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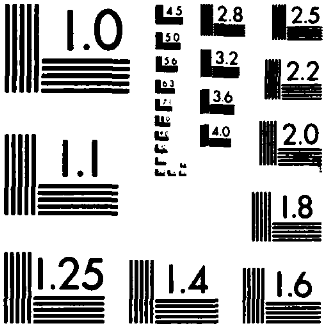

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April 1986

POLARIZATION RESISTANCE MEASUREMENTS OF COPPER NICKEL ALLOYS IN SEAWATER

C.M. Hanham - A.M. Quinn

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(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1. ORIGINATING ACTIVITY Defence Research Establishment Atlantic	2a. DOCUMENT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. DOCUMENT TITLE

Polarization Resistance Measurements of Copper Nickel Alloys in Seawater

4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Memorandum

5. AUTHOR(S) (Last name, first name, middle initial)

Hanham, C.M. and Quinn, A.M.

6. DOCUMENT DATE April 1986	7a. TOTAL NO. OF PAGES 35	7b. NO. OF REFS 32

8a. PROJECT OR GRANT NO.	9a. ORIGINATOR'S DOCUMENT NUMBER(S) DREA Technical Memoradum 86/211
8b. CONTRACT NO.	9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)

10. DISTRIBUTION STATEMENT

Unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING ACTIVITY DREA

13. ABSTRACT

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In a previous investigation, cast chromium modified 70/30 copper nickel exhibited erosion corrosion resistance, under severe conditions, equal to or better than that of the presently employed seawater piping system materials. In order to further understand this alloy's erosion corrosion behavior, its corrosion rate was measured in static seawater using the electrochemical polarization resistance technique. For comparison purposes, the corrosion rates of the present seawater piping system materials, wrought 90/10 copper nickel and cast leaded tin bronze (ASTM B61), and another potential replacement weldable alloy, cast niobium modified 70/30 copper nickel, were also measured.

The polarization resistance evaluation indicated that the cast chromium modified 70/30 copper nickel alloy had a similar level of resistance to corrosion in static seawater as the presently employed materials. Its corrosion resistance, however, did not consistently decrease with increasing temperature, as it did under severe erosive conditions.

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POLARIZATION RESISTANCE MEASUREMENTS OF COPPER NICKEL ALLOYS IN SEAWATER

C.M. Hanham A.M. Quinn

April 1986

Approved by B.F. Peters A/Director/Technology Division

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ABSTRACT

As a result of problems associated with the brazing of seawater piping systems on Canadian Forces surface ships, it has been proposed that future ships have welded systems. This proposal has necessitated the investigation of the properties and behavior of potential replacement weldable alloys for the nonweldable cast ASTM B61 leaded tin bronze presently used for fittings.

In a previous investigation, cast chromium modified 70/30 copper nickel exhibited erosion corrosion resistance, under severe conditions, equal to or better than that of the presently employed seawater piping system materials. In order to further understand this alloy's erosion corrosion behavior, its corrosion rate was measured in static seawater using the electrochemical polarization resistance technique. For comparison purposes, the corrosion rates of the present seawater piping system materials, wrought 90/10 copper nickel and cast leaded tin bronze (ASTM B61), and another potential replacement weldable alloy, cast niobium modified 70/30 copper nickel, were also measured.

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SOMMAIRE

A cause du problème de brasage des conduites sous-marines à bord des navires de surface des Forces canadiennes, on propose d'adopter des systèmes soudés sur les futurs bâtiments. Cette proposition a nécessité une étude des propriétés et du comportement d'alliages soudables qui pourraient remplacer la fonte non soudable de bronze au plomb et à l'étain ASTM B61 présentement utilisée pour les raccords.

Dans une étude antérieure, on a relevé que la fonte de cuivre et nickel 70/30 additionnée de chrome résistait aussi bien ou mieux à la corrosion par érosion, dans des conditions extrêmes, que les matériaux actuellement utilisés dans les conduites sous-marines. Pour mieux comprendre ce comportement de l'alliage, on a mesuré sa vitesse de corrosion dans de l'eau de mer stagnante au moyen de la technique de la résistance à la polarisation électrochimique. Pour fins de comparaison, on a aussi mesuré les vitesses de corrosion des matériaux des conduites sous-marines existantes, l'alliage cuivre-nickel 90/10 forgé et la fonte d'étain et de bronze au plomb (ASTM B61), et d'un autre alliage soudable potentiel de remplacement, la fonte de cuivre et de nickel 70/30 additionnée de niobium.

L'évaluation de la résistance à la polarisation a indiqué que la fonte de cuivre et nickel 70/30 additionnée de chrome résiste autant à la corrosion dans l'eau de mer stagnante que les matériaux utilisés actuellement. Sa résistance à la corrosion n'a toutefois pas diminué systématiquement en fonction de la température, comme ce fut le cas dans des conditions extrêmes d'érosion.

