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Corrosion Rates of Ferrous Alloys (Fe-Cr and Fe-Cr-Si) Measured by Polarization Technique

W. J. Schwerdtfeger

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A series of ferrous alloys containing chromium up to 18 percent and a similar series containing chromium with silicon (3 to 4 percent) were exposed from 2 to 3 months to city water to which had been added 3 percent by weight of sodium chloride.

Cathodic and anodic polarization curves were obtained during two entire exposure periods at periodic intervals. Previous studies by the author along these lines were confined almost exclusively to corrosion processes which were either under cathodic or mixed control. Data from the present study show that corrosion rates can be calculated from polarization curves, even though the corrosion reaction is under anodic control as was the case with alloys having about 14 and 18 percent of chromium.

1. Introduction

The author has shown by experiments during the past 10 yr that metal loss resulting from corrosion can be calculated from polarization curves. Most of the measurements were made in the laboratory on specimens of low-alloy iron or steel exposed to soils or to salt-water solutions where the corrosion currents were controlled primarily by cathodic polarization [1, 2].[1]

The method has been applied to predicting the relative behavior of metal bolts when coupled to pipe flanges underground which are anodic to the bolts [3]. Polarization measurements showing how corrosion currents are related to cathodic protection currents were described for steel corroding in salt water [4] and in a high resistivity soil [5].

Recently, the polarization technique of corrosion rate determination has been applied to the evaluation of inorganic coatings formed as a result of cathodic protection [6]. Even more recently, the same technique was used to measure the corrosion rates of steel and aluminum in situ (underground) over an exposure period of 16 months in a soil having a resistivity of 7,500 ohm-cm [7]. In addition to measuring the rates of corrosion of both the steel and the aluminum, the polarization data show how the type of corrosion control was influenced by gradual changes in the weather and by length of exposure time. In both papers, it was shown how the significant currents determined from polarization curves, at the break in the curves, were related to rates of polarization and how these in turn were related to corrosion rates (average weight losses).

The present study was carried out in the laboratory using iron alloys with chromium in amounts sufficient to have a marked influence on the corrosion rates (average weight losses). The results of others [8, 9] show that the addition of chromium to iron in the amount above 10–12 percent has a considerable effect on the solution potential. This indicates, and it was found by preliminary experiment, that with chromium in excess of 12 percent the corrosion current might be controlled mainly by anodic polarization. With these factors in mind, electrolytic iron was alloyed with chromium to form a series of alloys ranging from 0 to 18 percent chromium. Thus, this investigation was designed to determine whether, by exposing such a series to a 3 percent sodium chloride solution, the metal loss resulting from corrosion could be determined from polarization curves and how these curves would be affected by going from cathodic perhaps through mixed to anodic control. A second set of specimens was also exposed later having approximately the same amounts of chromium as the first set but in addition a relatively fixed percentage (3–4) of silicon. The amount of silicon chosen was such as to probably affect the corrosion rates [2] but not appreciably change the mechanical properties of the alloys.

2. Experimental Procedure

2.1. Preparation and Exposure of Specimens

A series of Fe–Cr and of Fe–Cr–Si alloys were sand cast at the National Bureau of Standards using electrolytic iron as the basis metal. The compositions of these alloys as determined by spectrochemical analyses are given in table 1.[3] The castings were about 0.9 in. in diam by 15 in. long. All castings were given an annealing treatment at 1600 °F, held at temperature for 2 hr and then furnace cooled. Next, the castings were machined to form specimens 0.625 in. in diam by 12 in. long.

Preliminary exposure of a few ferrous alloys containing from 16 to 18 percent of chromium revealed the fact that the method of mounting a specimen

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

[2] In this paper, corrosion rate is based on the total area of a specimen exposed to the electrolyte and is derived either from the actual weight loss of the specimen or from the calculated weight loss using Faraday's law and assuming 100 percent corrosion efficiency.

[3] Throughout this paper, the series of specimens designated A and AA are considered as being without silicon and the B series are referred to as those having silicon.

TABLE 1. *Composition of alloys*

Fe-Cr alloys				Fe-Cr-Si alloys			
Specimen	Composition, percent			Specimen	Composition, percent		
	Cr	Si	Al		Cr	Si	Al
1A	0	0.2	0.2	1B	0	3.3	0.2
2A	0.6	.2	<.1	2B	0.5	3.1	<.1
3A	1.6	.2	<.1	3B	2.5	3.4	.2
4A	2.0	.1	1.0	4B	1.4	3.3	<.1
5A	4.1	.2	0.8	5B	2.1	3.3	.2
6A	6.8	.2	.5	6B	6.4	3.9	.4
6AA	7.1	.2	.4	7B	7.9	3.0	<.1
7A	9.0	.2	.1	8B	10.6	2.1	.4
8A	11.4	.3	.4	9B	13.8	3.8	.3
8AA	11.1	.3	.6	10B	18.2	3.4	.4
9A	14.3	.3	.1				
10A	18.3	.4	.3				

NOTE: From 0 to about 6 percent, the values for chromium are probably within ± 0.1 percent; above 6 percent, the accuracy may be somewhat less for the chromium. The values for silicon and for aluminum are probably accurate to within ± 0.1 percent.

was in itself a problem to be solved before proceeding with the study in mind. Plastic tape can be used on plain ferrous metals in order to prevent accelerated corrosion at the waterline and to keep a fixed area exposed to the electrolyte as the solution level changes because of evaporation. In the preliminary exposure tests with chromium-iron alloys, it was observed that most of the corrosion took place under tape edges. The same effect was experienced with organic coatings. These experiences led to the idea of completely submerging the specimens, but brought up the problem of how to maintain electrical contact with the specimen. After some trials, it was decided to submerge the specimens by suspension with Nichrome wire (No. 30 B and S gage, .010-in. diam), depending for electrical continuity upon the weight of the specimen in contact with the wire looped through a hole drilled near the top. A 0.19-in. hole was drilled through each specimen 0.16 in. from one end for the suspension wire. The area of the surface of the specimen was about 0.167 ft^2.

The effect of galvanic action also had to be considered before deciding upon the scheme for suspension. This was resolved by measuring galvanic currents which would appear to be associated with the couple formed by the specimen and the wire. A length of Nichrome wire, equivalent to that which would be used for suspension, was exposed to a 3-percent sodium chloride solution. Its corrosion potential was observed to be cathodic to that of any specimen which would be used. Then the applied currents, which had to be used to cathodically polarize the wire to the anticipated range of corrosion potentials of the specimens, were measured. As will be observed later, this range was between —.2 and —.75 v measured with reference to a saturated calomel electrode. The applied currents measured to polarize the suspension wire to —.35, —.50, and —.75 v were, respectively, 2, 8, and 39 μa. Based on experience, it was presumed that the galvanic currents would become smaller as exposure time increased. Later, when the magnitude of the corrosion currents is noted, it will be seen that the above galvanic currents were probably less than 5 percent of the total corrosion current associated with any one specimen. Also, preliminary suspension for a few weeks in the salt water of an unalloyed ferrous specimen revealed no nicks at the points of contact between the specimen and the wire.

