CORRELATION OF ELECTRODE POTENTIAL MEASUREMENTS WITH CORROSION RATES

by

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SUMMARY

The object of this thesis is to determine if the irreversible electrode potentials of copper-base alloys can be correlated with the resistance of alloys to corrosion by orthophosphoric acid, (H_3PO_4).

The study of the correlation of electrode potentials with corrosion data was undertaken with the hopes that it would be possible to use electrode potentials in predicting the relative rates of corrosion of a series of similar alloys.

The electromotive force, which is directly proportional to the electrode potential, was determined for three series of special cast copper-base alloys, and one series of commercial copper-base alloys. The electromotive force was measured between the alloy specimens and a glass electrode in an aqueous solution of orthophosphoric acid. The specimens were suspended in a solution at room temperature (approx. 30°C), which was not stirred or aerated for 15 minutes before the potentiometer reading was taken.

The corrosion data were determined as a separate project by K. Elliott working under the supervision of D.J. Mack.

The electomotive force-composition curves and the corrosion rate-composition curves are plotted on the same axes. The two curves are similar in the case

of the copper-zinc alloys, leaded-brasses, and iron bearing-red brasses. However, there is only a slight similarity in the case of the commercial brasses and bronzes.

It is concluded from the results of the work that electrode potentials determined for copper-base alloys in an aqueous orthophosphoric acid solution will correlate with corrosion rates of the same alloys.

To investigate farther the possibility of the correlation of electrode potentials with corrosion rate, it is suggested that several other alloys be used.

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INTRODUCTION

The need of information as to the relative durability of metallic materials has led to the widespread use of corrosion tests. These tests vary widely in character from exposure for prolonged periods to the actual environment in which the metals are to be used to laboratory tests of great variety. Such tests, while of considerable assistance in the selection of suitable materials for given purposes, have not generally furnished sufficient information as to the processes of corrosion to permit the prediction as to what will happen under slightly different conditions.

The relatively long period of time required to obtain measurable results on metal specimens exposed to natural environments led to an interest in accelerated corrosion tests in which the rates of reaction are accelerated by increasing the temperature, the humidity, or by otherwise modifying the natural environment. The more recent trend in corrosion investigations has been in the direction of the study of corrosion processes with experimental techniques of sufficient sensitivity to measure the actual rates of reaction occurring in the natural environments. These methods have the advantages of both accelerated and natural environment tests in that the test requires a reasonable short time and does

not involve the danger of distortion introduced by accelerating the rates of reaction.

One method of determining the rate of reaction that occurs when a metal corrodes in an aqueous solution is the determination of its electrode potential. The electrode potential method was used in this study of the correlation of corrosion rates with electrode potentials.

GENERAL THEORY AND PREVIOUS WORK ON ELECTRODE POTENTIALS

The basis of any electrochemical treatment of the subject of corrosion is, of necessity, the "electromotive force series", an arrangement of the elements in the order of their solution tendencies. The standard potentials are those determined for the elements in solutions containing in effect one atomic weight in grams of ions in 1,000 grams of water at 25° C. These potentials are referred to hydrogen which is designated arbitrarily as zero. By experiment it has been shown that reversible electrode potentials* determined in this way are of little value in corrosion studies. For instance, the presence of cyanides or similar compounds cause serious departure from the E.M.F. series. Metals like aluminum and stainless steel, which cover themselves with protective films or develop passivity will also display a behavior utterly inconsistent with their places in the E.M.F. series.[5]

Corrosion of metals can be classified under two main divisions: (1) Direct combination of the metal ions with oxygen, chlorine or similar elements: (2)[5]

* Reversible electrode potentials obey Nernst's law; that is, they are the potentials at equilibrium conditions. At equilibrium conditions only an infinitesimal current is consumed, so that the greatest possible electrical work is obtained from the cell. This work is definite and is of great value in thermodynamical calculations.[7] Irreversible cells are not at an equilibrium condition.

the replacement of hydrogen or another metal from solution. The corrosion of copper-base alloys in aqueous environment comes under class (2).

It has been well established that, in the corrosion of a metal in aqueous environment, two reactions take place simultaneously upon its surface; metal ions pass into solution and hydrogen ions pass out of solution, depositing on the metal. This deposit of hydrogen changes the potential of the metal surface and is called polarization. However, inasmuch as ions are matter and have dimensions, it is evident that both reactions cannot take place at the same point and that there must be two kinds of areas, those at which metal dissolves, and those at which hydrogen ions are discharged. These reactions continue until equilibrium is reached. In order that the reactions continue (i.e. that the metal continues to corrode) this equilibrium must be destroyed in either of two ways: (a) by self discharge of the hydrogen as gas, as usually happens when metals are attacked by acids: or (b), by removal of the hydrogen with (OH^-) ions to form H_2O. The (OH^-) ions are formed by the following reaction:

$$O_2 + 2H_2O + 4e \longrightarrow 4(OH)^-$$

This removal of the H^+ ions by the (OH^-) ion to form water depends upon the presence of O_2 dissolved in the electrolyte and is usually known as corrosion by O_2 depolarization.

