

# Corrosion Rates of Binary Alloys of Nickel and Iron Measured by Polarization Methods

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Specimens of ten binary alloys of nickel and iron containing 3, 5, 10, 16, 20, 30, 36, 50, 57, and 81 percent Ni and of the metals nickel and iron were immersed for 7 months in 265 gallons of city water to which had been added 3 percent by weight of sodium chloride.

Cathodic and anodic polarization curves of the specimens were obtained at about 22 periodic intervals throughout the exposure period. Corrosion currents, calculated from currents at breaks in the curves, were converted to corrosion rates expressed as weight losses by applying Faraday's law. The calculated weight losses were in reasonable agreement with the actual weight losses.

The polarization rates,  $\Delta V/\Delta I$ , of the specimens calculated from cathodic polarization curves (cathodic control prevailed) at several intervals throughout the exposure period were plotted on logarithmic coordinates with respect to the corrosion current densities calculated from breaks in the same curves. Similarly, the averages of these  $\Delta V/\Delta I$  values were also plotted on logarithmic coordinates versus the actual corrosion rates expressed as weight losses. Both plots conformed to the theoretical slope of  $-1$ .

Key Words: Corrosion rates, Ni-Fe alloys, polarization techniques, polarization rate, polarization resistance, polarization circuits, Ni-Fe pitting.

## 1. Introduction

A few years ago, it was demonstrated experimentally that the corrosion rates of a series of ferrous alloys, containing chromium additions up to 18 percent and a similar series with 3 percent of silicon in addition to the chromium, exposed to a 3 percent sodium chloride solution, could be calculated from currents associated with changes of slope (breaks) in polarization curves [1].<sup>1</sup> The sensitivity of the method was shown by the fact that the weight loss of the 18 Cr alloy attributed to corrosion was measured satisfactorily even though the apparent area affected by corrosion was less than 1 percent of the entire surface. The polarization curves of the alloys showed that the known critical change in corrosion rate (expressed as weight loss) for this range of chromium occurred when the corrosion reaction changed from cathodic to anodic control, between 11.4 and 14.3 percent Cr.

The reason for the laboratory measurements described in this paper, using binary alloys of nickel and iron, was to explore further the practicability of polarization techniques as methods of evaluating rates of corrosion. The corrosion rates of several binary alloys between 3 and 81 percent nickel, including the unalloyed metals, were measured by the above technique and also by a method which has been called "polarization resistance" but is referred to by this writer as polarization rate  $\Delta V/\Delta I$ .

The significance of the slope,  $\Delta V/\Delta I$ , of the controlling polarization curve was observed by the author and related to the break method [2] but was never further pursued until after Skold and Larson [3] found the method favorable. They observed that a linear relationship existed when corrosion rate (expressed as weight loss) was plotted versus  $\Delta V/\Delta I$  on logarithmic coordinates. Shortly thereafter, Stern provided a theoretical basis for the polarization resistance method [4]. These methods among others have also been discussed by Phelps [5]. The writer has found it desirable to use both techniques simultaneously as an aid in interpreting and checking data [6, 7] and this procedure was followed in the measurements about to be described.

## 2. Experimental Procedure

### 2.1. Preparation and Exposure of Specimens

The binary alloys were forged and heat treated by the Armco Steel Corporation. Their compositions according to analysis are shown in table 1. Forgings, 0.875 in.  $\times$  0.875 (2.2 cm  $\times$  2.2 cm) in cross section, were machined into specimens 0.625 in. (1.59 cm) diam  $\times$  12 in. (30 cm) long. A hole, 0.25 in. (6.3 mm) diam centered 0.32 in. (8.1 mm) from one end, was drilled through the specimen to permit insertion of a Nichrome wire, No. 30 B & S gage, 0.010 in. (0.25 mm) diam, which served as a loop to hold the specimen in suspension below the surface of the corrodent. All edges were

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

rounded, particularly at the hole, in order to assure accuracy in weight loss measurements. This precaution also prevented nicking of the suspension wire and provided good electrical contact as this wire also conducted the polarizing current.

The method used in suspending the specimens and the reasons therefor were previously described [1]. The Nichrome was always cathodic to the specimens, even to the nickel specimen, and galvanic action, if any, was insignificant as previously observed with the Fe-Cr alloys.

Before exposure, the specimens were degreased, scrubbed with scouring powder, rinsed, rubbed with fine-grit abrasive, scrubbed under running hot water, dried by air-blast and then weighed to the nearest 2 mg.

Twelve specimens, each of different composition (table 1) were exposed to Washington, D.C. city water to which was added 3 percent by weight of sodium chloride. The salt water was contained by an open cylindrical vat, 66 in. (16.7 dm) diam. The depth of the water was maintained at 18 in. and the volume of water about 265 gal. The specimens, about 13 in. (33 cm) apart, were staggered and suspended in two rows across the center of the vat, the tops of the specimens being 2 in. (5 cm) below the water surface. Electrical contact with a given specimen was made through a terminal strip mounted on the outside of the vat from which wires were permanently connected to the Nichrome suspension loops by battery clips. The temperature of the water was not controlled but was measured regularly during exposure.

TABLE 1. *Composition of alloys*

Specimen	Composition, percent*	
	Iron	Nickel
1	100	0
2	97	3
3	95	5
4	91	10
5	85	16
6	81	20
7	70	30
8	64	36
9	49	50
10	43	57
11	21	81
12	0	100

\*Analyzed by x-ray fluorescence techniques for iron and nickel in each specimen. Iron and nickel were determined separately. Values as measured were within  $\pm 0.5$  percent and are rounded off to the nearest 1 percent. Two specimens, 1 and 11, were analyzed by a qualitative spectrochemical method for impurities, resulting in the following: Specimen 1 had Ni, Cu, Si, Ti, each between 0.01–0.1 percent, Al < 0.01 percent. Specimen 11 had Si between 0.1–1.0 percent, Cu, Co, Ti, each between 0.01–0.1 percent, Al, Mn each < 0.01 percent.