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NOTATION

b_a	anodic Tafel constant
b_c	cathodic Tafel constant
b'_{1a}	forward oxidation reaction mechanism constant
b'_{1c}	reverse oxidation reaction mechanism constant
b'_{2a}	forward reduction reaction mechanism constant
b'_{2c}	reverse reduction reaction mechanism constant
df	degrees of freedom
EW	equivalent weight
i_{corr}	corrosion current density
i_{o1}	reversible oxidation reaction exchange current density
i_{o2}	reversible reduction reaction exchange current density
i_1	reversible oxidation reaction current density
i_{1a}	forward oxidation reaction current density
i_{1c}	reverse oxidation reaction current density
i_2	reversible reduction reaction current density
i_{2a}	forward reduction reaction current density
i_{2c}	reverse reduction reaction current density
n	number of repeated measurements in sample
R_p	polarization resistance
s_1	standard deviation of sample 1

NOTATION (continued)

s_2	standard deviation of sample 2
t	statistical t value
Δx	difference between two sample means
ϕ	potential
ϕ_{corr}	corrosion potential
ϕ_{o1}	characteristic oxidation reaction reversible potential
ϕ_{o2}	characteristic reduction reaction reversible potential
ρ	density

1. INTRODUCTION

The seawater piping system on a warship is designed to quickly supply large quantities of seawater for fighting fires in addition to its normal function of delivering seawater to systems such as condensers and heat exchangers. The choice of materials for a warship's seawater system is important because both maximum operational reliability and minimum maintenance must be guaranteed.

Materials for seawater piping systems are chosen, based on:

1. their ability to resist corrosion over the range of flow speeds that may be encountered,
2. their galvanic compatibility with metals used for associated components such as valve bodies and pump casings,
3. their resistance to fouling by marine organisms,
4. their ease of fabrication by conventional practices, including casting, bending, and joining, and
5. their cost.

At the time of the design of the DDH 280 class ships, leaded tin bronze was chosen as the fitting material for the seawater piping systems because of its defect-free castability, corrosion resistance, availability on the Canadian market and its supposed ease of brazing. However, problems associated with the brazing technique did appear. Joint leakage and liquid metal embrittlement, as described elsewhere[1,2], led to the proposal by the Director, Maritime Engineering Support that future seawater systems be of an all welded construction. An all welded system is potentially easier to fabricate and repair and is capable of handling greater loads than a silver brazed system.

Two weldable alloys were investigated as potential replacement materials for the cast fittings that would still be required in an all welded system: standard cast niobium modified 70/30 copper nickel (C96400) and non-standard cast chromium modified 70/30 copper nickel (IN768). A thorough study of the alloys' foundry characteristics, weldability and mechanical properties was completed by Energy, Mines and Resources Canada[3-6] and an investigation of their erosion corrosion resistance was conducted at the Defence Research Establishment Atlantic (DREA)[1,2]. The quality of the castings and gas metal arc welds of the two alloys was found to be satisfactory and the erosion corrosion resistance of the chromium modified alloy was determined to be greater than that of the niobium modified alloy and equal to or better than that of the presently employed seawater piping system materials: cast ASTM B61 leaded tin bronze and wrought 90/10 copper nickel.

This report describes the evaluation of the corrosion resistance of these same alloys in static seawater by an electrochemical technique called polarization resistance. In addition to measuring the corrosion rates of the metals at various temperatures in static seawater, this study was initiated in order to provide a further understanding of the alloys' erosion corrosion behavior.

2. POLARIZATION RESISTANCE MEASUREMENTS

Polarization resistance measurements, for determining corrosion rates, make use of the concept of mixed potential theory, which was first proposed by Wagner and Traud[7]. In the mixed potential theory, it is assumed that metallic corrosion is the result of two or more independent electrochemical reactions. In the most elementary case the metal, M, is oxidized,

$$M \longrightarrow M^{+} + e^{-} \qquad (1)$$

and another species, X^+, either contained in the metal or it's surrounding environment, is reduced.

$$X^+ + e^- \longrightarrow X \qquad (2)$$

A metal acquires a corrosion potential (ϕ_{corr}) when it is corroding in contact with a solution containing oxidizing agents. At this potential, the rate of oxidation of the metal is equal to the rate of reduction of the species. The current, representing the corrosion rate of the metal, is exactly balanced by an equal current, representing the reduction rate of the oxidizing agent. The net current (I, the current observed by an external device) is zero. However, if the metal is polarized either anodic or cathodic to the corrosion potential, a current flow can be measured.