In postulating such a situation it is necessary to assume that the interface between a metal and its environment is not entirely homogeneous; otherwise there would be no basis for the selection and establishment of these two kinds of areas. There are, in other words, two types of interface between metal and environment at which different corrosion tendencies must exist. The known resistance of spectroscopically pure metals to solution in acid is the results of the homogeneity of the metal-acid interface and not of a lesser tendency of the metals to dissolve.

Unless specially prepared, metal surfaces contain areas which are chemically or physically different from the rest of the surface. The presence of metallic impurities, oxides, and differences in crystal structure and physical strain, which in turn lead to differences in solution tendencies, cannot readily be avoided. In actual practice, therefore, it is safe to assume that perfectly homogeneous metals are not commercially available: and even if they were, the chances of their environment being equally homogeneous are rather remote.

These areas of different solution tendency can be shown experimentally to have different electrode potentials.[5] In the "galvanic cells" so formed, the areas which favor metal solution are the anodes and those which favor hydrogen-ion discharge are the cathodes.

The quantity of current which passes through these cells is proportional to the amount of metal which dissolves. This "couple" action provides the mechanism by means of which corrosion takes place.

The preferable experimental approach to determining the rate of corrosion would be to measure the characteristics of individual corrosion cells, since the current which flows in these cells in a given time is a direct measure of the rate of corrosion. The measuring of the characterisitcs of individual corrosion cells requires a highly specialized technique.[2-3] However, it is a simple matter to determine a composite of the resultant potentials, which is the electrode potential of the metal.

If this composite of the resultant potentials can be shown to be reproducible, then it is possible to use these potentials in determining the relative rate at which the specimens tend to corrode. Therefore, for a series of alloys, the potential of each alloy will indicate its tendency to go into solution. The less positive the potential the greater the tendency to go into solution. (The more electro-negative metals are sodium, zinc, etc.) These potential measurements cannot be used to determine thermodynamic quantities since they are irreversible. However, if the potentials correlate with corrosion data then it can be assumed

that they can be used to determine the corrosion rates in any one series of alloys.

Since the electrode potential is directly proportional to the measured E.M.F., for purposes of corrosion study it is not necessary to determine the irreversible electrode potentials in relation to hydrogen providing the same electrode and same electrolyte are used for any one series of measurements.

The change of electrode potential with time has been used by R.M. Burns[4] in determining the relative rates of sulfation of lead alloys. R.H. Brown, W.L. Flink, and M.S. Hunter[1] used electrode potential measurements in the determination of phase fields of an aluminum-copper alloy. Electrode potential measurements has been used by Schumacker and Souden[8] in studying the corrosion of iron-copper alloys; by Tamman and Sotter[10] in investigating alloys of iron-molybdenum and iron-chromium; by Strauss[9] on iron-chromium alloys.

In these applications of the use of electrode potential measurements the writers stress the fact that the electrode potentials can be correlated with actual service corrosion rates only when the potentials are measured in certain experimentally determined solutions.

MATERIALS AND EQUIPMENT

Three of the four series of copper-base alloys used in the study were special copper-base alloy castings prepared from pure metals. The other one was a series of commercial cast brasses and bronzes which was purchased from Crane Co. Tables No. 1,2,3, and 4 show a tabulation of the four series giving designation and composition. The leaded-red brass series and iron bearing-red brass series consist of lead and iron as shown in tables (2) and (3). The remainder of the alloys is red brass. (Red brass has a composition of 85% Cu and 15% Zn) The analysis of the commercial series is the "as desired" analysis taken from the purchase order.

The equipment used in this study consists of a Leeds and Northrup #7661-A-1 Universal pH Potentiometer Assembly. (See direction books Std. 11257 and 11258 by Leeds and Northrup Company, Philadelphia, Pa.)

Analysis of Alloys Studied

Table 1

Copper-zinc series

Alloy number	%Zn	%Cu
Z1	1.0	99.0
Z2	2.5	97.5
Z3	5.0	95.0
Z4	8.0	92.0
Z5	14.3	85.7
Z6	20.0	80.0
Z7	31.5	68.5

Table 2

Leaded-red brass series

Alloy number	%Pb
ZL1	0.08
ZL2	0.55
ZL3	1.10
ZL4	5.20
ZL5	9.00
ZL7	20.30

Remainder is 85% copper-15% zinc brass

Table 3

Iron bearing red brass series

Alloy number	% Fe
ZF1	0.16
ZF2	0.47
ZF3	0.77
ZF4	1.90

Remainder is 85 copper- 15 zinc brass.