## 2.2. Electrical Measurements

Potentials were measured with reference to a saturated calomel half-cell. Contact between the salt water and the half-cell was by an agar-salt bridge in the form of a 5-ft (152 cm) length of flexible tubing containing a mixture of agar and potassium chloride. The electrical continuity of the agar-salt bridge was assured

by a cotton cord saturated with potassium chloride. The cord extended the entire length of the tube enveloped by the agar-salt mixture. The end of the tube was placed into the water through a sleeve mounted about 6 in. (15 cm) from the wall inside of the vat. The distance between the tip of the salt-bridge and a specimen varied between 18 in. (46 cm) and 40 in. (101 cm), depending on the location of the specimen. When electrical measurements were not in progress, the salt-bridge was removed from the water. When polarization measurements were being made, auxiliary electrodes consisting of two strips of zinc sheet, 4 in. (10 cm) wide  $\times$  18 in. (46 cm) long, were hung over the wall of the vat.

Measurements were made on about 22 occasions during the exposure period of 210 days. The measurements involved corrosion potential and the running of cathodic and anodic polarization curves. For a given specimen, an interval of several hours, sometimes 24 hr, was permitted between cathodic and anodic polarization runs, not necessarily in that order, but usually so.

Corrosion potentials were measured with a high resistance voltmeter and polarization was measured and recorded with a two-pen (current and potential) strip-chart recorder. The length of time required for obtaining a polarization curve varied from about 15 to 30 min. Most of the polarization data were obtained by using the galvanodynamic method and about 25 percent using a potentiodynamic method for comparison. The schematic circuit diagrams for these methods are shown in figures 1 and 2, respectively. Both circuits incorporate the Holler bridge for balancing out undesirable voltage drop (IR) from the recorded potentials [8]. In figure 1, the polarizing current is steadily increased by varying the applied voltage at a linear rate by means of the ten-turn motor-driven potentiometer  $R_1$  with resistor  $R_3$  set for a predetermined range of polarizing current. In figure 2, initially the applied voltage between the specimen and the reference electrode is manually adjusted by setting  $R_4$  to a value equal to the corrosion potential after which  $R_4$  becomes motor-driven and sweeps the range of potential required for polarization while  $R_3$  is set at a comparatively low value of resistance so as to not unduly limit the applied current. In viewing the recorder charts, the break in the curve is more evident on the potential plot than on the current plot with the galvanodynamic method, while the reverse is true when the potential sweep circuit (fig. 2) is used.

## 2.3. Removal of Corrosion Products

Following removal from the salt water, the specimens were held under running hot water and scrubbed with a stiff fiber-bristle brush. They were then placed into an ultrasonic cleaning tank (for 10 min) containing a 10 percent solution, at 150 °F, of ammonium citrate made alkaline (pH 9–10) by the addition of ammonium hydroxide. Then, the specimens were again brushed under running hot water, dried under an air

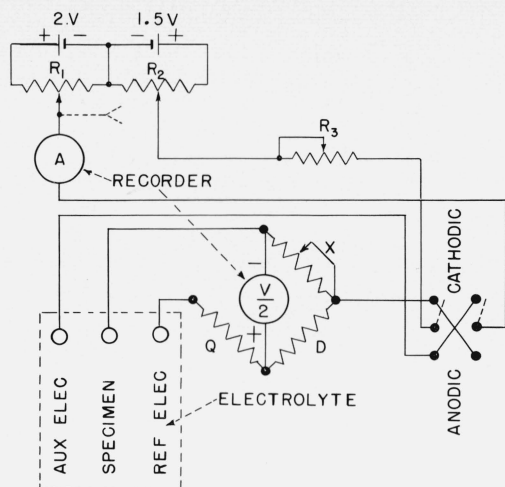


FIGURE 1. Polarization circuit-galvanodynamic method.

$R_1 = 25\Omega - 10$  turn (motor driven  $-0.2$  RPM),  $R_2 = 100\Omega - 10$  turn,  $R_3 = 10,000\Omega$ ,  $X = 100\Omega - 10$  turn,  $Q = D = 100,000\Omega$ .

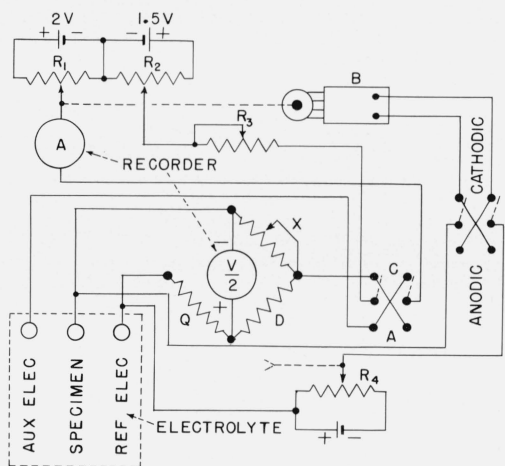


FIGURE 2. Polarization circuit-potentiodynamic method.

$R_1 = 50\Omega - 10$  turn (motor driven-variable speed-reversible),  $R_2 = 100\Omega - 10$  turn,  $R_3 = 10,000\Omega$ ,  $R_4 = 25\Omega - 10$  turn (motor driven  $-0.2$  RPM reversible),  $X = 100\Omega - 10$  turn,  $Q = D = 100,000\Omega$ ,  $B =$  motor (controlled by voltage differential).

blast and weighed to the nearest 2 mg. After repeating this procedure the third time, there was no significant change in weight; the final weights were then subtracted from the original weights in computing the actual metal loss attributed to corrosion.