Wagner and Traud's mixed potential theory[7] provides a means for relating current density and potential. This relationship holds for both oxidation and reduction and is represented as

$$i_1 = i_{1a} + i_{1c} = i_{o1}\left[\exp\left(\frac{\phi - \phi_{o1}}{b'_{1a}}\right) - \exp\left(-\frac{\phi - \phi_{o1}}{b'_{1c}}\right)\right] \qquad (3)$$

for oxidation, and

$$i_2 = i_{2a} + i_{2c} = i_{o2}\left[\exp\left(\frac{\phi - \phi_{o2}}{b'_{2a}}\right) - \exp\left(-\frac{\phi - \phi_{o2}}{b'_{2c}}\right)\right] \qquad (4)$$

for reduction, where the constants b' are dependent on reaction mechanisms; the partial current densities i_{1a} and i_{1c} are related to the forward and reverse reaction rates of equation (1); i_{2a} and i_{2c} are related to the forward and reverse reaction rates of equation (2); i_o is the exchange current density of each partial reaction; and ϕ_o is the characteristic reversible potential. Hence, the externally observed current density at any potential is described as

$$i = i_{1a} + i_{1c} + i_{2a} + i_{2c} \qquad (5)$$

or

$$i = i_{o1}\left[\exp\left(\frac{\phi - \phi_{o1}}{b'_{1a}}\right) - \exp\left(-\frac{\phi - \phi_{o1}}{b'_{1c}}\right)\right] + i_{o2}\left[\exp\left(\frac{\phi - \phi_{o2}}{b'_{2a}}\right) - \exp\left(-\frac{\phi - \phi_{o2}}{b'_{2c}}\right)\right] \qquad (6)$$

The corrosion potential that a metal establishes in a corrosive environment is a mixed potential which must lie between the reversible potentials of the partial electrochemical reactions. One can therefore eliminate the insignificant current densities associated with the metal ion reduction reaction (i_{1c}) and the reducible species oxidation reaction (i_{2a}). Therefore, equation (6) reduces to

$$i = i_{o1}\exp\left(\frac{\phi - \phi_{o1}}{b'_{1a}}\right) - i_{o2}\exp\left(-\frac{\phi - \phi_{o2}}{b'_{2c}}\right) \tag{7}$$

As indicated above, the net current observed by an external device at the corrosion potential is zero. Therefore, at $\phi = \phi_{corr}$,

$$i_{1a} = \left|i_{2c}\right| = i_{corr} \tag{8}$$

where i_{corr} is defined as the corrosion current density. Then,

$$i_{corr} = i_{o1}\exp\left(\frac{\phi_{corr} - \phi_{o1}}{b'_{1a}}\right) = i_{o2}\exp\left(-\frac{\phi_{corr} - \phi_{o2}}{b'_{2c}}\right) \tag{9}$$

Combining equations (7), (8), and (9) gives

$$i = i_{corr}\left[\exp\left(\frac{\phi - \phi_{corr}}{b'_{1a}}\right) - \exp\left(-\frac{\phi - \phi_{corr}}{b'_{2c}}\right)\right] \tag{10}$$

As first pointed out by Wagner and Traud[7] and later discussed by Oldham and Mansfeld[8], the form of this equation suggests another method for determining corrosion current densities. It was shown[8,9] that differentiation of equation (7) with respect to potential gives

$$\frac{\partial i}{\partial \phi} = \frac{i_{o1}}{b'_{1a}}\exp\left(\frac{\phi - \phi_{o1}}{b'_{1a}}\right) + \frac{i_{o2}}{b'_{2c}}\exp\left(-\frac{\phi - \phi_{o2}}{b'_{2c}}\right) \tag{11}$$

Evaluating this at the corrosion potential and using equation (9) gives

$$\left(\frac{\partial i}{\partial \phi}\right)_{\phi_{corr}} = i_{corr}\left(\frac{1}{b'_{1a}} + \frac{1}{b'_{2c}}\right) \tag{12}$$

When equation (10) is graphically presented in a plot of ϕ versus log i, the resulting curve will display two straight line portions. By convention, the slopes of these lines are called the Tafel constants, b_a and b_c. These values are related to the constants, b', by

$$b = (\ln 10)\, b' \tag{13}$$

Then, equation (12) becomes

$$\left(\frac{\partial i}{\partial \phi}\right)_{\phi_{corr}} = i_{corr}\left[\frac{\ln 10\,(b_a + b_c)}{b_a\, b_c}\right] \tag{14}$$

The inverse of the gradient of a current density versus potential curve at the corrosion potential has been called the polarization resistance by Bonhoeffer[10] and Stern[11,12]. It is defined as

$$\left(\frac{\partial \phi}{\partial i}\right)_{\phi_{corr}} = R_p \qquad (15)$$

and is inversely proportional to the corrosion current density.