Table 4

Commercial series *

Alloy number	%Cu	%Sn	%Pb	%Zn	%Ni
C1	89.50	5.00	1.75	3.75	0.00
C2	85.00	5.00	5.00	5.00	0.00
C3	77.00	5.00	10.00	6.00	2.00
C4	83.00	4.00	6.00	7.00	0.00
C5	80.00	3.00	7.50	9.50	0.00
C6	77.00	3.00	10.00	10.00	0.00
C7	78.00	2.00	7.00	13.00	0.00

* These figures are the "as desired" analysis from the purchase requisition.

PROCEDURE

The samples used were disc cross sections (approx. 2 1/4" in diameter by 3/16" thick) cut from cast billets. Series Z, ZL, and ZF were cast in the University of Tennessee Chemical Engineering Laboratory, while series C was purchased in the billet form.

Treatment of Samples for Electrode Potential Measurements

1. Machine to smooth finish.
2. Finish on (0) metallographic emery paper.
3. Wash with soap and water, rinse in alcohol and allow to dry.
4. Coat approximately 2/3 of the sample with paraffin by dipping into molten paraffin.
5. Place in the solution so that the uncoated 1/3 is all below the surface.

In addition to this treatment, series Z was heat treated at approximately 1,000°F to relieve machine and casting stresses. The oxide film caused by the heating was removed by pickling in an aqueous solution of hydrochloric acid.

Treatment of Glass Electrode

1. Soak the electrode for about one hour in aqueous hydrochloric acid solution, then rinse in water.
2. Place the electrode in the solution, so that

approximately 1/3 of the length is submerged.

Measuring the E.M.F.

1. Balance the potentiometer against the standard cell.
2. Throw the switch to measure the E.M.F. and balance again.
3. Record the reading taken after the specimen has been in the solution for 15 minutes.

Procedure for Determining the Corrosion Rate of the Alloys as Expressed in Inches of Penetration Per Year

The corrosion rates were determined by K. Elliott,[6] working under the supervision of D.J. Mack, as a separate project.

After rough machining, the specimens were polished on grade (0) metallographic emery paper. They were then washed in soap and water, rinsed in alcohol and allowed to dry. After determining the weight, density, and dimensions of each specimen in a series, the entire series, held on a spool type specimen holder, was immersed for four hours in boiling 85% C.P. orthophosphoric acid at 156°C which was aerated with saturated air at a rate of 0.07 cubic feet per minute. Two liters of the acid were used in each test.

At the end of four hours the specimens were removed,

washed, scrubbed with a bristle brush and soap, and then reweighed. From the loss in weight, the density and dimensions the corrosion rate in inches of penetration per year was computed.

Explanation of Steps in Procedure

Other variables being fixed, the rate of corrosion varies inversely with the degree of finish a specimen has on its surface. This is due to the specimen having less exposed area when it has a smooth surface than when it has a rough surface. It was desired to have a uniform finish on all the samples in any one series, so that there would be no variation of electrode potential due to surface conditions. Grade (0) metallographic emery paper was arbitrarily chosen to polish the specimens.

The specimens were washed after being polished to remove the abrasive material and any oil that was on the surface. Any foreign material on the surface will cause a variation in electrode potential. The specimens were rinsed in alcohol to remove the water.

Approximately 2/3 of the specimen was coated with paraffin before it was suspended in the solution in order to eliminate the difference of potential existing at the air-liquid interface. This difference of potential is caused by the difference of concentrations of oxygen

in the solution and in the air. The paraffin coating which extended below the liquid level protected the specimen at and above the solution level from the air. Paraffin was used because it is easy to apply, and because it is chemically inert.

A glass electrode rather than a hydrogen or calomel electrode was used as a reference electrode because it is not affected by oxidizing solutions and it is simple to use.

The irreversible electrode potentials will not become constant because of film formation and polarization, therefore some arbitrarily chosen time must be used to take the readings. It was found that the change in potential with time remained fairly constant after the specimen had been in contact with the solution for 15 minutes.

RESULTS

The E.M.F. for each specimen is tabulated in tables No. 5,6,7, and 8, together with the corrosion rate in inches of penetration per year and the composition of the alloys. The E.M.F.- composition curves and the corrosion rate-composition curves which are plotted on the same axes are shown in figures No. 1,2,3,4, and 5. The curves are plotted on the same axes, so that the correlation between the electrode potential and the corrosion rates may be more easily seen.

Corrosion Rates and E.M.F.