Before exposure, the specimens were cleaned with carbon tetrachloride, polished with fine-grit abrasive cloth, scrubbed under hot water, dried, and weighed. They were exposed to tap water to which had been added 3 percent by weight of sodium chloride. The salt water was contained by an open cylindrical wooden vat, 66 in. in diam and 19 in. high and was kept at a depth of 18 in., the volume being about 265 gal. The temperature of the water was not controlled but was measured regularly during the exposure periods. Ten specimens, one without chromium and nine each with different amounts of chromium, were exposed for a period of 65 days. Later a second set of 12 specimens was exposed to a fresh solution of the same electrolye for 80 days. Ten of these specimens were of about the same composition as the first set except that each also contained an added fixed percentage of silicon and the other two had no added silicon but chromium only, about 7 and 11 percent.

Figure 1 shows how the specimens (rods) were mounted for exposure. The photograph is of 4 of the second set of specimens taken on the last day of exposure. The rods shown are in the chromium range from 8 to 14 percent, the one on the right containing 14 percent of Cr with Si. The tops of the specimens were 2 in. below the surface of the water and the minimum space between them was 9 in. The wire clips shown in the photograph were left connected throughout exposure. All leads were brought to a terminal block mounted on the side of the vat so as not to disturb the specimens while while making electrical measurements.

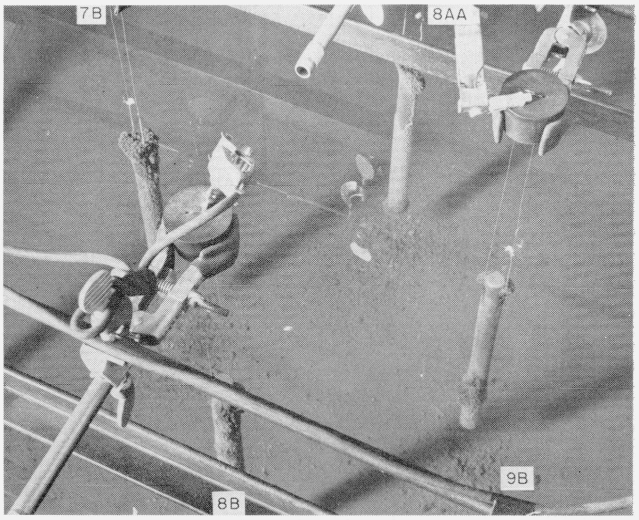

FIGURE 1. *Arrangement of specimens suspended in salt water.* Shown are 4 of the second set of 12 specimens, from left to right: 7B(7.0 Cr, 3.0 Si); 8B(10.6 Cr, 2.1 Si); 8AA(11.1 Cr); 9B(13.8 Cr, 3.8 Si).

2.2. Electrical Measurements

The specimens were suspended under water in two rows, each row being 3 in. from the centerline of the vat. Auxiliary electrodes consisting of 0.5-in.-diam steel rods were fastened vertically on the wall inside of the vat. A group of six electrodes, spaced 6 in. apart, were mounted facing one row of specimens and another group of six, similarly mounted, diagonally opposite faced the other row. One group of electrodes was used to conduct polarizing current for any one specimen in the adjacent row.

All potentials were measured with reference to a saturated calomel half-cell. Electrical contact between the salt water and the half-cell was made through a 5 ft flexible agar-salt bridge. The free end of the flexible tube was slipped into the salt water about 8 in. below the surface through a hard rubber sleeve mounted vertically and partially in the water about 6 in. from the wall of the vat. The salt bridge was left in the water only while potentials were being measured.

Measurements made on any one day comprised corrosion potential, polarization arising from applied currents, and salt-water temperature. Data were obtained more frequently on the first set of specimens exposed than on the second set. On the second set, the frequency of measurements was determined by the need rather than by any given interval of time. For both exposures, more data were obtained the first week or two than later. On some specimens cathodic and anodic polarization curves were not always recorded on the same day. Emphasis was placed on the kind of polarization which controlled the rate of corrosion of a given specimen. When the corrosion control was mixed, the attempt was made to automatically record both curves on the same day or within two successive days.

Corrosion potentials were measured with a 200,000-ohm/v voltmeter. Polarization data were obtained with a two-pen (current and potential) strip chart recorder. The polarizing current resulted from linear increments in applied voltage which were obtained with a synchronously driven 10-turn potentiometer. The Holler bridge [5], used in conjunction with the recorder made it possible to balance out undesirable resistance in the system.

2.3. Removal of Corrosion Products

At the conclusion of exposure, specimens were removed from the salt solutions and scrubbed under running hot water with a fiber-bristle brush. A motor-driven, fiber-bristle brush was used to remove corrosion products from the mounting holes. Then, the specimens were submerged for 4 hr in a 10-percent solution of warm ammonium citrate neutralized with ammonium hydroxide and again scrubbed under hot water. Compressed air was used for cleaning and blowing water out of the pitholes. Finally, the specimens were vigorously hand brushed with a brass-bristle brush, then lightly with a steel-bristle brush and weighed. Measurements were made of pit depths using a pit-depth gage and also of the apparent area affected by corrosion.

3. Results and Discussion

The data were recorded automatically and after about 2 months of exposure plotted on semilogarithmic coordinates for interpretation and convenience as shown in figure 2. The vertical dashes in the figure indicate the values of polarizing current (I_p and I_q, cathodic and anodic, respectively) used in calculating the corrosion currents i_o. The values of current I_q for the 4 specimens containing less than 12 percent Cr (1A through 8A) were taken directly from the recorder charts because the changes-in-slope (breaks) were more evident than on the semilogarithmic coordinates when applied current I_q was several times the magnitude of the current I_p. These specimens containing chromium, 0 through 11.4 percent, were under cathodic control; therefore, the values of I_p have a greater bearing on the calculated corrosion currents than do the values of I_q. The transition from cathodic to anodic control which occurred between 11.4 and 14.3 percent Cr is very evident in figure 2.

The polarization data for the 10 specimens having chromium in varying amounts, 0 through 18 percent, together with calculated and actual weight losses resulting from corrosion are given in table 2. The electrochemical equivalent, K (footnote c, table 2), used in Faraday's law for calcu-

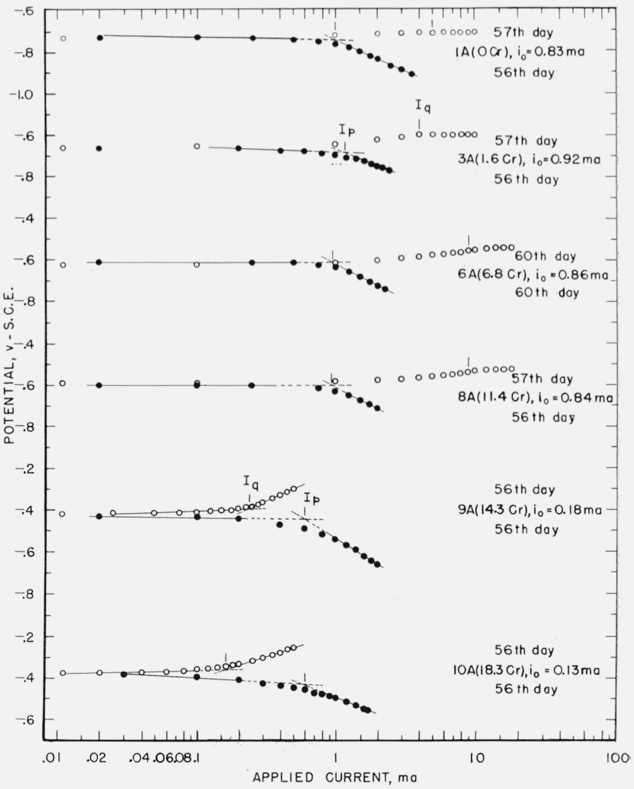

FIGURE 2. *Polarization curves of some of the Fe-Cr specimens after about 2 months exposure to city water containing 3 percent of sodium chloride.*

