on the 28th day of exposure when breaks in the potential curves appeared at substantially the same values of current as revealed by curves D. The specimen was then removed from the salt solution. The little evidence of rust was readily removed with a wire brush.

That eq (3) is fairly well substantiated by the results obtained from the polarization curves is shown by the data (table 5). This is particularly so for the data from curves C and D where values are given for both I_p and I_q. Excessive IR drop, if included in the polarized potentials, would disturb the relation, but in the experiment under discussion it can be seen that the IR component, as can be estimated from the decay curves (fig. 6) following the removal of polarizing current, was only a small part of the potential change.

As previously mentioned, the values of I_p and I_q from curves D (table 5) represent a condition that is substantially stabilized for longer periods of exposure. Therefore, by substituting these values of I_p and I_q into eq (2) and using the resultant value of i_0 in Faraday's equation, the weight-loss equivalent figures out to be about 0.055 $(oz/ft^2)/yr$. That this is a realistic value can be judged by comparing it with weight-loss measurements on high-silicon cast iron made by Logan [8] after approximately 12 years of underground exposure. The average weight loss was 0.031 $(oz/ft^2)/yr$ on specimens buried in 35 soils ranging in resistivity from 60 to 45,000 ohm-cm.
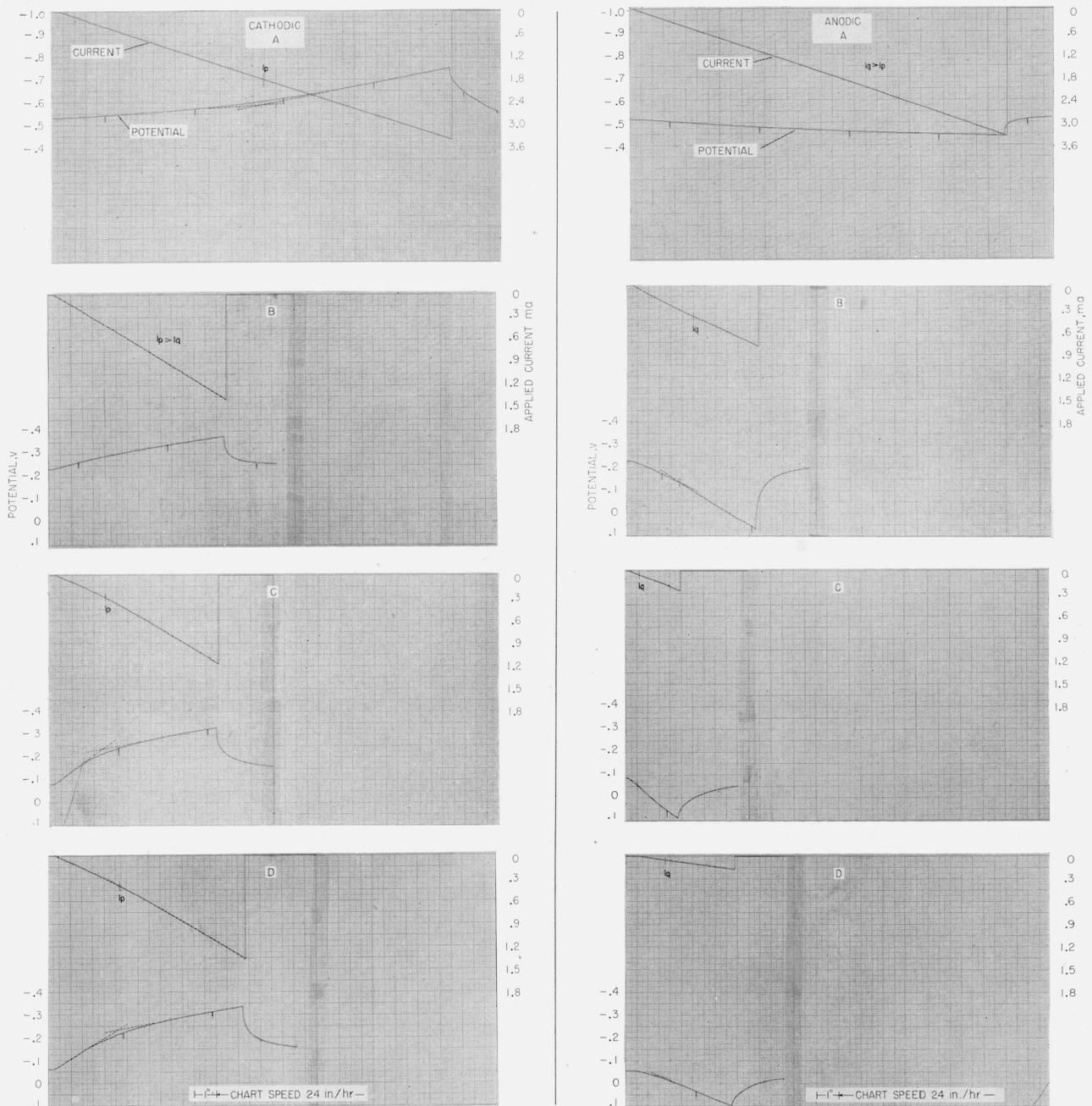
FIGURE 6. *Polarization of high-silicon cast iron exposed to a stagnant 0.2-percent sodium chloride solution.*