### 3. Results and Discussion

On the 210th day of exposure the specimens were removed from the salt water. Although the object of the experimental work was primarily that of evaluating the corrosion rate measuring techniques, the data in table 2 show how the results to be described are related to the apparent areas corroded and to the depths of the

pits. Note, that all apparent corrosion on the nickel (specimen 12) seems to have been confined to one pit.

Polarization curves from data on recorder charts obtained on the 202d day of exposure are shown in figures 3 and 4 on semilogarithmic and rectangular coordinates, respectively. While such data, ordinarily, are shown on semilogarithmic coordinates, the rectangular plot helps to verify the break in the curve and the value of applied current at which it occurs. The absence of a break on the latter would place doubt on the extrapolated semilogarithmic value. The values of  $I_p$  (break in the cathodic curve) and of  $I_q$  (break in the anodic curve) chosen in calculating the corrosion currents (table 3) are marked  $I_p$  and  $I_q$  in figures 3 and 4 and are indicated by vertical dashes (where dashed lines intersect). It will be noted that there is reasonably good agreement between figures 3 and 4 for a given specimen in the values of  $I_p$ , but apparently not as good agreement in the values of  $I_q$ .

TABLE 2. Appearance of the binary alloys of nickel and iron after cleaning which followed 210 days of exposure to salt water

Specimen	Apparent area corroded	Remarks, pit depths
1 (100 Fe)	Percent 85	General corrosion (0-3 mils*).
2 (3 Ni)	70	General corrosion (0-3 mils), except for one pit (5 mils).
3 (5 Ni)	80	General corrosion (0-3 mils).
4 (10 Ni)	75	General corrosion (0-3 mils).
5 (16 Ni)	65	General corrosion (0-5 mils).
6 (20 Ni)	50	General corrosion (0-8 mils).
7 (30 Ni)	40	Lower 4.5 in. (11 cm) (opposite suspension end) of specimen length not corroded, otherwise—general corrosion (0-8 mils).
8 (36 Ni)	50	Spotty corrosion to 10-mil depths.
9 (50 Ni)	15	8 in. (20 cm) of the specimen measured from the lower end was not corroded. Spotty corrosion (8-12 mils) on the upper 4 in. (10 cm). Pits to 45 mils in depth at the top end.
10 (57 Ni)	< 1	Scattered pits (2-6 mils) in about 24 places. One pit (50 mils) at the top end.
11 (81 Ni)	< 0.05	Three pits (5-25 mils) on the surface. One pit (50 mils) inside of the mounting hole.
12 (100 Ni)	< 0.02	No corrosion, except for one pit (60 mils deep) inside the mounting hole.

\*mil = 0.001 in. (25.4  $\mu$ ).

The values of  $I_q$ , pertaining to these data, selected from the rectangular coordinates are considered the more significant, except for specimens 11 (81 Ni) and 12 (100 Ni). The actual values of  $I_p$  and  $I_q$  were obtained before compressing the scales (particularly the ordinates) as shown in figures 3 and 4. The data for all specimens are shown on one figure so that the reader can get an overall picture of what the curves portray for different rates of corrosion. When calculating the corrosion current (see the equation, footnote b, table 3), the smaller current, whether it be  $I_p$  or  $I_q$ , is the more significant (controlling) and fortunately can be extrapolated with the greater degree of accuracy.

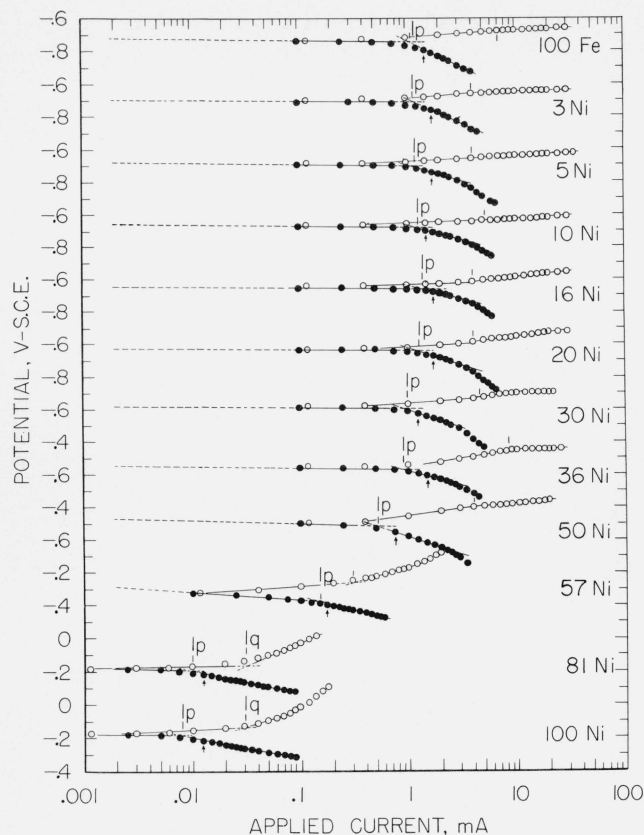


FIGURE 3. Polarization curves of iron, nickel, and binary alloys of nickel and iron obtained on the 202d day of exposure to city water having added 3 percent by weight of sodium chloride.

NOTE: Values of  $I_p$  and  $I_q$  actually used for the calculations (table 3) are marked  $I_p$  and  $I_q$  (figs. 3 and 4), for example,  $I_p$  (fig. 3) is used with  $I_q$  (fig. 4) for the 100 Fe specimen. In the case of the 100 Ni specimen,  $I_p$  and  $I_q$  of figure 3 are used, etc. The ordinates (figs. 3 and 4) are compressed to save space. In going up the scale, the potentials become less negative. Thus, for the 30 Ni specimen, the corrosion potential is about  $-0.58$  V (see fig. 4).