○ anodic ● cathodic

TABLE 2. *Corrosion weight losses calculated from polarization data obtained on iron specimens containing chromium exposed to a 3-percent sodium chloride solution*

Specimen	Exposure time	Polarizing current at break in curve [a]		Corrosion [b] current i_o	Weight loss [c]	
		Cathodic I_p	Anodic I_q		Calculated cumulative	Actual
	days	*ma*	*ma*	*ma*	*mg*	*mg*
1A (0 Cr)	0 [d]	1.6	8.0	1.3	---------	
	3	2.6	13.0	2.2	127	
	7	1.6	8.0	1.3	307	
	11	1.2	6.0	1.0	417	
	18	1.2	6.0	1.0	592	
	25	1.1	5.5	0.92	760	
	31	1.2	6.0	1.0	904	
	37	0.97	4 9	0.81	1,039	
	44	1.0	5.0	.83	1,182	
	53	0.94	4.7	.78	1,362	
	63	.95	4.8	.79	1,557	
	65	---------	---------	---------	1,597	1,630
2A (0.6 Cr)	0 [d]	1.3	6.5	1.1	---------	
	3	2 2	11.0	1.8	105	
	7	1.6	8.0	1.3	265	
	10	1.4	7.0	1.2	355	
	18	1.4	5.5	1.1	595	
	25	1.1	3.0	0.81	761	
	31	1.3	4.0	.98	895	
	37	1.2	4.8	.96	1,040	
	44	1.2	4.8	.96	1,208	
	53	1.2	4.8	.96	1,424	
	63	1.2	4.5	.95	1,661	
	65	---------	---------	---------	1,708	1,555
3A (1.6 Cr)	0 [d]	1.2	6.0	1.0	---------	
	3	2.5	12.5	2.1	112	
	7	1.9	9.5	1.6	302	
	10	1.4	7.0	1.2	407	
	18	1.3	3.0	0.91	627	
	25	1.1	2.5	.76	772	
	31	1.2	3.5	.89	897	
	37	1.3	4.0	.98	1,036	
	44	1.0	3.0	.75	1,188	
	53	1.2	3.5	.89	1,373	
	63	1.2	3.5	.89	1,595	
	65	---------	---------	---------	1,639	1,500
4A (2.0 Cr)	0 [d]	1.8	9.0	1.5	---------	
	3	2.7	13.5	2.2	135	
	7	2.0	10.0	1.7	335	
	10	1.3	4.5	1.0	433	
	18	1.4	4.5	1.1	653	
	25	1.2	4.8	0.96	828	
	31	1.5	6.0	1.2	993	
	37	1.2	3.3	0.88	1,143	
	44	1.1	3.3	.83	1,293	
	50	0.90	2.7	.68	1,405	
	56	.94	2.8	.70	1,509	
	63	.70	2.1	.52	1,616	
	65	---------	---------	---------	1,642	1,685
5A (4.1 Cr)	0 [d]	1.9	9.5	1.6	---------	
	3	2.6	13.0	2.2	142	
	7	1.8	9.0	1.5	322	
	11	1.3	4.5	1.0	452	
	18	1.2	4.5	0.95	622	
	25	1.0	3.5	.78	774	
	31	1.3	7.5	1.1	915	
	37	0.90	4.5	0.75	1,053	
	44	.87	4.3	.72	1,181	
	53	.85	5.0	.73	1,345	
	63	.72	4.0	.61	1,513	
	65	---------	---------	---------	1,544	1,580
6A (6.8 Cr)	1	1.6	4.5	1.2	30	
	5	1.2	4 5	0.95	140	
	8	1.5	6.0	1.2	223	
	11	1.2	6.0	1.0	306	
	18	1.0	5.0	0.83	465	
	27	0.90	3.6	.72	638	
	34	.80	3.2	.64	757	
	43	.82	9.0	.75	912	
	50	.80	7.0	.72	1,040	
	60	.95	9.0	.86	1,237	
	64	.90	8.0	.81	1,321	1,470
7A (9.0 Cr)	0 [d]	1.5	3.0	1.0	--------	
	3	2.7	3.0	1.4	90	
	7	2.0	3.5	1.3	230	
	11	1.3	4.0	0.98	340	
	18	1.4	3.5	1.0	513	
	25	1.1	2.8	0.79	670	
	31	1.5	8.0	1.3	820	
	37	0.98	3.0	0.74	970	
	44	1.0	5.0	.83	1,107	
	56	1.9	10.0	1.6	1,467	
	63	0.87	8.0	0.79	1,677	
	65	---------	---------	---------	1,716	1,800
8A (11.4 Cr)	0 [d]	1.8	3.3	1.2	--------	
	3	2.4	3.0	1.3	90	
	7	2.4	4.0	1.5	230	
	10	1.4	3.5	1.0	328	
	18	1.6	6.4	1.3	548	
	25	1.1	4.4	0.88	740	
	31	1.3	5.2	1.0	881	
	37	0.98	3.9	0.78	1,014	
	44	.92	8.0	.83	1,156	
	49	.85	7.0	.76	1,256	
	56	.93	9.0	.84	1,396	
	63	.80	8.0	.73	1,533	
	65	---------	---------	---------	1,569	2,025
9A (14.3 Cr)	0 [d]	0.60	0.14	0.11	---------	
	4	.53	.090	.077	9	
	8	.90	.12	.11	18	
	11	.58	.025	.024	23	
	18	.70	.38	.25	47	
	24	.48	.28	.18	80	
	32	.43	.26	.16	114	
	37	.32	.22	.13	133	
	44	.40	.22	.14	156	
	51	.75	.24	.18	184	
	56	.60	.24	.18	206	
	65	.60	.22	.16	244	510
10A (18.3 Cr)	0 [d]	.50	.15	.12	---------	
	4	.85	.17	.14	13	
	8	1.0	.18	.15	27	
	11	.75	.18	.14	38	
	18	.80	.27	.20	68	
	24	.39	.18	.12	92	
	30	.66	.28	.20	116	
	37	.44	.22	.15	146	
	44	.50	.23	.16	174	
	51	.45	.19	.13	198	
	56	.60	.16	.13	214	
	65	.60	.17	.13	243	255

[a] See the text.

[b] $i_o = I_p I_q/(I_p + I_q)$.

[c] Calculated weight loss (g)$=Kti$, where $K=2.8938\times10^{-4}$ g/coulomb, $i=i_o=$ average current (amp) for the period (t in sec) between successive readings. The value of i_o at the instant of exposure and at the end of exposure is taken as the initial and final values, respectively as calculated. Weight loss (mg) is approximately equal to 25 ti_o; where t=days, i_o=ma. For effects of chromium, see the text.

[d] From 3 to 6 hr after initial exposure.