There are two different approaches to the determination of the polarization resistance, R_p, from polarization resistance data. Some experimentalists[13] follow Stern and Geary's original work[14] and propose the determination of R_p from linearization of polarization curves in the vicinity of the corrosion potential. Others[8,9,15-17] use the tangent of a polarization curve at the corrosion potential to determine a more exact R_p[18].

Stern and Geary[14] developed the relationship

$$i_{corr} = \left[\frac{b_a b_c}{\ln 10 (b_a + b_c)}\right] \cdot \frac{1}{R_p} \qquad (16)$$

which is a combination of equations (14) and (15), on the basis of two assumptions. They assumed that for small values of $\Delta\phi$, terms above and including $\Delta\phi^2$ in the series expansion for exp $\Delta\phi$ could be ignored. The supposed linearity of the potential/current density relationship close to ϕ_{corr} stems directly from this assumption. Stern and Geary[14] emphasized that the linear relationship exists only because the difference between two logarithmic functions of current density approximates to a linear function when they are of the same order of magnitude.

Oldham and Mansfeld[8] proposed a much more rigorous definition of linearity and derived a mathematically exact expression for the curvature of a polarization curve at the corrosion potential. They demonstrated that there is no theoretical reason for polarization curves, an example of which is shown in Figure 1, to be linear at the corrosion potential and that the curve must display curvature in the vicinity of the corrosion potential for the Stern-Geary relationship to be valid. It can be shown that the second derivative of the Stern-Geary relationship is an equation which demonstrates that there is only one point (a point of inflection, corresponding to a minimal slope) at which the polarization curve has no curvature. In other words, the i versus ϕ plot can only be linear at the corrosion potential when the Tafel slopes are fortuitously equal. Mansfeld has argued[15,17] that the polarization resistance, R_p, and the corrosion current density, i_{corr}, can only be determined from the gradient of the polarization curve at the corrosion potential.

There has been some disagreement[13,19-20] with Oldham and Mansfeld's claim that "there is no theoretical reason for polarization curves to be linear at the corrosion potential". Jones[19] states that the polarization curve is linear because the difference between two exponential terms is approximately linear (and appears linear experimentally) as the difference approaches zero. He supports the expectation to find linearity of polarization curves near the corrosion potential. It all hinges on the mathematically correct definition of linearity. Oldham and Mansfeld's intention was to demonstrate that the gradient of the curve at the corrosion potential has to be used to determine the corrosion current density. This is especially true for polarization curves which are nonlinear (or far from linear) at the corrosion potential.

The name, polarization resistance, has been given to a determinable parameter as well as an experimental technique of measuring corrosion data. The characteristic which differentiates a polarization resistance experiment from a potentiodynamic polarization experiment or a Tafel experiment is the potential range over which the data are obtained, that is, the amount that the metal is polarized away from its corrosion potential.

A metal may be anodically polarized as much as 1.2 V from its corrosion potential during a potentiodynamic polarization experiment. The data from such experiments are most useful for determining a metal's ability to form and maintain a stable, protective film. A portion of the data may also be used to determine the metal's polarization resistance, but, as indicated below, this is not considered to be accurate.

During a Tafel experiment, a metal is polarized 250 mV from its corrosion potential, first in the cathodic direction and then in the anodic direction. The data from each branch of the experiment can be used to determine each of the Tafel slopes and a portion of the data can be further used to determine the polarization resistance. Again, this approach is not considered to be accurate.

A polarization resistance measurement begins 25 mV cathodic to a metal's corrosion potential and ends 25 mV anodic to its corrosion potential, covering only a 50 mV range. Traditionally, it was felt that only a value of polarization resistance could be determined from this data, necessitating the separate determination of the Tafel slopes in order to determine the corrosion current density. It has more recently been shown[15,16], however, that the Tafel constants, polarization resistance and the corrosion current density can be determined simultaneously from one polarization resistance measurement.

Jankowski et al.[21] describe a number of limitations of the polarization resistance method for determining corrosion rates, as it was first introduced by Wagner and Traud[7] and developed by Stern and Geary[14]. The most serious among them are the necessity for knowledge of the Tafel slopes, the narrow linear range associated with with large differences between the values of the Tafel slopes and the error associated with the corrosion potential's closeness to one of the equilibrium potentials determining the corrosion process.

There are advantages of determining corrosion current densities from polarization resistance measurements. For example, polarization is conducted linearly with time, typically at 0.6 V/hour. A polarization resistance measurement over a 50 mV range will therefore take 5 minutes while a Tafel experiment over a 500 mV range will take 50 minutes. The shorter time factor alone is an advantage. Also, when a metal is anodically polarized, its surface will dissolve, its roughness will increase and corrosion product films will form. In addition, during cathodic polarization, surface films formed at the corrosion potential might be reduced. The degree to which these reactions will occur depends on the amount a metal is polarized away from its corrosion potential. Clearly, surface changes will be minimal during polarization resistance measurements and the measurement process will not interfere with the quantity to be measured.