All the values of  $I_p$  and  $I_q$ , calculated corrosion currents, calculated weight losses, and actual weight losses for all specimens are tabulated in table 3. In calculating weight losses, the electrochemical equivalent for ferrous iron was chosen for the alloys with less than 50 percent of nickel, and that of nickel for the alloys having 50 percent or more of nickel. Actually, the equivalent value chosen is not significant here as the difference (about 5%) in results obtained is within the limit of accuracy with which the polarization curves can be evaluated.

In table 3, beginning with the 78th day of exposure and on through the 117th day, all data were obtained using the potentiodynamic method of polarization. It will be noted that the data pattern fits in quite well with the pattern before and after this period obtained using the galvanodynamic polarization technique. For specimens 1 through 6, the change from  $I_q = 10 I_p$  to lesser values of  $I_q$  is not believed to be significant. The potentiodynamic method offered no advantage in obtaining these data and required more instrumentation.

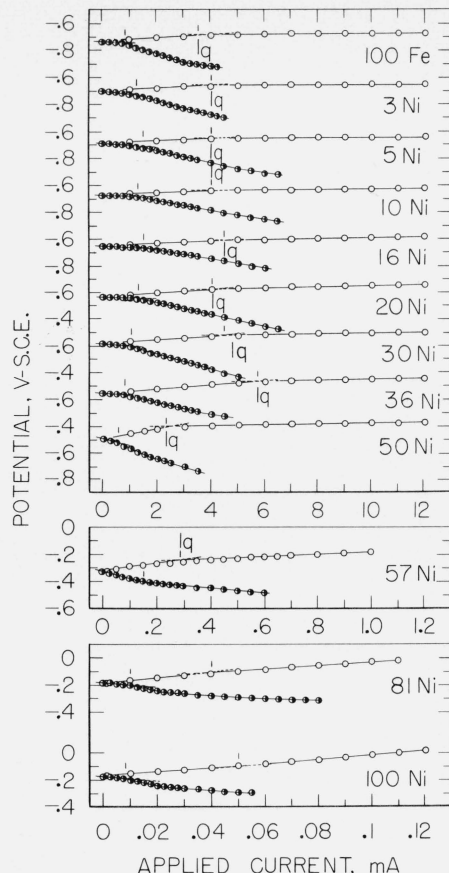


FIGURE 4. Same data as in figure 3, plotted on rectangular coordinates.

○ anodic, ● cathodic. See "Note" figure 3.

Figure 5 shows how the corrosion rates vary with the nickel content and how the calculated and actual values compare. The biggest reduction in corrosion rate occurred in changing from 50 Ni to 57 Ni. For the particular environment, nickel in amounts up to 20 percent seem to offer no advantage from the standpoint of corrosion resistance. Pettibone [9] demonstrated an advantage in the corrosion resistance of 36.53 Ni steel over mild steel in four sea water environments for exposure periods varying from 5 to 15 years. It has also been reported that the corrosion rate of a 26 percent Ni alloy of iron and nickel was about one-third that of wrought iron in sea water as well as in the atmosphere [10].

When specimen 8 (36 Ni) was initially exposed, the corrosion current was about one-eighth that of the specimens with lesser amounts of nickel (table 3). Between the 4th and 7th days, the corrosion potential of specimen 8 changed from  $-0.355$  V to  $-0.540$  V (potentials are not shown in the table) and the corrosion current increased fivefold. On specimen 9 (50 Ni), a low rate of corrosion prevailed through the 34th



TABLE 3. Corrosion weight losses calculated from polarization data obtained on a series of alloys containing nickel and iron exposed to a 3-percent sodium chloride solution for 7 months

Specimen	Exposure time	Polarizing current at break in curve <sup>a</sup>		Corrosion current <sup>b</sup>	Weight loss <sup>c</sup>	
		Cathodic $I_p$	Anodic $I_q$	$i_o$	Calculated cumulative	Actual
	Days	<i>mA</i>	<i>mA</i>	<i>mA</i>	<i>mg</i>	<i>mg</i>
1 (100 Fe)	4	1.8	$10I_p^d$	1.6	160	
	14	1.0	$10I_p^d$	0.91	470	
	20	0.75	$10I_p^d$	0.68	590	
	28	1.0	$10I_p^d$	0.91	750	
	34	0.93	$10I_p^d$	0.84	920	
	41	1.1	$10I_p^d$	1.0	1100	
	46	1.0	$10I_p^d$	0.91	1200	
	54	0.95	$10I_p^d$	0.86	1400	
	62	1.1	$10I_p^d$	1.0	1600	
	70	1.2	$10I_p^d$	1.1	1800	
	78	1.1	6.0	0.93	2000	
	88	1.2	8.2	1.0	2200	
	95	1.1	8.0	0.96	2400	
	102	1.3	7.3	1.1	2600	
	117	1.2	7.8	1.0	3000	
	125	1.1	9.0	0.98	3200	
	137	1.0	7.0	0.88	3400	
	145	0.80	4.7	0.68	3600	
	159	1.2	4.5	0.95	3900	
	172	1.1	4.5	0.88	4200	
	202	1.1	3.5	0.84	4800	
	210				5000	4590
2 (3 Ni)	4	1.6	$10I_p^d$	1.4	140	
	14	1.3	$10I_p^d$	1.2	460	
	20	0.95	$10I_p^d$	0.85	610	
	28	1.2	$10I_p^d$	1.1	810	
	34	1.1	$10I_p^d$	1.0	970	
	41	1.1	$10I_p^d$	1.0	1100	
	46	1.0	$10I_p^d$	0.91	1300	
	54	0.95	$10I_p^d$	0.85	1400	
	62	1.2	$10I_p^d$	1.1	1600	
	70	1.3	$10I_p^d$	1.2	1900	
	77	1.3	7.5	1.1	2100	
	88	1.3	8.0	1.1	2400	
	95	1.2	7.5	1.0	2500	
	102	1.3	6.8	1.1	2700	
	117	1.4	8.8	1.2	3200	
	125	0.95	6.0	0.82	3400	
	137	1.3	6.0	1.1	3600	
	145	1.1	4.0	0.86	3800	
	159	1.3	9.0	1.1	4200	
	172	1.2	4.0	0.92	4500	
	202	1.1	4.0	0.86	5200	
	210				5300	4660
3 (5 Ni)	4	1.6	$10I_p^d$	1.4	140	
	14	1.0	$10I_p^d$	0.91	410	
	20	0.80	$10I_p^d$	0.73	540	
	28	1.2	$10I_p^d$	1.1	720	
	34	1.1	$10I_p^d$	1.0	890	
	41	1.3	$10I_p^d$	1.2	1100	
	46	1.1	$10I_p^d$	1.0	1200	
	54	0.98	$10I_p^d$	0.89	1400	
	62	1.3	$10I_p^d$	1.2	1600	
	70	1.5	$10I_p^d$	1.4	1900	
	78	1.3	8	1.1	2100	
	88	1.2	8.3	1.0	2400	
	95	1.5	7.5	1.3	2600	
	102	1.5	7.3	1.2	2800	
	118	1.3	8.0	1.1	3300	
	125	1.1	7.0	0.96	3400	
	137	1.3	9.0	1.1	3700	
	145	1.2	5.0	0.97	3900	
	159	1.3	4.5	1.0	4300	
	172	1.2	4.2	0.93	4600	
	202	1.2	4.0	0.92	5300	
	210				5500	4860