NOTE: All specimens were completely submerged and exposed at the same time in an open vat containing approximately 265 gal of salt water. Mean solution temperature=68 °F, min=64 °F, max=72 °F. Area of specimen=1/6 ft².

lating the weight losses of each specimen is that for ferrous iron only. Krystow and Balicki [10] observed that when 18–8 stainless steel was exposed to a 2*N* boiling nitric and sulfuric acid mixture the percentage of the total corrosion attributable to iron was above 99 percent.

The appearance of the Fe–Cr specimens after 65 days of exposure and after cleaning is shown in figure 3. The apparent area corroded and the pit depths are given in table 3 to enable one to better evaluate the sensitivity of the polarization technique of corrosion rate measurement. The corroded area of most specimens is readily apparent in figure 3, but on a few specimens, e.g., 9A and 10A, pitting inside of the mounting holes accounted for most of the weight loss. Evidently, the film on the surface of the hole was more vulnerable to oxygen deficiency than that on the exterior surface of the specimen. Specimens 9A and 10A were under anodic control during the entire exposure period (table 2). No appreciable corrosion is attributed to galvanic action between the suspension wires and the specimens as there was no evidence of such corrosion on the specimens low in chromium (fig. 3) where the effect should be greatest because of the greater potential difference between the Nichrome suspension wire and the specimen.

TABLE 3. *Appearance after removal of the corrosion products of the iron specimens alloyed with chromium*

Specimen	Apparent area corroded	Remarks, pitting
	%	
1A (0 Cr)	82	General corrosion (0–1 mil), except for one pit (10 mils) in center of specimen.
2A (0.6 Cr)	62	General coorrsion (0–1 mil).
3A (1.6 Cr)	86	General corrosion (0–1 mil).
4A (2.0 Cr)	15	Corrosion on side of rod near top and center (0–5 mils).
5A (4.1 Cr)	24	Corrosion in spots (0–10 mils).
6A (6.8 Cr)	12	Corrosion in spots (5–10 mils).
7A (9.0 Cr)	5	Top end of rod corroded, with one pit of 70 mils. Bottom end pitted around the edge. Corrosion from mounting hole down the side about 2 in. (13 mils). Spots along entire surface (12–35 mils).
8A (11.4 Cr)	5	Corrosion on top and bottom ends, also on side below mounting hole for about 1 in. Some corrosion inside mounting hole. Several pits (12–56 mils) on the entire surface.
9A (14.3 Cr)	1	Most corrosion inside of the mounting hole (two pits of 70 mils). Only two small pits (23 and 30 mils) on the surface.
10A (18.3 Cr)	≪1	Most corrosion confined to one narrow pit (100 mils) inside of the mounting hole. Two tiny pits (10 and 17 mils) on the side of rod about 2 in. up from the lower end.

The film-forming properties of silicon when added to stainless steel have been reported on by Rhodin [11]. Under the conditions of his experiments, he observed remarkable improvement in corrosion resistance both from the standpoint of weight loss and of pitting when silicon-modified Type 316L stainless steel contained silicon in amounts between 2.41 and 4.67 percent. The effects of silicon have been also discussed by Speller [9] and by others. The primary reason for including silicon in some of the alloys of the present study was to find out whether the effects mentioned by other investigators could be measured and how the shapes of the polarization curves would be affected.

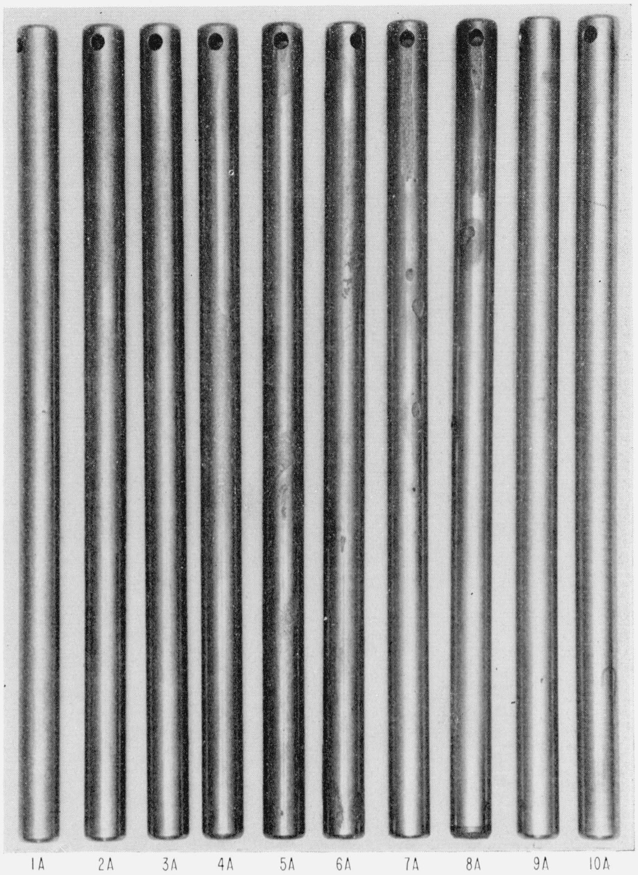

FIGURE 3. *Ferrous alloys containing varying amounts o chromium—after 65 days of exposure to salt water and afte cleaning.*

For composition, see table 1.

Data, similar to those given for the Fe–Cr alloys. are given for the Fe–Cr–Si alloys in table 4. Attention is again directed to the fact that the exposure period was for 80 days while that for the Fe–Cr alloys was 65 days. The two additional specimens 6AA (7.1 Cr) and 8AA (11.1 Cr) have essentially the same chromium content as have specimens 6B and 8B, respectively, except that the former are without silicon. It was felt that comparisons could be made by including them in the same exposure where effects due to silicon might be revealed by polarization measurements.

Data from both exposures, based on actual weight losses and plotted to a common scale, are shown in figure 4. A similar comparison, based on polarization data obtained during the final 3 weeks of the first exposure (without silicon) and the corresponding 3 weeks of the second exposure period, is shown in figure 5. The addition of silicon seems to have had the effect of reducing the critical range of chromium from 10 to 12 percent to around 2 to 3 percent. The somewhat higher corrosion rates of the silicon-bearing specimens containing up to 6 percent chromium might be attributed to the higher water temperature during the second exposure (fig. 4).