It has been emphasized[22] that in using equation (14) for determining corrosion current densities, the Tafel slopes have to be known at the corrosion potential. The simultaneous determination of Tafel slopes and the corrosion current density from polarization resistance measurements accomplishes this.

Corrosion current densities can be determined by graphical analysis of polarization resistance curves[23], and by computer analysis of current density versus potential curves using both linear[15,16] and nonlinear[24] least squares fitting techniques. The computerized approach using a linear least squares fitting technique[15,16] consists of truncating a Taylor series expansion of

$$i = \frac{b_a b_c}{\ln 10 \, R_p (b_a + b_c)} \left[\exp \frac{\ln 10 \, (\phi - \phi_{corr})}{b_a} - \exp \frac{-\ln 10 \, (\phi - \phi_{corr})}{b_c} \right] \qquad (17)$$

which is a combination of equations (10), (14) and (15), and providing an initial estimate of one of the unknown parameters. This treatment results in an expression which is linear with respect to the unknown parameters and which can be solved by a linear least squares method. Values for the parameters are then incremented and the linear least squares fit is repeated. This procedure is iterated until changes in the parameters are acceptably small.

Gerchakov et. al.[24] developed a nonlinear least squares fitting technique which, unlike Mansfeld's technique[15], accepts initial estimates for all of the parameters and applies the Gauss-Newton method to generate a new set of parameter estimates. This procedure is repeated until a calculated nonlinear residual error does not change by more than a preset value. Successive iterations on a computer lead to the desired values of Tafel constants, polarization resistance and the corrosion current density. This method requires sophisticated computer analysis.

It has been shown by metal sample weight loss measurements and by solution analysis after electrochemical polarization resistance measurements[16] that the method of determining corrosion current densities from polarization resistance measurements without prior knowledge of Tafel slopes is accurate. The method has great potential for comparing the corrosion rates of a variety of materials in a controlled environment or for studying the effect of variable environmental conditions on the corrosion rate of one material. Polarization resistance measurements are suitable for the laboratory because of their high sensitivity, accuracy and speed, but are also suitable for in-situ monitoring because they can be used remotely and continuously without disturbing the specimen.

3. EXPERIMENTAL PROCEDURE

The descriptions of the seven different materials evaluated in this study are given in Table I, and the chemical compositions of the parent metals and the GMAW electrodes, from which samples were made, are found in Tables II and III respectively. The samples required for this study were sectioned and machined to a length of 2 cm and a diameter of 1.5 cm from cast and welded test blocks produced by CANMET/PMRL[3-6]. The chromium modified Monel 451 weld sample, the niobium modified Cuprotrode 521 weld sample, and the Monel 67 weld sample were taken from the centres of welds made in parent metal test blocks as listed in Table I. One end of each sample was drilled and tapped for 3-48 N.C. threads to accommodate an electrode holder. Within one hour prior to immersion in the electrolyte, samples were polished with 400 and 600 grit silicon carbide paper, washed with tap water, degreased in boiling toluene for five minutes, and then rinsed with distilled water.

The electrolyte used for all of the experiments came from a single batch of natural Halifax harbour seawater. The seawater was filtered to 3 microns and its measured pH ranged between 7.5 and 7.9. The corrosion cell containing the electrolyte was maintained at 1, 15, and 25°C in a Haake Model F3-K refrigerated bath.

A deaerated condition was obtained by purging the electrolyte with nitrogen for one hour before and one hour after immersing the sample. The nitrogen purge was terminated for one hour prior to and also during the measurement. A Model 340 Dissolved Oxygen Analyzer (Weston and Stack) with a Model 60 Probe and Flow Cell (Rexnord) was used to monitor the depletion of the dissolved oxygen from the electrolyte throughout the experiment. The dissolved oxygen concentration did not increase substantially when the sample was immersed in the electrolyte after the first hour of the purge.

The polarization resistance experiments were conducted in an EG&G Princeton Applied Research (PAR) Model K47 Corrosion Cell (Figure 2) which accommodates two high-density graphite counter electrodes, a working electrode (sample), a reference electrode bridge tube (Luggin probe) with a fitted saturated calomel (mercury-mercurous chloride) reference electrode, and a gas inlet/outlet purge tube. The experiments were monitored and the polarization resistance data were collected by a microprocessor-controlled EG&G PAR Model 350 Corrosion Measurement System[25].