Table 5

Z Series

Alloy #	%Zn	Corrosion rate	E.M.F. volts	E.M.F.* volts
Z1	1.0	0.71 in./yr.	0.303	0.315
Z2	2.5	.71 "	.312	.329
Z3	5.0	.70 "	.312	.329
Z4	8.0	.57 "	.302	.322
Z5	14.3	.56 "	.292	.303
Z6	20.0	.58 "	.299	.320
Z7	31.5	.45 "	.315	.328

* These voltages were taken in a three normal solution.

Table 6

ZL Series

Alloy #	%Pb.	Corrosion rate	E.M.F. volts
ZL1	0.08	0.076 in./yr.	0.308
ZL2	.55	.079 "	.302
ZL3	1.10	.085 "	.300
ZL4	5.20	.150 "	.400
ZL5	9.00	.380 "	.565
ZL7	20.30	.660 "	.738

Table 7

ZF Series

Alloy #	%Fe	Corrosion rate	E.M.F. volts
ZF1	0.16	0.19 in./yr.	0.304
ZF2	.47	.19 "	.305
ZF3	.77	.18 "	.305
ZF4	1.90	.19 "	.302

Table 8

C Series

Alloy #	%Pb	%Zn	Corrosion rate	E.M.F. volts
C1	1.75	3.75	0.086 in./yr.	0.308
C2	5.00	5.00	.144 "	.494
C3	10.00	6.00	.294 "	.450
C4	6.00	7.00	.174 "	.306
C5	7.50	9.50	.267 "	.320
C6	10.00	10.00	.269 "	.565
C7	7.00	13.00	.218 "	.592

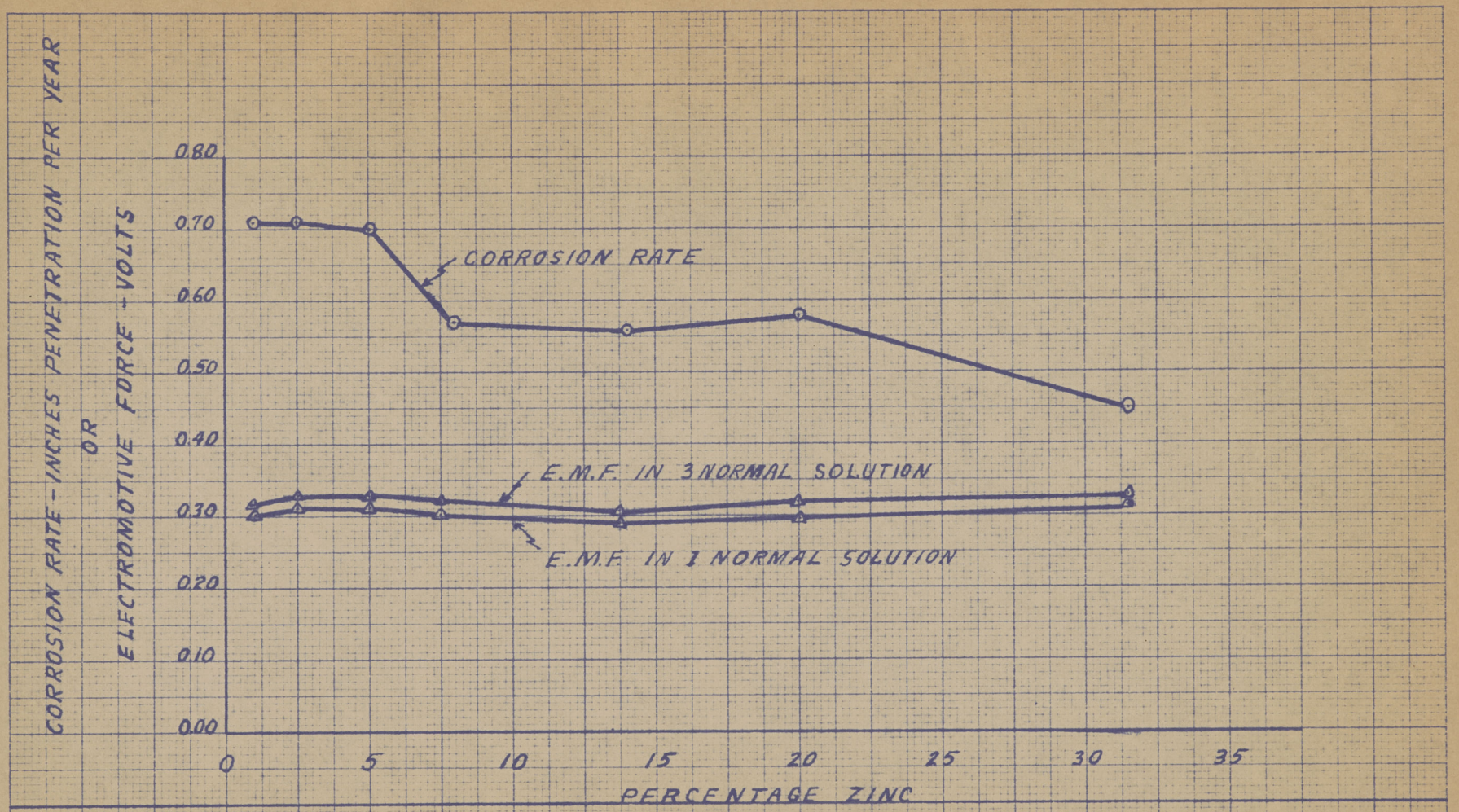

FIGURE 1

ALLOY COMPOSITION VS E.M.F AND CORROSION RATE

Z SERIES - EFFECT OF ZINC CONTENT

LONG, R.B.