TABLE 4. *Corrosion weight losses calculated from polarization data obtained on iron specimens containing chromium and silicon exposed to a 3 percent-sodium chloride solution*

Specimen	Exposure time	Polarizing current at break in curve [a]		Corrosion [b] current i_o	Weight loss [c]	
		Cathodic I_p	Anodic I_q		Calculated cumulative	Actual
	Days	*ma*	*ma*	*ma*	*mg*	*mg*
1B (0 Cr, 3.3 Si)	1	2.5	12.5	2.1	52	
	6	1.6	8.0	1.3	264	
	9	1.4	7.0	1.2	358	
	14	1.5	7.5	1.2	508	
	21	1.2	6.0	1.0	700	
	27	1.2	6.0	1.0	850	
	37	1.2	6.0	1.0	1,100	
	48	1.3	6.5	1.1	1,388	
	55	1.1	5.5	0.92	1,565	
	62	1.2	5.0	.97	1,730	
	69	1.0	4.0	.80	1,885	
	76	1.0	4.0	.80	2,025	
	80	---------	---------	---------	2,105	2,045
2B (0.5 Cr, 3.1 Si)	1	2.3	11.5	1.9	47	
	6	1.8	9.0	1.5	260	
	9	1.7	8.5	1.4	369	
	14	1.9	9.5	1.6	557	
	21	1.6	8.0	1.3	811	
	27	1.4	7.0	1.2	998	
	37	1.5	7.5	1.2	1,298	
	48	1.5	6.5	1.2	1,628	
	55	1.1	4.4	0.89	1,810	
	62	1.5	4.0	1.1	1,985	
	69	1.2	3.5	0.90	2,160	
	76	1.3	3.5	.95	2,322	
	80	---------	---------	---------	2,417	2,245
3B (2.5 Cr, 3.4 Si)	1	2.4	12.0	2.0	50	
	6	2.5	12.5	2.1	306	
	9	2.2	11.0	1.8	452	
	14	2.1	10.5	1.7	671	
	21	1.8	9.0	1.5	951	
	27	1.7	8.5	1.4	1,169	
	37	1.6	8.0	1.3	1,506	
	48	1.3	5.3	1.0	1,822	
	55	1.6	6.4	1.3	2,023	
	62	1.3	4.0	0.98	2,223	
	69	1.5	3.5	1.0	2,396	
	76	1.5	3.7	1.1	2,580	
	80	---------	---------	---------	2,690	2,340
4B (1.4 Cr, 3.3 Si)	1	2.4	12.0	2.0	50	
	6	2.0	10.0	1.7	281	
	9	2.0	10.0	1.7	408	
	14	2.1	10.5	1.7	620	
	21	1.6	8.0	1.3	882	
	27	1.6	6.4	1.3	1,077	
	37	1.7	6.8	1.4	1,415	
	48	1.3	4.0	0.98	1,742	
	55	1.3	4.0	.98	1,913	
	62	1.6	3.0	1.0	2,086	
	69	1.3	2.5	0.85	2,248	
	76	1.6	3.5	1.1	2,418	
	80	---------	---------	---------	2,528	2,520
5B (2.1 Cr, 3.3 Si)	1	2.0	10.0	1.7	42	
	6	2.1	10.5	1.8	261	
	9	2.0	10.0	1.7	392	
	14	2.1	10.5	1.8	611	
	21	2.1	10.5	1.8	926	
	27	1.7	8.5	1.4	1,166	
	37	1.5	4.5	1.1	1,479	
	48	1.4	5.0	1.1	1,781	
	55	1.5	4.0	1.1	1,973	
	62	1.6	3.0	1.0	2,157	
	69	1.1	3.0	0.80	2,314	
	76	1.6	3.0	1.0	2,471	
	80	---------	---------	---------	2,571	2,480
6B (6.4 Cr, 3.9 Si)	1	2.5	7.5	1.9	47	
	6	2.5	10.0	2.0	291	
	9	1.6	3.9	1.1	407	
	14	2.0	4.5	1.4	563	
	21	1.4	4.5	1.1	782	
	27	1.2	4.0	0.92	933	
	37	1.1	4.0	.86	1,155	
	48	0.95	3.0	.72	1,372	
	55	1.0	3.0	.75	1,501	
	62	1.1	2.6	.77	1,634	
	69	1.0	3.0	.75	1,767	
	76	0.88	1.7	.58	1,886	
	80	---------	---------	---------	1,947	2,120
7B (7.9 Cr, 3.0 Si)	1	1.9	6.0	1.5	38	
	6	2.2	6.6	1.6	232	
	9	1.7	2.4	0.99	329	
	14	1.6	3.0	1.0	453	
	21	1.3	3.9	0.98	620	
	27	1.3	3.0	.91	770	
	37	1.1	3.2	.82	986	
	48	1.0	2.8	.74	1,200	
	55	1.0	3.5	.78	1,333	
	62	1.2	2.0	.75	1,467	
	69	0.7	2.2	.53	1,579	
	76	.9	1.5	.56	1,673	
	80	---------	---------	---------	1,729	1,720
8B (10.6 Cr, 2.1 Si)	1	1.0	0.68	0.41	10	
	6	1.2	.62	.41	61	
	9	0.73	.75	.37	90	
	14	1.1	2.2	.73	159	
	21	1.1	3.7	.85	297	
	27	0.86	1.5	.55	402	
	37	.78	1.6	.52	536	
	48	.85	3.5	.68	701	
	55	.70	1.3	.45	800	
	62	.88	2.5	.65	896	
	69	.98	1.6	.61	1,006	
	76	.90	1.2	.51	1,104	
	80	---------	---------	---------	1,155	1,330
9B (13.8 Cr, 3.8 Si)	1	0.92	0.70	0.40	10	
	6	1.1	.57	.38	59	
	9	1.1	.50	.34	86	
	14	1.2	.52	.36	130	
	21	0.96	.40	.28	186	
	27	.80	.32	.23	224	
	37	.56	.17	.13	269	
	48	.78	.25	.19	313	
	55	.70	.32	.22	249	
	62	.80	.33	.23	388	
	69	.82	.28	.21	427	
	76	.80	.32	.23	466	
	80	---------	---------	---------	489	650
10B (18.2 Cr, 3.4 Si)	1	0.43	0.25	0.16	4	
	6	.16	.080	.053	17	
	9	.15	.080	.052	21	
	14	.12	.095	.053	28	
	21	.11	.060	.039	36	
	27	.36	.21	.13	48	
	37	.22	.035	.030	68	
	48	.050	.031	.019	75	
	55	.064	.029	.020	79	
	62	.068	.050	.029	83	
	69	.16	.19	.087	93	
	76	.16	.090	.058	106	
	80	.045	.029	.018	110	145
6AA (7.1 Cr)[d]	1	2.2	13.2	1.9	47	
	6	1.6	9.6	1.4	253	
	9	1.4	5.6	1.1	347	
	14	1.4	5.0	1.1	485	
	21	1.0	5.0	0.83	654	
	27	1.2	5.0	.83	779	
	37	1.2	5.0	.83	994	
	48	0.82	5.5	.71	1,206	
	55	.74	3.3	.60	1,321	
	62	.78	3.8	.65	1,430	
	69	.80	3.5	.65	1,544	
	76	.90	3.0	.69	1,661	
	80	---------	---------	---------	1,730	1,825
8AA (11.1 Cr)[d]	1	2.4	9.6	1.9	47	
	6	1.6	6.4	1.3	247	
	9	2.4	3.6	1.4	348	
	14	1.6	8.0	1.3	517	
	21	2.1	4.5	1.4	753	
	27	1.4	3.5	1.0	933	
	37	1.3	5.0	1.0	1,183	
	48	0.73	3.5	0.60	1,403	
	55	.66	2.7	.53	1,502	
	62	.90	3.0	.69	1,609	
	69	.83	3.0	.65	1,726	
	76	.94	2.8	.70	1,844	
	80	---------	---------	---------	1,914	2,155

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[a] See the text. [b] $i_0=I_pI_q/(I_p+I_q)$.