The experimental procedure used for the polarization resistance experiments was a modification of the ASTM G-5 standard[26]. After measuring the exposed surface area of the sample in order to convert the current measurements to current density measurements, the sample was immersed in the electrolyte and the reference electrode bridge tube tip was placed within 5 mm of the sample surface. After an additional hour of gas purging, the gas purge was terminated and the sample was allowed to come to equilibrium for one hour.

The potentiodynamic scan was started at 25 mV cathodic to the sample's corrosion potential, which was measured at the end of its one hour equilibrium period, and continued at a scan rate of 0.167 mV/sec. The current required to maintain the sample at its controlled potentials was measured every 0.5 mV throughout the linear scan. The 50 mV scan was completed at 25 mV anodic to the sample's equilibrium corrosion potential.

At the completion of each experiment the data were stored on digital tape by the EG&G PAR Model 355 Tape Storage Module and then transferred through the EG&G PAR Model 350 Corrosion Measurement System to the DREA DEC-20 computer through the use of a Fortran program, <STAAL>C11A20[27]. The polarization resistance data were analyzed by the method of nonlinear least squares using a Pascal computer program, CORROS[27].

CORROS is a computer program which finds the corrosion potential, the anodic and cathodic Tafel constants, the polarization resistance and the corrosion current density from polarization resistance data obtained from the mixed potential region around the corrosion potential. The program's basic routine is a nonlinear least squares fit of the data. The output includes the corrosion parameters, their standard deviations, and the relative root mean squared error of the fitted data.

The corrosion current density was determined, along with the anodic and cathodic Tafel slopes, the corrosion potential, the polarization resistance, and the error associated with each parameter. Three seperate experiments were conducted on each sample under each of the three different temperature conditions. Examples of the polarization resistance data obtained and the computer fits to the data are given in Figure 3. One of three measurements at each of the three temperatures is presented for the chromium modified 70/30 copper nickel parent metal sample.

The corrosion current density values were converted to corrosion rates according to Faraday's Law[28].

$$\text{corrosion rate } (\mu\text{m/year}) = \frac{3.27\ i_{corr}\ (\mu\text{A/cm}^2) \cdot \text{EW (g/equiv)}}{\rho\ (\text{g/cm}^3)} \qquad (18)$$

Representative equivalent weights (EW) of the samples were calculated from their chemical compositions (Tables II and III). The average corrosion rates were statistically analyzed using the t-test[29]. This test is used to determine if there is a significant difference between the sample means of two populations. The t for each pair of populations was calculated using:

$$t = \Delta x \left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2} \right)^{-1/2} \qquad (19)$$

where Δx is the difference between the sample means, and s_1 and s_2 are the sample standard deviations.

The number of degrees of freedom of the t distribution was also calculated:

$$\frac{1}{df} = \left(\frac{s_1^2}{s_1^2 + s_2^2}\right)^2 \frac{1}{n_1 - 1} + \left(\frac{s_2^2}{s_1^2 + s_2^2}\right)^2 \frac{1}{n_2 - 1} \qquad (20)$$

The calculated t values were compared with tabulated t distribution values[30] at various confidence intervals. When a calculated t value was greater than a tabulated t value, it meant that there was a significant difference between the sample means of the two populations being tested.

4. RESULTS

The corrosion current densities, along with their associated root mean square errors from the curve fitting technique, determined from each of three repeated polarization resistance measurements for each material at three temperatures, are tabulated in Table IV. The average corrosion rates, calculated from the corrosion current density measurements using Faraday's Law, are tabulated in Table V and plotted as a function of temperature in Figures 4 and 5. The standard deviations in the corrosion rates are listed in Table V but, for reasons of graphical clarity, are not shown in Figures 4 and 5.

Each population of data, which consists of three repeated polarization measurements on one of seven samples at one of three temperatures (a total of twenty-one populations), was statistically compared with every other population of data, using the t-test at four confidence levels: 99, 95, 90, and 80%. The results of these statistical comparisons are presented in Figures 6, 7, 8 and 9. Pairs of populations which have a significant difference between their mean corrosion rates are indicated by an x. The increasing occurrence of a significant difference between the mean corrosion rates with decreasing confidence level is seen from Figure 6 to Figure 9. At the 99% confidence level, there is little significant difference between any of the samples at any temperature, while at the 80% confidence level, a large number of the samples have significantly different corrosion rates.

Although Figures 4 and 5 visually indicate that the average corrosion rates of all of the samples increase with increasing temperature, this is not statistically the case at a high level of confidence. If the standard deviations in the average corrosion rates were lower and there had been a greater number of repeated polarization resistance measurements , this would be the case. There is also statistically little significant difference between the corrosion rates of the different samples at a high level of confidence. All of the samples corrode essentially at the same rate in static, deaerated seawater over a temperature range of 1°C to 25°C.