A, 3 to 5 hr after initial exposure; B, after 24 hr of exposure; C, after 5 days of exposure; D, after 14 days of exposure.

5. Summary

The corrosion of carbon steel in a 0.2-percent sodium chloride solution was found to be cathodically controlled to the extent that the ratio between corrosion and cathodic protection currents was relatively constant, being about 0.9. This value corresponds to an average ratio, 0.83, previously found applicable for carbon steel exposed to a variety of corrosive soils [1].

The sensitivity of the cathodic-polarization technique, as a means for measuring relative rates of corrosion, was studied by simultaneously exposing aluminum- and silicon-killed carbon steels, having approximately the same composition, to the 0.2-percent sodium chloride solution for 14 days. Also included were additional specimens of the same steels after water-quenching from 1,650° F. Neither the polarization nor the weight-loss measurements revealed any differences in the corrosion rates of

aluminum-killed or silicon-killed steel specimens, but both methods of measurement showed that quenching presumably caused the rates of corrosion to be slightly increased.

The use of polarization curves for measuring rates of corrosion is also shown by strip chart records made with a two-pen electronic recorder. Preliminary measurements illustrated the effect of increasing the rate of corrosion of carbon steel exposed to a 0.2-percent salt solution when air was bubbled into the electrolyte. Zinc used as the auxiliary anode was also found to be satisfactory as a reference electrode for the range of polarizing current involved.

The sensitivity of polarization curves in measuring rates of corrosion was further explored by using automatic equipment for recording the cathodic polarization on simultaneously exposed low and medium carbon steels. Some of the medium carbon specimens were heat-treated before exposure. The corrosion rates calculated from the polarization curves were within ± 5 percent of the corrosion rates shown by the actual weight losses.

Upon exposing a specimen of high-silicon cast iron to the 0.2-percent sodium chloride solution, the control of the corrosion reaction was observed to shift from cathodic to anodic within a period of 24 hr; automatic recording equipment was used. After 14 days of exposure, the corrosion rate appeared to be quite stable; and, based on breaks in the polarization curves, chiefly the anodic curves, the corrosion rate was estimated as being about 0.055 $(oz/ft^2)/yr$. This value is shown to be comparable to the corrosion rate of the same material based on 12 years of underground exposure, thus showing the value of polarization curves in quickly estimating rates of corrosion that could not be measured accurately by weight loss for short periods of exposure.

It is not suggested that the measurement of polarization curves be used as a substitute for long-time-exposure tests, as one is unable to extrapolate with a high degree of certainty the corrosion rates over long periods of time. However, it is believed that the polarization technique of corrosion-rate measurement is a good way of screening materials for underground- or marine-exposure studies.

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6. References

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