[c] Same as footnote c in table 2. Note: Exposure was the same as for the exposure of the specimens (table 2), except at a different time and to a freshly prepared solution for a period of 80 days. Mean salt water temperature=77° F, min=68° F, max=85° F. Exposed area of specimen=1/6 ft^2.

[d] No silicon added.

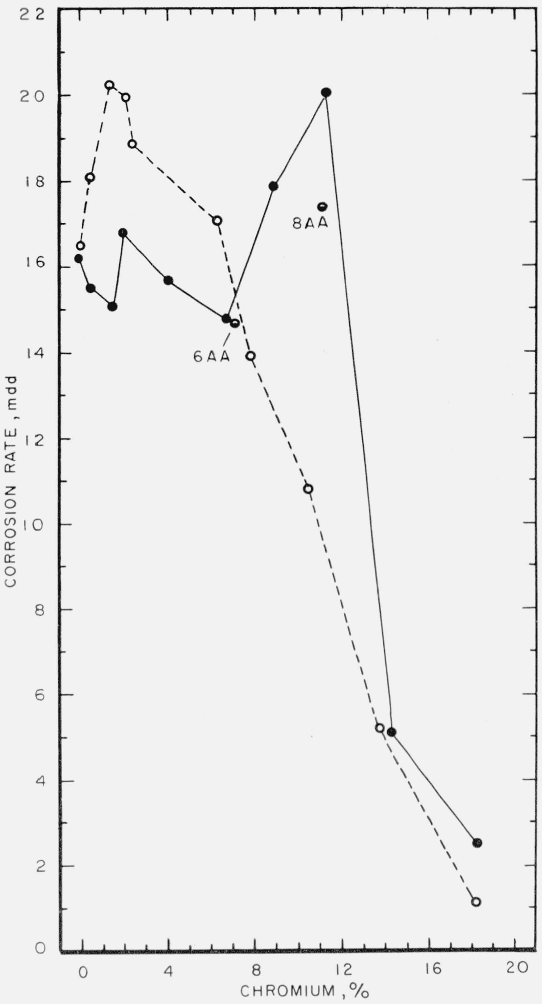

FIGURE 4. *Effect of chromium and of chromium with silicon (3 to 4 percent) on the corrosion rates (based on actual weight losses) of iron alloys exposed between 2 and 3 months to city water containing 3 percent of sodium chloride.*

● Without silicon—1st set of specimens, mean solution temp 68 °F.
○ With silicon—2d set of specimens, mean solution temp 77 °F.
◒ Without silicon—2d set

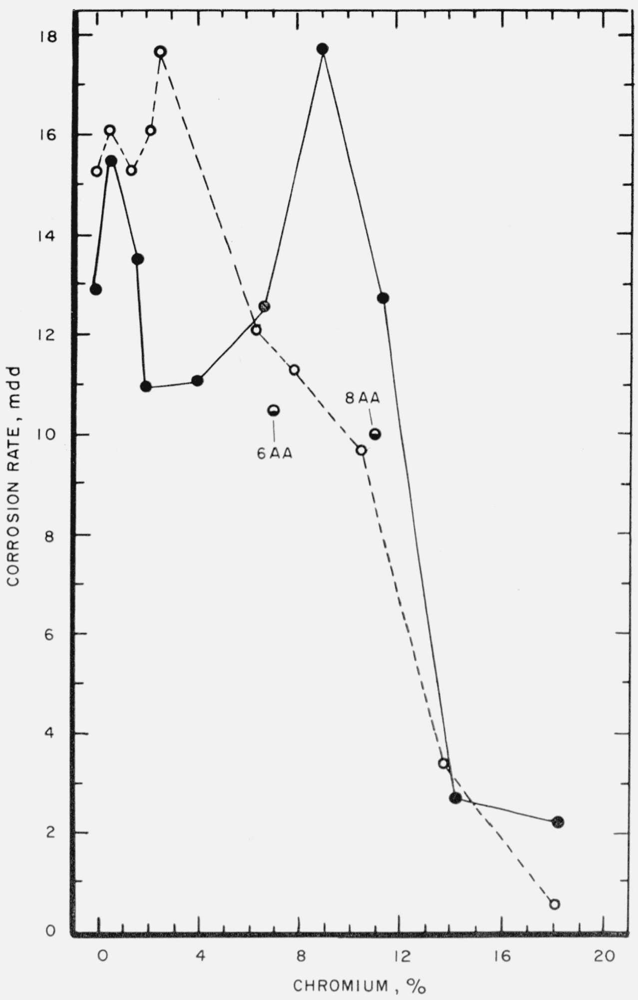

FIGURE 5. *Effect of chromium and of chromium with silicon (3 to 4 percent) on the corrosion rates (based on polarization curves) of iron alloys (fig. 4) near the end of the exposure periods to salt water.*

● Specimens without silicon, based on 3 or 4 pairs of curves (anodic and cathodic) from 43d through 65th days of exposure.
○, with silicon; ◒, without silicon, based on 4 pairs of curves from 48th through 69th days of exposure.

Comparative polarization data on those alloys having about 7 and 11 percent chromium, with and without silicon, are illustrated by figure 6. The added silicon seems to have caused a shift from cathodic toward mixed control and lower rates of corrosion. This is especially noticeable by comparing specimens 8B and 8AA. In general, the data appear to indicate that for iron having 8 percent or more of chromium, the addition of from 3 to 4 percent of silicon is beneficial in further reducing corrosion weight loss (fig. 4).

The 10 specimens containing silicon are shown (corrosion products removed) in the photograph, figure 7, after 80 days of exposure. Data on the apparent area corroded and remarks on pitting are given in table 5. As with the alloys containing no silicon, the suspension wires caused no nicking at points of contact with the specimens. Four of the specimens (7B, 8B, 8AA, and 9B) described in table 5 are shown during exposure in figure 1 with corrosion products intact. The corrosion products around the pits, especially on 9B, are clearly visible in the photograph.

The relation between corrosion potential and exposure time for about half of the specimens is shown in figure 8. With the exception of specimens 9A (first set of specimens) and 10B (second set), the potentials are relatively constant with time. The effects produced by marked changes in potential (specimens 9A and 10B) on the polarizing characteristics and corrosion rates are shown, respectively, in figures 9 and 10. In figure 9, it will be noted that the corrosion current, i_o, increased tenfold as the corrosion potential shifted from about —0.2 v (11th day) to —0.4 v (18th day). The shift in corrosion potential was also associated with a change from

TABLE 5. *Appearance after removal of the corrosion products of the iron specimens containing chromium and silicon*

Specimen	Apparent area corroded	Remarks, pitting
	%	
1B (0 Cr, 3.3 Si)	70	General corrosion (0–1 mil).
2B (0.5 Cr, 3.1 Si)	69	General corrosion (0–1 mil).
3B (2.5 Cr, 3.4 Si)	77	General corrosion (0–1 mil), except for a cluster of pits (0–7 mils) in a cathodic area.
4B (1.4 Cr, 3.3 Si)	69	General corrosion (0–1 mil). Two small groups of pits (0–5 mils) in a cathodic area.
5B (2.1 Cr, 3.3 Si)	79	General corrosion (0–1 mil). Also, about six groups of pits (3–5 mils).
6B (6.4 Cr, 3.9 Si)	15	Top end of rod all corroded with 45 mil pits, also bottom end with 5 mil pits. About 15 places on surface with pits (5–20 mils).
7B (7.9 Cr, 3.0 Si)	4	Corrosion confined to top end of rod (10–30 mils) and to sides just below the mounting hole (5–30 mils).
8B (10.6 Cr, 2.1 Si)	2	Eight pits (30–80 mils) on the surface and severe pitting (50 mils) inside of mounting hole.
9B (13.8 Cr, 3.8 Si)	<2	Most of the corrosion concentrated in one pit (130 mils) about one-third way up from the bottom end and in a cluster of pits (10–40 mils) nearby.
10B (18.2 Cr, 3.4 Si)	<1	Two pits (50 mils) in middle of rod. Slight corrosion inside of mounting hole.
6AA (7.1 Cr) [a]	9	Top and bottom ends pitted to 12 mils. About 12 areas on surface pitted (5–20 mils). Slight corrosion inside mounting hole.
8AA (11.1 Cr) [a]	5	Top and bottom ends corroded with pits to 30 mils. Severe corrosion around edges of mounting hole. Four pits (30–50 mils) on the surface.