At a lower level of confidence, 80%, all of the samples display increasing corrosion rates with increasing temperature. There is little difference between the magnitudes of any of the samples' corrosion rates at 1°C. At 15°C, however, the niobium modified Cuprotrode 521 weld sample's corrosion rate was approximately 50% higher than all of the other samples. At 25°C, the ASTM B61 leaded tin bronze sample and the 90/10 copper nickel sample have lower corrosion rates than all of the other samples. The niobium modified Cuprotrode 521 weld sample again has the highest corrosion rate overall.

5. DISCUSSION

The average corrosion current densities determined from the polarization resistance measurements range from as low as 15.7 to as high as 279.2 nanoamperes per square centimeter as shown in Table V. These extremely low measurements correspond to extremely low corrosion rates ranging between 0.3 and 5.4 microns per year.

The statistical analysis of the data shows that there is limited confidence in there being any significant difference between any of the samples' corrosion rates in deaerated, static seawater. The expected relationship between corrosion rates and temperature is not shown for each sample until the 80% confidence level. This fact, along with the observations of the significant standard deviations in the determined corrosion current densities and the lack of reproducibility amongst the repeated polarization resistance measurements, suggests that the low magnitude measurements themselves may be responsible for the low confidence levels at which significant differences are shown.

Callow et al.[31] reviewed various fundamental and experimental factors which contribute to inaccuracy in the polarization resistance technique of determining corrosion rates. The factors reviewed include errors inherent in the theoretical basis of the technique, deviations from linearity of polarization data in the vicinity of the corrosion potential, polarization data obtained close to reversible potentials, errors resulting from test solution resistance, failure to achieve steady state during polarization, time dependent corrosion potentials and Tafel slopes, electrode perturbation, and probe element differences resulting from localized corrosion.

They suggest that the factors which have received the most attention in the literature, namely deviations from linearity of polarization data close to the corrosion potential and uncertainty in the determination of Tafel constants, are unlikely to contribute errors in calculated corrosion rates greater than a factor of times two. They indicate that this would be acceptable, particularly when monitoring corrosion rates in industrial on-stream situations, because the alternative techniques for measuring corrosion rates also have problems of reproducibility and reliability.

Although many of their reviewed errors are directly relevant to industrial on-stream corrosion monitoring, some of the factors, notably errors inherent in the theoretical basis of the technique, failure to achieve steady state during polarization and time dependent corrosion potentials and Tafel slopes, would be considered relevent to our polarization resistance measurements. All of the average corrosion current densities determined are within a factor of two of the individual measurements made.

Some trends are displayed with decreasing confidence level. The niobium and chromium modified parent metal samples have essentially the same corrosion rate at both 1°C and 15°C, while the chromium modified parent metal sample has a higher corrosion rate at 25°C. At 1°C, the niobium and chromium modified parent metal samples have the lowest corrosion rates, and at 25°C, the 90/10 and B61 samples have the lowest corrosion rates. The parent metal samples do not have consistently lower rates than the weld metal samples at all temperatures.

Erosion corrosion studies[1,2] on the same alloys showed that the chromium modified parent metal was more resistant to erosion corrosion than the niobium modified parent metal, the welded chromium modified metal was more resistant than the welded niobium modified metal, welds produced with Monel 67 GMAW electrodes were more resistant than welds produced with niobium modified Cuprotrode 521 GMAW electrodes, and seawater temperature had a significant effect on the susceptibility of all the alloys to erosion corrosion.

The erosion corrosion evaluations were conducted on samples exposed to direct impingement of seawater, entrained with 3.4% air, at 12.2 m/sec while the polarization resistance measurements were conducted on samples exposed to static, deoxygenated seawater. The significant difference between these two sets of exposure conditions is very important.

The lack of qualitative consistency between the jet impingement results and the polarization resistance results supports our previous suggestion[1,2] that the enhanced erosion corrosion resistance of the 70/30 copper nickel alloys can be attributed to their high hardness and strength. If their electrochemical superiority in their ability to form protective films had been predominantly responsible for their superior erosion corrosion resistance, it would have been apparent as a result of the polarization measurements. In other words, an alloys's ability to resist corrosion by forming a protective film is dependent on the exposure conditions. Any difference between the abilities of the different alloys to form protective films should have been easily observable under the static conditions of the polarization resistance measurements. Since all of the alloys behaved essentially equally under static conditions, the enhanced erosion corrosion resistance of the 70/30 copper nickel alloys must have been due to their high hardness and strength, factors independent from the conditions of the test.

Polarization measurements conducted on the same alloys after exposure for a longer period of time may show a significant difference between these alloys' behavior due to their relative abilities to form protective films. Exposure to less severe erosion corrosion may also show that the electrochemical behavior of an alloy has a role in its resistance to erosion corrosion.