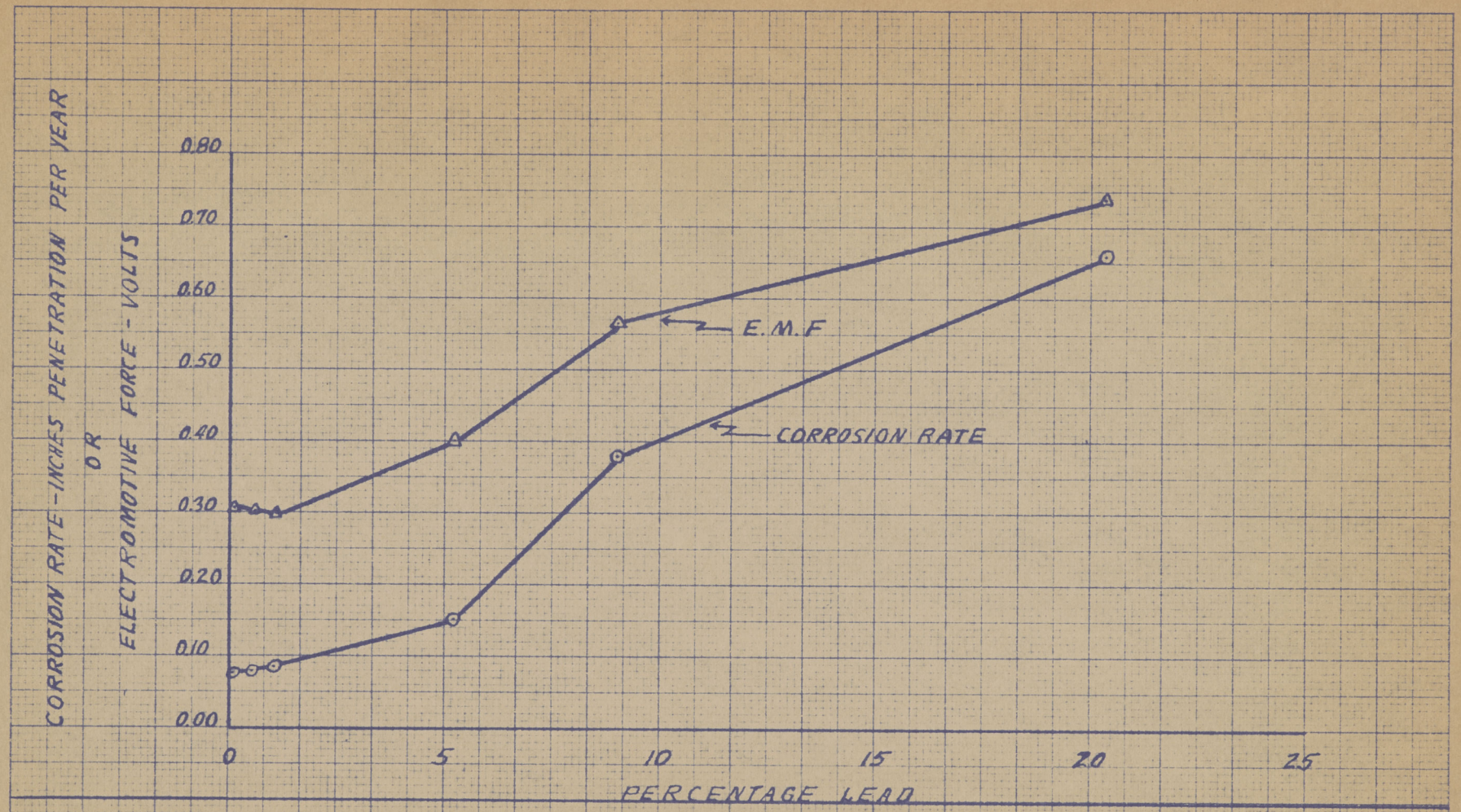

FIGURE 2

ALLOY COMPOSITION VS E.M.F AND CORROSION RATE

ZL SERIES - EFFECT OF LEAD CONTENT

LONG, R.B.