[a] No silicon added.

anodic to mixed corrosion control. For specimen 10B (fig. 10), a shift in the corrosion potential of about 100 mv in the anodic direction, between the 22d and 28th days of exposure, increased the corrosion current threefold; whereas, a change in the corrosion potential of about 100 mv in the cathodic direction (77th to 80th day) resulted in a threefold reduction in the corrosion current.

The relation between corrosion potential and percentage of chromium toward the end of exposure, with and without silicon, is shown in figure 11. For the data without silicon, the trend of the corrosion potential to become more noble, with increasing amounts of chromium, was irregular until the amount exceeded 11.4 percent. It will be recalled that it was in excess of 11.4 percent chromium where the transition from cathodic to anodic control occurred with a resultant large reduction in corrosion rate (fig. 2); with lesser amounts of chromium the corrosion rate fluctuated (figs. 4 and 5). As for the specimens with silicon (fig. 11), there is a regular trend in the potential towards more noble values as the percentage of chromium increases above 2.5 percent and also a consistent reduction

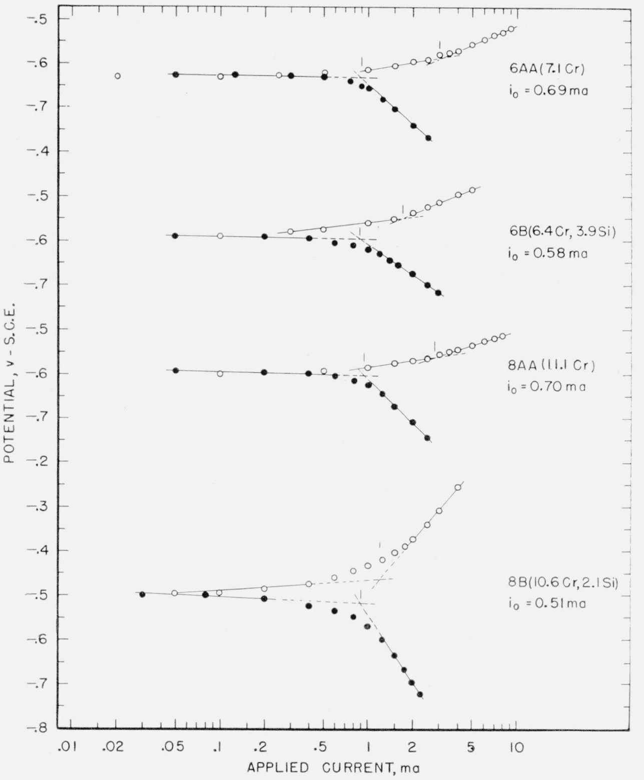

FIGURE 6. *Polarization curves of iron specimens having about 7 and 11 percent chromium (with and without silicon) on the 76th day of simultaneous exposure to salt water.*

○ anodic ● cathodic

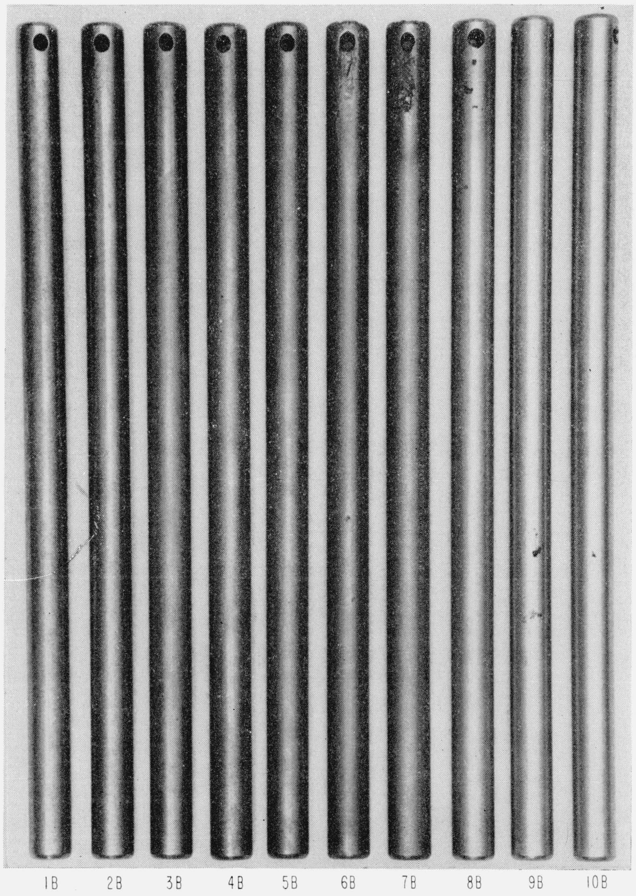

FIGURE 7. *Ferrous alloys (corrosion products removed) containing varying amounts of chromium and silicon (3 to 4 percent) after 80 days of exposure to salt water.*

For composition, see table 1.

in the corrosion rates (figs. 4 and 5). The data shown in figures 4, 5, and 11 indicate that, with about 8 percent or more of chromium, the addition of 3.5 percent silicon has the effect of making the potential more noble and perhaps advantageously affecting corrosion rate. The data resulting from the simultaneous exposure of 2 specimens (6AA and 8AA) without silicon and the specimens with silicon having about the same percentage of chromium tend to reinforce this statement, keeping in mind that the salt water temperature was higher than it was when the first set of specimens without silicon were exposed.

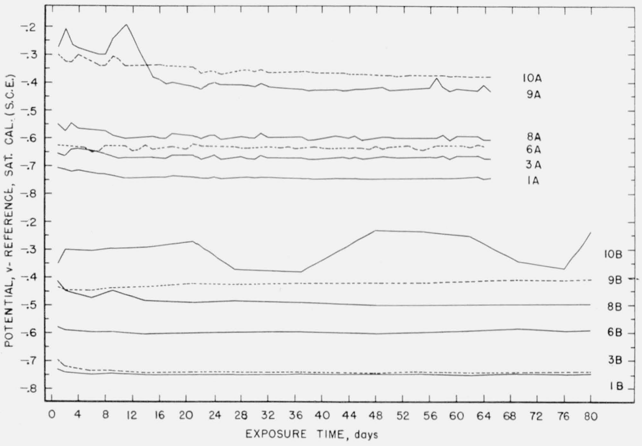

FIGURE 8. *Potential versus time curves for some of the Fe–Cr and Fe-Cr-Si alloys exposed to salt water.*

For composition of the alloys, see table 1.