TABLE 3. Corrosion weight losses calculated from polarization data obtained on a series of alloys containing nickel and iron exposed to a 3-percent sodium chloride solution for 7 months—Continued

Specimen	Exposure time	Polarizing current at break in curve <sup>a</sup>		Corrosion current <sup>b</sup>	Weight loss <sup>c</sup>	
		Cathodic $I_p$	Anodic $I_q$	$i_o$	Calculated cumulative	Actual
	Days	<i>mA</i>	<i>mA</i>	<i>mA</i>	<i>mg</i>	<i>mg</i>
4 (10 Ni)	4	1.5	$10I_p^d$	1.4	140	
	14	1.3	$10I_p^d$	1.2	470	
	20	1.0	$10I_p^d$	0.91	630	
	28	1.3	$10I_p^d$	1.2	830	
	34	1.3	$10I_p^d$	1.2	1000	
	41	1.1	$10I_p^d$	1.0	1200	
	46	1.2	$10I_p^d$	1.1	1300	
	55	1.2	$10I_p^d$	1.1	1600	
	62	1.2	$10I_p^d$	1.1	1800	
	70	1.3	$10I_p^d$	1.2	2000	
	78	1.2	7.5	1.0	2200	
	88	1.2	9.0	1.1	2500	
	95	1.2	8.0	1.0	2600	
	102	1.3	8.0	1.1	2800	
	117	1.3	7.0	1.1	3200	
	125	1.2	7.0	1.0	3400	
	137	1.5	14.0	1.4	3800	
	145	1.2	5.0	0.97	4000	
	159	1.3	4.0	0.98	4400	
	172	1.3	4.2	0.99	4700	
	202	1.3	4.0	0.98	5400	
	210				5600	4880
5 (16 Ni)	4	1.9	$10I_p^d$	1.7	170	
	14	1.4	$10I_p^d$	1.3	550	
	20	1.2	$10I_p^d$	1.1	720	
	28	1.5	$10I_p^d$	1.4	980	
	34	1.0	$10I_p^d$	0.90	1100	
	41	1.2	$10I_p^d$	1.1	1300	
	46	1.2	$10I_p^d$	1.1	1500	
	55	1.3	$10I_p^d$	1.2	1700	
	62	1.5	$10I_p^d$	1.4	1900	
	70	1.5	$10I_p^d$	1.4	2200	
	78	1.4	8.7	1.2	2500	
	88	1.5	9.0	1.3	2800	
	95	1.4	8.0	1.2	3000	
	102	1.7	7.1	1.4	3200	
	117	1.6	8.4	1.3	3700	
	125	1.4	6.0	1.1	4000	
	137	1.5	5.0	1.1	4300	
	145	1.5	4.5	1.1	4500	
	159	1.4	4.0	1.0	4900	
	172	1.5	4.0	1.1	5200	
	202	1.4	4.5	1.1	6100	
	210				6300	5350
6 (20 Ni)	5	2.0	$10I_p^d$	1.8	220	
	12	1.5	$10I_p^d$	1.4	500	
	20	1.1	$10I_p^d$	1.0	740	
	28	1.5	$10I_p^d$	1.4	990	
	34	1.2	$10I_p^d$	1.1	1200	
	41	1.1	$10I_p^d$	1.0	1400	
	46	1.1	$10I_p^d$	1.0	1500	
	55	1.2	$10I_p^d$	1.1	1700	
	62	1.1	$10I_p^d$	1.0	1900	
	70	1.2	$10I_p^d$	1.1	2100	
	77	1.2	8.3	1.0	2300	
	88	1.3	7.7	1.1	2600	
	95	1.3	7.3	1.1	2800	
	102	1.3	8.0	1.1	3000	
	117	1.5	6.8	1.2	3400	
	125	1.1	6.3	0.94	3600	
	137	1.4	6.0	1.1	3900	
	145	1.0	4.0	0.80	4100	
	159	1.3	6.0	1.1	4400	
	172	1.2	4.2	0.93	4800	
	202	1.3	4.0	0.98	5500	
	210				5700	4440