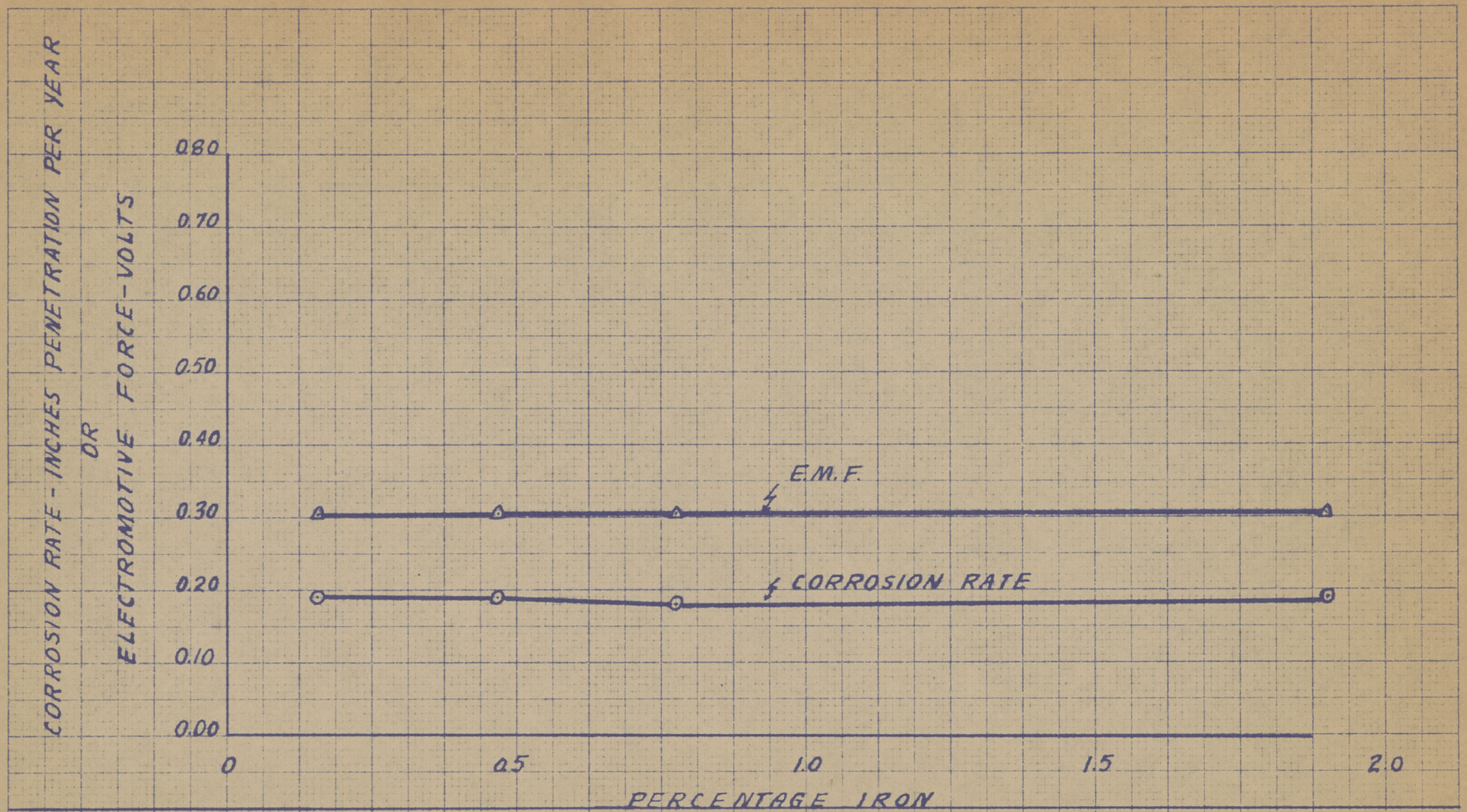

FIGURE 3

ALLOY COMPOSITION VS E.M.F. AND CORROSION RATE

ZF SERIES - EFFECT OF IRON CONTENT

LONG, R.B.