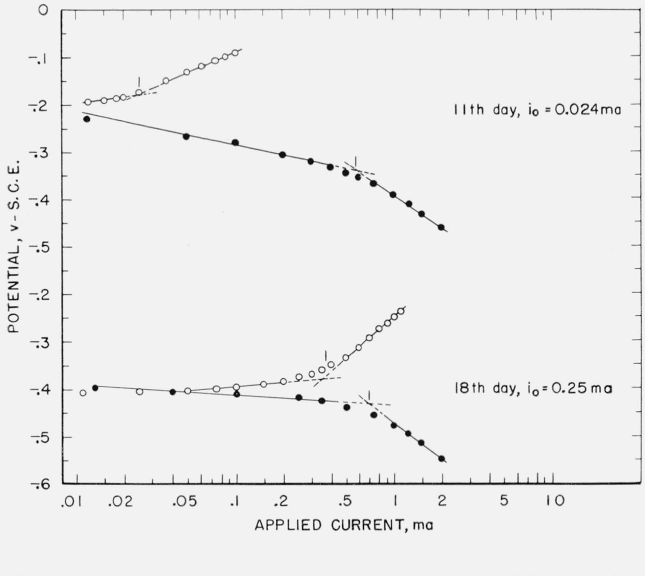

FIGURE 9. *Relationship between corrosion potential and polarizing characteristics of specimen 9A (14.3 Cr) at different times during exposure.*

○ anodic ● cathodic

4. Summary

Electrolytic iron alloyed with chromium in varying amounts between 0 and 18 percent was exposed for 65 days to city water having added 3 percent by weight of sodium chloride. Similar specimens with substantially the same chromium content but having in addition between 3 and 4 percent of silicon were exposed for 85 days to a new salt solution.

For both exposures, weight losses calculated from average corrosion currents, derived from polarization curves obtained periodically, agreed reasonably well with the actual weight losses.

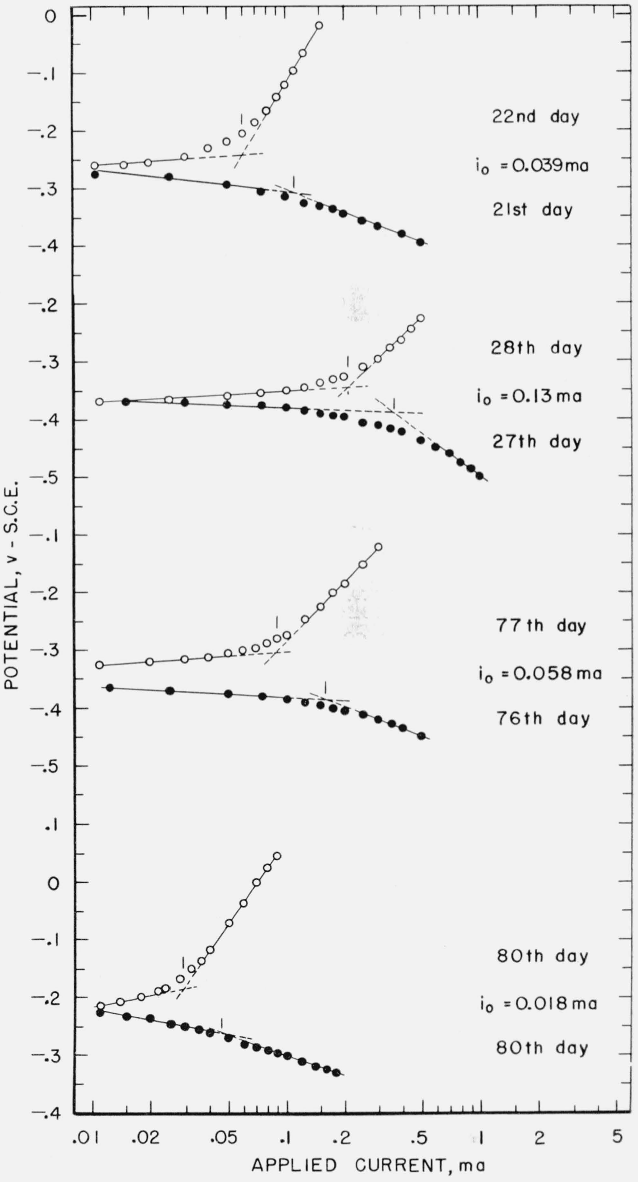

FIGURE 10. *Relationship between corrosion potential and polarizing characteristics of specimen 10B (18.2 Cr, 3.4 Si) at different times during exposure.*

○ anodic ● cathodic

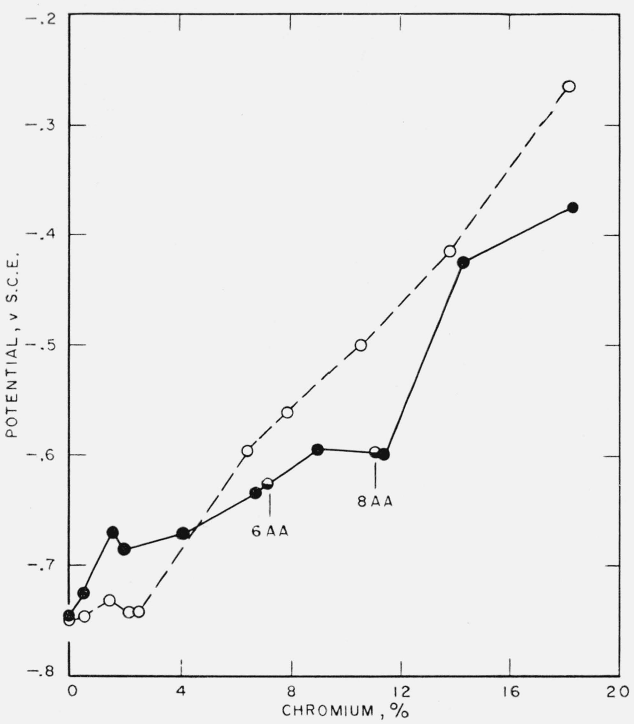

FIGURE 11. *Average potential of each specimen (22 specimens, both exposures) for 3-week period near the end of exposure.*

● Without silicon—1st set, 43d through 65th day.
○ With silicon—2d set, 48th through 69th day.
◒ Without silicon—2d set, 48th through 69th day.

As the chromium content of specimens increased the corrosion control became mixed, that is, more influenced by anodic polarization, especially so for the specimens with silicon and there was a definite transition to anodic control between about 11 and 14 percent chromium. The change from cathodic control as chromium content was increased resulted in the corrosion being confined to smaller areas. On the specimens having 18 percent chromium, the corroded area was apparently about 1 percent or less of the total area exposed.

The addition of silicon to the alloys seems to have had the effect of reducing the critical range (reduction in weight loss) of chromium from between 11 to 14 percent to 8 percent or probably less.

The critical ranges for chromium were accompanied by abrupt shifts in corrosion potential in the cathodic direction. Marked reductions in corrosion rate were associated with shifts of corrosion potential to more noble values.

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