TABLE 3. Corrosion weight losses calculated from polarization data obtained on a series of alloys containing nickel and iron exposed to a 3-percent sodium chloride solution for 7 months—Continued

Specimen	Exposure time	Polarizing current at break in curve <sup>a</sup>		Corrosion current <sup>b</sup>	Weight loss <sup>c</sup>	
		Cathodic $I_p$	Anodic $I_q$	$i_0$	Calculated cumulative	Actual
	Days	<i>mA</i>	<i>mA</i>	<i>mA</i>	<i>mg</i>	<i>mg</i>
7 (30 Ni)	4	1.7	5.0	1.3	130	
	12	1.5	7.5	1.1	370	
	20	1.0	7.0	0.87	570	
	28	1.2	10 $I_p^d$	1.1	760	
	34	1.1	10 $I_p^d$	1.0	920	
	40	1.1	10 $I_p^d$	1.0	1100	
	47	0.93	10 $I_p^d$	0.85	1200	
	55	1.1	10 $I_p^d$	1.0	1400	
	62	1.1	5.0	0.90	1600	
	70	1.0	6.0	0.86	1800	
	78	1.1	9.2	0.98	1900	
	88	1.2	11.5	1.1	2200	
	95	1.1	8.0	0.97	2400	
	102	1.2	9.0	1.1	2500	
	117	1.0	8.8	0.90	2900	
	125	0.95	5.3	0.81	3100	
	137	1.0	6.5	0.87	3300	
	145	0.90	4.0	0.74	3500	
	159	0.98	2.5	0.70	3700	
	172	1.1	2.5	0.76	4000	
	202	1.0	4.5	0.82	4600	
	210	.....	.....	.....	4700	4100
8 (36 Ni)	4	0.20	0.90	0.16	16	
	7	1.1	4.4	0.88	55	
	12	1.4	8.2	1.2	180	
	21	0.75	5.0	0.65	390	
	29	1.3	5.5	1.1	560	
	34	0.90	4.3	0.74	680	
	41	1.0	5.8	0.85	820	
	47	0.80	3.7	0.66	930	
	55	0.90	5.5	0.77	1100	
	62	0.90	5.0	0.76	1200	
	70	1.0	5.0	0.83	1400	
	78	1.0	5.5	0.85	1500	
	88	1.1	6.0	0.93	1800	
	95	1.2	5.0	0.97	1900	
	102	1.2	4.8	0.96	2100	
	117	1.2	5.0	0.97	2500	
	125	1.2	6.0	1.0	2600	
	137	0.50	6.5	0.79	2900	
	145	0.90	5.2	0.77	3100	
	159	1.3	6.0	1.1	3400	
	173	0.90	5.0	0.76	3700	
	202	0.90	5.7	0.78	4300	
	210	.....	.....	.....	4400	3110
9 (50 Ni)	4	0.18	0.30	0.11	12	
	7	0.11	0.11	0.055	18	
	12	0.15	0.30	0.10	28	
	18	0.32	0.14	0.097	43	
	28	0.26	0.30	0.14	75	
	34	0.29	0.25	0.13	96	
	40	1.4	3.0	0.95	180	
	46	1.3	3.0	0.91	330	
	54	0.75	2.1	0.55	480	
	62	1.0	2.5	0.71	610	
	70	1.0	6.0	0.85	780	
	78	0.90	6.0	0.78	950	
	88	0.82	6.5	0.73	1100	
	95	0.75	6.5	0.67	1300	
	102	0.88	5.9	0.76	1400	
	117	0.60	6.8	0.55	1700	
	125	0.55	2.5	0.45	1800	
	137	0.65	4.0	0.56	1900	
	145	0.60	2.8	0.49	2000	
	159	0.60	2.0	0.46	2200	
	173	0.67	2.5	0.53	2400	
	202	0.52	2.3	0.42	2700	
	210	.....	.....	.....	2800	2860

TABLE 3. Corrosion weight losses calculated from polarization data obtained on a series of alloys containing nickel and iron exposed to a 3-percent sodium chloride solution for 7 months—Continued