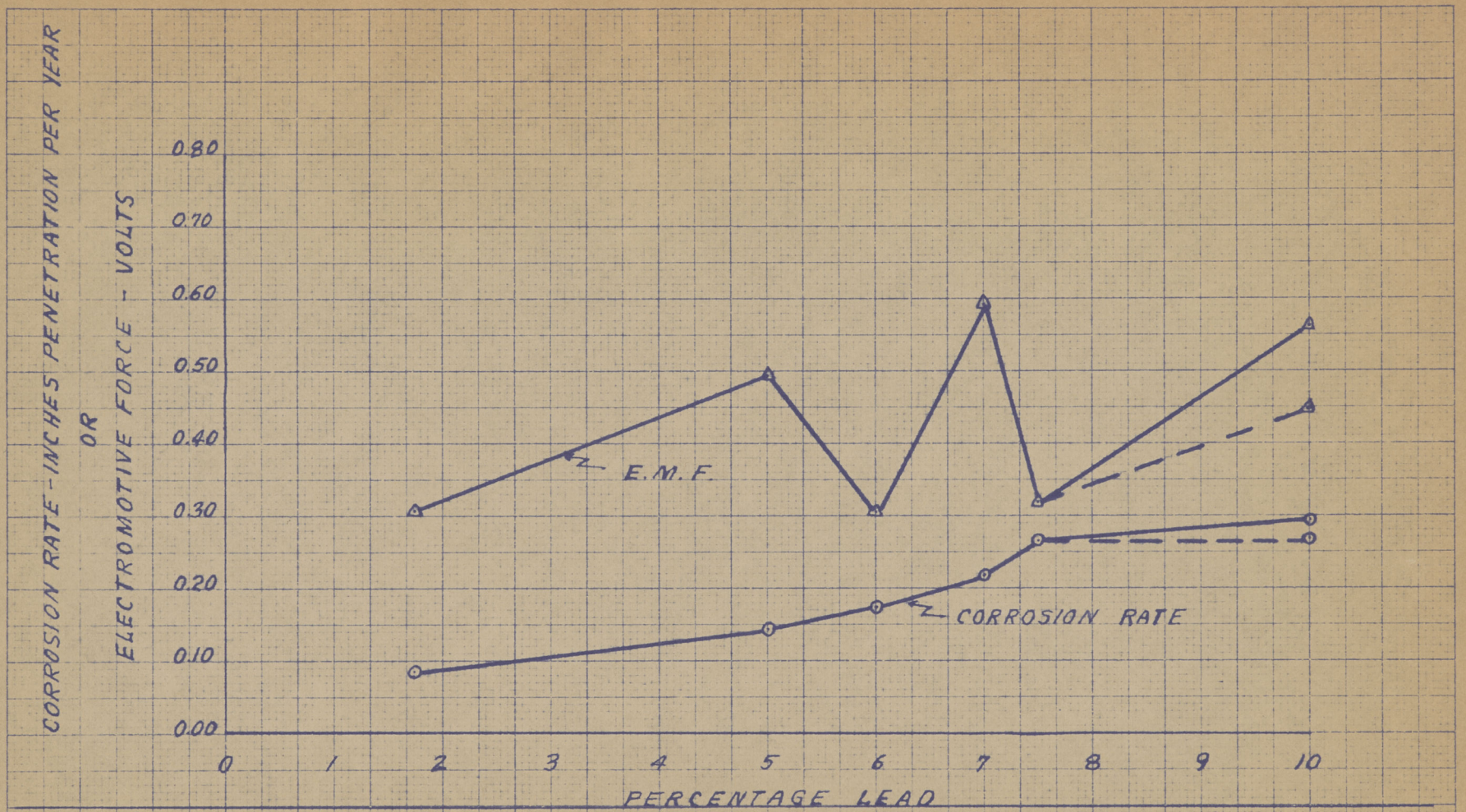

FIGURE 4

ALLOY COMPOSITION VS E.M.F AND CORROSION RATE

C SERIES - EFFECT OF LEAD CONTENT

LONG, R.B.