Specimen	Exposure time	Polarizing current at break in curve <sup>a</sup>		Corrosion current <sup>b</sup>	Weight loss <sup>c</sup>	
		Cathodic $I_p$	Anodic $I_q$	$i_0$	Calculated cumulative	Actual
	Days	<i>mA</i>	<i>mA</i>	<i>mA</i>	<i>mg</i>	<i>mg</i>
10 (57 Ni)	4	0.10	0.25	0.071	7.5	
	7	0.08	0.13	0.049	12	
	12	0.18	0.32	0.11	23	
	21	0.20	0.09	0.062	43	
	29	0.15	0.13	0.07	57	
	34	0.13	0.12	0.065	66	
	40	0.29	0.14	0.094	78	
	46	0.15	0.15	0.075	91	
	54	0.15	0.19	0.084	110	
	62	0.15	0.25	0.094	130	
	70	0.21	0.41	0.14	150	
	78	0.20	0.35	0.13	180	
	88	0.18	0.25	0.10	210	
	95	0.16	0.25	0.098	230	
	102	0.14	0.41	0.10	250	
	117	0.17	0.17	0.12	290	
	125	0.13	0.56	0.11	320	
	137	0.11	0.55	0.092	350	
	146	0.17	0.38	0.12	370	
	159	0.16	0.30	0.10	410	
	173	0.13	0.25	0.085	440	
	202	0.15	0.28	0.097	510	
	210	.....	.....	.....	530	332
11 (81 Ni)	4	0.036	0.070	0.024	2.5	
	7	0.009	0.010	0.0047	3.7	
	12	0.025	0.027	0.013	4.9	
	18	0.011	0.019	0.007	6.5	
	29	0.010	0.014	0.0059	8.4	
	34	0.0095	0.016	0.0060	9.2	
	40	0.011	0.020	0.0071	10	
	46	0.010	0.018	0.0064	11	
	54	0.012	0.022	0.0078	13	
	62	0.009	0.022	0.0064	14	
	70	0.010	0.027	0.0073	16	
	78	0.011	0.027	0.0078	17	
	88	0.012	0.033	0.0088	20	
	95	0.012	0.030	0.0086	21	
	102	0.011	0.040	0.0085	23	
	117	0.012	0.042	0.0094	26	
	125	0.0085	0.027	0.0064	28	
	137	0.0095	0.026	0.0070	30	
	145	0.011	0.026	0.0077	32	
	159	0.0082	0.025	0.0062	34	
	173	0.012	0.030	0.0086	37	
	202	0.010	0.030	0.0075	43	
	210	.....	.....	.....	45	61
12 (100 Ni)	4	0.050	0.038	0.022	2.3	
	7	0.0070	0.012	0.0044	3.3	
	12	0.010	0.025	0.0071	4.0	
	18	0.0088	0.028	0.0067	5.1	
	29	0.010	0.011	0.0052	7.8	
	34	0.0095	0.011	0.0051	8.5	
	40	0.010	0.020	0.0067	9.4	
	46	0.0075	0.020	0.0055	10	
	54	0.0060	0.020	0.0046	11	
	62	0.0090	0.020	0.0062	13	
	70	0.0090	0.022	0.0064	14	
	78	0.010	0.030	0.0075	16	
	88	0.010	0.026	0.0072	17	
	95	0.011	0.030	0.0080	19	
	102	0.011	0.030	0.0080	20	
	117	0.012	0.033	0.0088	24	
	125	0.0080	0.021	0.0058	25	
	138	0.011	0.026	0.0077	27	
	145	0.0088	0.030	0.0068	29	
	159	0.0083	0.034	0.0067	31	
	173	0.0090	0.027	0.0067	34	
	202	0.0080	0.030	0.0063	39	
	210	.....	.....	.....	40	54

<sup>a</sup> See the text.

<sup>b</sup>  $i_0 = I_p \cdot I_q / (I_p + I_q)$ .

<sup>c</sup> Calculated weight loss (g) =  $Kti$ ,  $K$  = electrochemical equivalent (for specimens 1–8, assumed  $K = 2.8938 \times 10^{-4}$  g/coulomb; for specimens 9–12, assumed  $K = 3.0409 \times 10^{-4}$  g/coulomb;  $i$  = average of corrosion currents (A) for the exposure period ( $t$  in sec) between successive readings). The values of  $i_0$  at the beginning and end of exposure are taken as the initial and final values, respectively, as calculated.

<sup>d</sup> Assumed.

NOTE: All specimens were completely submerged and exposed at the same time in an open vat containing about 265 gal of salt water. Mean solution temp., 73 °F; min, 64 °F; max, 81 °F. Area of specimen, 1/6 ft<sup>2</sup> (155 cm<sup>2</sup>).

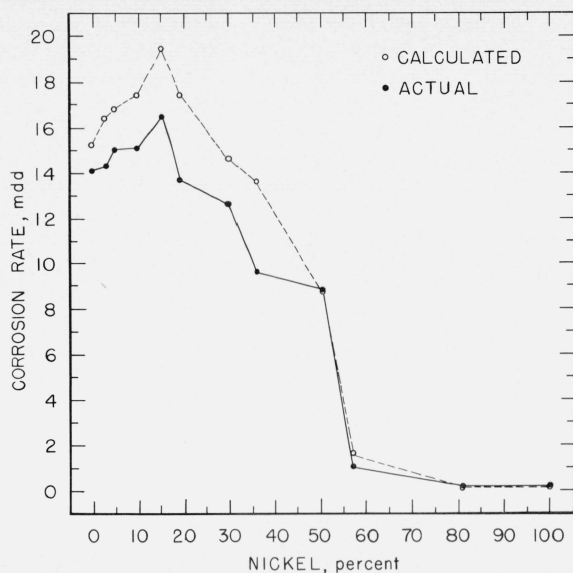


FIGURE 5. Effect of nickel alloyed with iron on the corrosion rates of alloys exposed for 7 months to Washington, D.C. city water to which was added 3 percent by weight of sodium chloride.

● based on the actual weight loss for 210 days.  
○ based on the cumulative weight loss as calculated from the breaks in polarization curves (table 3).

day (table 3) after which the corrosion potential changed from  $-0.343$  V to  $-0.495$  V and the corrosion current increased sevenfold. The corrosion current pertaining to specimen 9 was minimum when its corrosion potential was the least active ( $-0.285$  V) on the 7th day of exposure. For a comparison of the corrosion potentials of all alloys on the 202d day of exposure, see figure 4 (at zero current). Perhaps, the still water surrounding the specimens, where a greater chance for oxygen depletion occurred, may have prevented a continuation of the film-forming tendencies initially exhibited by the 36 and 50 Ni alloys. In moving water, the oxide films would probably have been more stable and might have prevailed.

The relationship between the two corrosion rate measuring techniques is shown in figure 6. The line through the points is drawn with a slope of  $-1$ , the theoretical basis for which was given by Stern [4]. The values of  $\Delta V/\Delta I$  are based on the change in potential caused by the increase of applied current from zero to a value slightly larger than the current  $I_p$ , as indicated by arrows in figure 3 when the corrosion current is zero or negligible as indicated by the increase polarization rate. Selecting values of applied current smaller than  $I_p$  could result in erroneous values of  $\Delta V$  because the changes in potential might be too small for reliable measurement. Once a relationship, as in figure 6, is established for a given environment, corrosion rates can be approximated simply by measuring  $\Delta V/\Delta I$ .

As the corrosion currents were controlled by the cathodic reactions, almost without exception (table 3), the values  $\Delta V/\Delta I$  were calculated from the cathodic polarization curves. The relationship between the

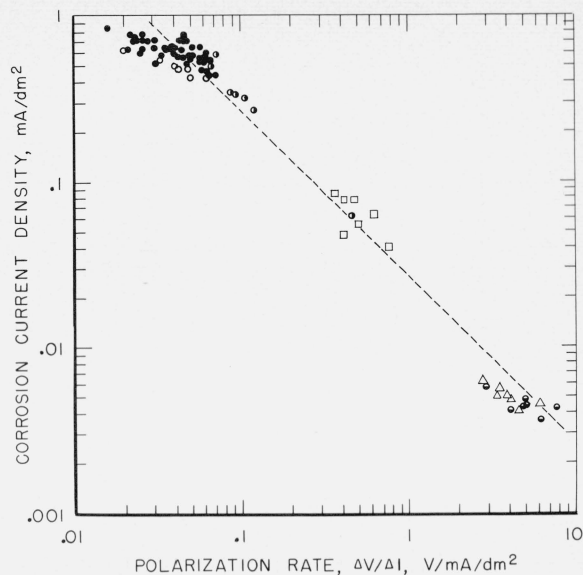


FIGURE 6. Logarithmic relationship between the corrosion current density, calculated from breaks in cathodic and anodic polarization curves, and the controlling polarization rate (cathodic) of nickel, iron, and binary alloys of nickel and iron.

Sublegend: Seven values are shown for each specimen based on measurements made at periodic intervals during the 210-day exposure period.

●	Specimens 1 through 7, 0–30 Ni.
○	Specimen 8, 36 Ni.
●	Specimen 9, 50 Ni.
□	Specimen 10, 57 Ni.
△	Specimen 11, 81 Ni.
●	Specimen 12, 100 Ni.

polarization rates  $\Delta V/\Delta I$  and the actual corrosion rates (weight losses) of the 12 specimens is shown in figure 7, the line through the points again being drawn with slope of  $-1$ .

## 4. Summary

Ten binary alloys of nickel and iron (series of 3 to 81% Ni) and the metals nickel and iron, 12 specimens in all, were exposed for 210 days to about 265 gals of still Washington, D.C., tap water (64–81 °F) to which was added 3 percent by weight of sodium chloride. Corrosion currents were calculated periodically from breaks in polarization curves, averaged for each of the 22 periods and converted to cumulative weight losses by Faraday's law. The calculated weight losses differed from the actual weight losses (resulting from corrosion) by from 1 to 61 percent, averaging 22 percent for the 12 specimens. The iron lost about 85 times as much weight as did the nickel while the ratio of the respective areas apparently corroded was about 4000 to 1. Corrosion of the nickel seemed to be confined to one pit about 0.064 in. (1.6 mm) diam.

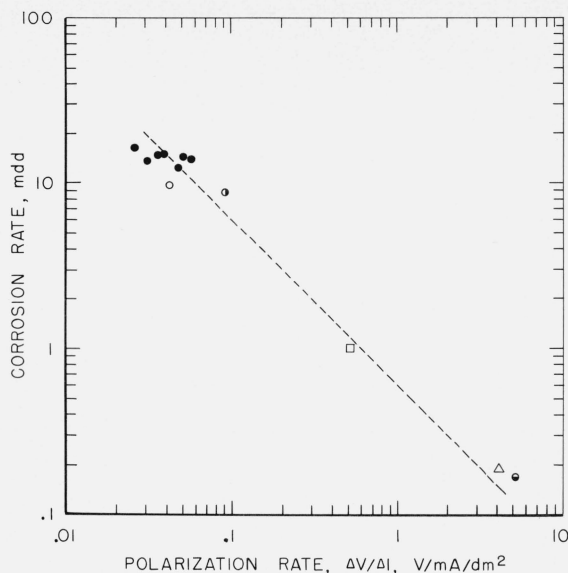


FIGURE 7. Logarithmic relationship between corrosion rate based on actual weight loss and the controlling polarization rate of nickel, iron, and binary alloys of nickel and iron.

Sublegend: Each point pertains to a specimen and the polarization rate is the average of seven measurements made at periodic intervals during the 210-day exposure period.

- Specimens 1 through 7, 0-30 Ni.
- Specimen 8, 36 Ni.
- Specimen 9, 50 Ni.
- Specimen 10, 57 Ni.
- △ Specimen 11, 81 Ni.
- Specimen 12, 100 Ni.

Polarization rates,  $\Delta V/\Delta I$ , of the 12 specimens, referred to by most investigators as polarization resistance, were plotted on logarithmic coordinates against corrosion current densities calculated from the same curves by the break method and found to fit a curve having the theoretical slope of  $-1$ . Similarly, the actual weight losses of the 12 specimens plotted on logarithmic coordinates versus their average polarization rates also revealed a slope of  $-1$ . Thus, once having established the relationship between corrosion current density (from breaks in polarization curves) and polarization rates,  $\Delta V/\Delta I$ , corrosion current densities can be approximated for other alloys in the particular environment by simply measuring  $\Delta V/\Delta I$ .

The primary purpose of the laboratory work was to evaluate two polarization techniques as methods for measuring rates of corrosion in an aqueous solution. Of secondary interest to the author was the observation that the biggest benefit in corrosion resistance occurred in changing from 50 to 57 percent Ni. Both the calculated and the actual weight losses revealed a reduction in corrosion of over 80 percent for the 57 Ni alloy over that of the 50 Ni alloy.

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