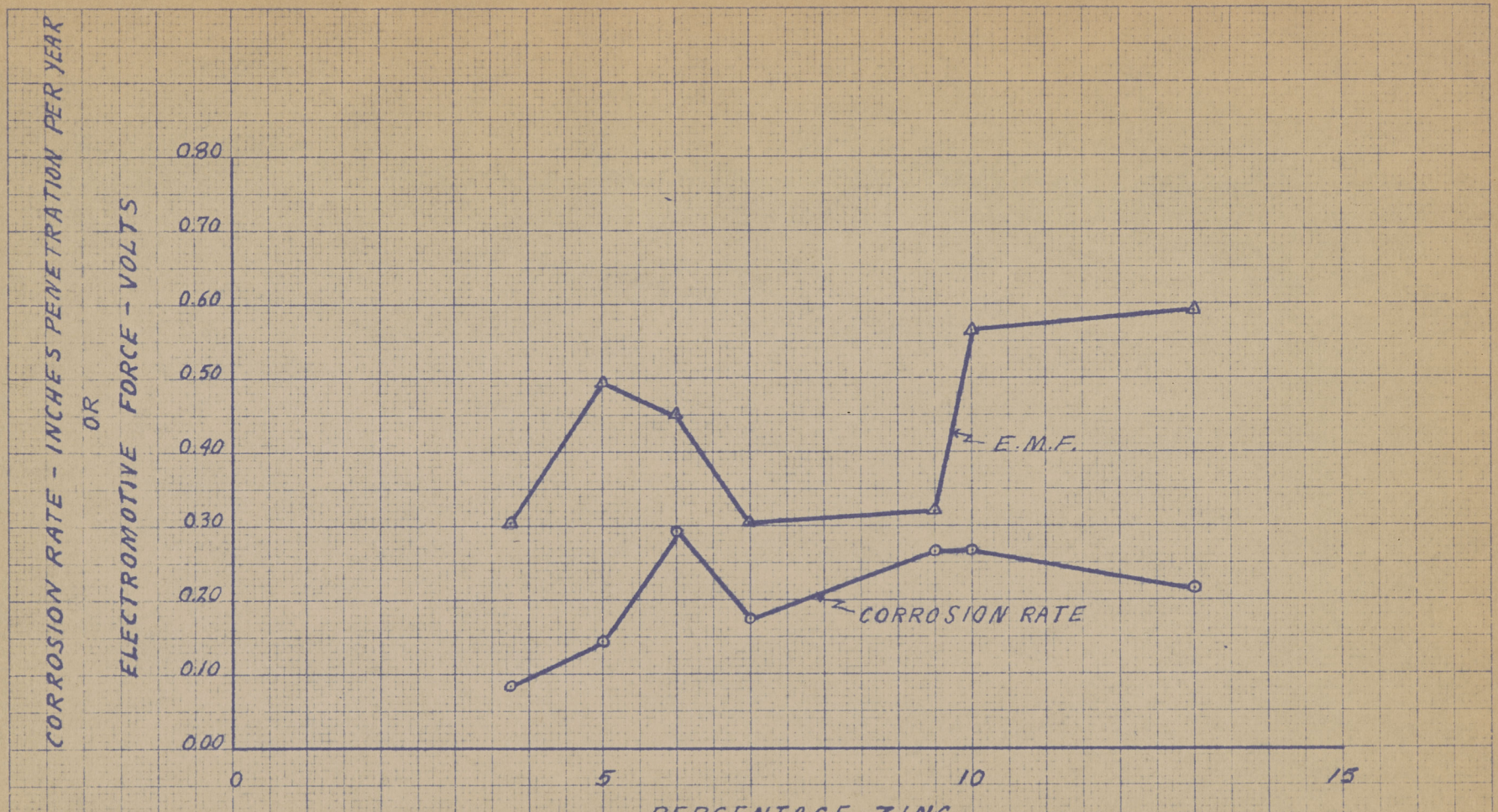

FIGURE 5

ALLOY COMPOSITION VS E.M.F. AND CORROSION RATE

C SERIES - EFFECT OF ZINC CONTENT

LONG, R.B

DISCUSSION AND CONCLUSIONS

The alloy composition vs. E.M.F. and corrosion rate curves shown in figure (1) are for the Z series. This series is a copper-zinc alloy with the percentage zinc varying from 1% to 31.5%. The corrosion rate curve shows a minimum at approximately 15% zinc and another at 31.5%. However, there is some doubt about the correctness of the corrosion rate value for the 31.5% specimen. The E.M.F.-composition curves have a minimum value at approximately 15% zinc only. The two curves for the one normal and the three normal solution are similar. The one for the three normal solution is just moved up the scale.

The curves in figure (2) are for the leaded brasses. The lead in this alloy series is present in the free metallic state, that is, it is not a true alloy, but a dispersion of the red brass and lead. The two curves, which show a steady increase in corrosion rate and E.M.F. with increase in lead content, correlate well.

Figure (3) shows the E.M.F. and corrosion rate vs. composition curves for the iron bearing red brasses. The percentage of iron present is comparatively small, varying from .16% to 1.9%. The curves show no change with the change in iron content. The two curves correlate well.

Figures (4) and (5) show the curves for the

commercial brasses and bronzes. Curves in figure (4) show how the corrosion rate and E.M.F. vary with the percentage lead in the alloy, while curves in figure (5) shows the variation with the change of zinc content. In figure (4) there are two specimens that have 10% lead. The difference in the values of the E.M.F. and corrosion rate for the two specimens is possibly due to the fact that the other metals present in the alloy are not present in the same amounts in the two specimens.

The results as a whole are considered favorable since for all the series of alloys there is some correlation. For the simple alloys the correlation is remarkably good. The reason for the correlation not being very good in the commercial series is believed to be due to the complexity of the alloy series. Also the analysis of this series is the "as desired" compositions as obtained from the purchase order, but it is believed to be essentially correct. However, it is possible that there are traces of other metals present, which could have a marked effect on the electrode potentials.

It is concluded from the results of this work that the irreversible electrode potentials determined in orthophosphoric acid solution as the electrolyte can be correlated with corrosion data determined by a four hour boil test in orthophosphoric acid, but that no absolute value for prediction of corrosion rate can so far be made on the basis of electrode potentials.

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APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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