Another study[32] of the effects of oxygen concentration on the corrosion of 70/30 and 90/10 copper nickel alloys showed that for oxygen concentrations less than 6.6 ppm, the corrosion rate of 70/30 copper nickel is considerably less than that of 90/10. At higher oxygen concentrations, however, the corrosion rate of 70/30 copper nickel increases to a value that is comparable to that of 90/10 copper nickel. The results of our investigation did not, however, show a significant difference between the 90/10 sample and 70/30 alloy samples at low oxygen concentrations.

Copper based alloys are chosen for marine applications because of their good corrosion resistance. The measurements conducted in this study indicate that all of the alloys would be equally suitable for marine application. The data demonstrate that there is very little substantial difference in behavior in static deoxygenated seawater between the alloys presently used in the DDH 280 class firemain system, namely wrought 90/10 copper nickel and cast ASTM B61 leaded tin bronze, and possible replacement cast alloys such as niobium and chromium modified 70/30 copper nickel. Although these findings are inconsistent with previous comparisons of the alloys' erosion corrosion resistance in severely turbulent seawater, the acceptability of the possible replacement alloys in this environment, substantiates their potential usefulness.

6. CONCLUSIONS

Polarization resistance measurements have been conducted to evaluate the corrosion rate of seven copper based alloy samples in static, deoxygenated seawater. The principle findings are:

(a) the niobium and chromium modified parent metal samples have essentially the same corrosion rate at both 1°C and 15°C, but the chromium modified parent metal sample has a higher corrosion rate at 25°C,

(b) the niobium and chromium modified parent metal samples have the lowest corrosion rates at 1°C,

(c) the 90/10 and B61 samples have the lowest corrosion rates at 25°C, and

(d) the parent metal samples do not have consistently lower corrosion rates than the weld metal samples at all temperatures.

Comparison with previous results from erosion corrosion experiments in turbulent, oxygen-rich seawater indicate that the 70/30 copper nickel alloys' superior strength and hardness, and not their ability to electrochemically form protective oxide films, were responsible for their erosion corrosion resistance under the severe conditions to which they were exposed.

TABLE I

SAMPLE DESCRIPTIONS

Sample Name	Parent Metal	GMAW Electrode
Niobium Modified 70/30 Copper Nickel Parent	UNS C96400	-
Chromium Modified 70/30 Copper Nickel Parent	IN 768	-
Monel 67 Weld	UNS C96400	Monel 67
Niobium Modified Cuprotrode 521 Weld	UNS C96400	Cuprotrode 521
Chromium Modified Monel 451 Weld	IN 768	Monel 451
ASTM B61 Leaded Tin Bronze	UNS C92200	-
90/10 Copper Nickel	UNS C70600	-

TABLE II

CHEMICAL COMPOSITIONS OF THE PARENT METALS

	Cu	Ni	Fe	Mn	Si	Nb	Cr	Zr	S	Pb	Sn	C	Ti	Zn	P
UNS C96400 CAST Nb MODIFIED 70/30 COPPER NICKEL	65-69	28-32	.25-1.5	1.5 max	.5 max	.5-1.5	-	-	-	.03 max	-	.15 max	-	-	-
IN 768 CAST Cr MODIFIED 70/30 COPPER NICKEL	bal	28-33	1.0 max	.4-1.0	.3-.6	-	1.4-2.0	.05-.15	.02 max	.01 max	-	.07 max	.1 max	-	.02 max
UNS C92200 ASTM B61 LEADED TIN BRONZE	86-90	1.0 max	0.25 max	-	.005 max	-	-	-	.05 max	1.0-2.0	5.5-6.5	-	-	3.0-5.0	.05 max
UNS C70600 WROUGHT 90/10 COPPER NICKEL	86.5 min	9.0-11.0	1.0-1.8	1.0 max	-	-	-	-	-	.05 max	-	-	-	1.0 max	-

TABLE III

CHEMICAL COMPOSITIONS OF THE GMAW ELECTRODES

	Cu	Ni	Fe	Mn	Si	Nb	Cr	Zr	S	Pb	C	Ti	Zn	P
MONEL 67 *	68.08	30.11	0.57	0.82	0.05	-	-	-	0.002	-	0.03	0.34	-	-
CUPROTRODE 521 **	66.93	30.72	0.51	0.79	0.40	1.02	-	-	0.005	0.005	0.43	-	0.009	-
MONEL 451 *	66.12	30.20	0.15	2.00	0.48	-	2.17	0.036	0.005	-	<0.02	0.09	-	<.005

* Manufacturer's Certified Analysis
** CANMET Wet Chemical Analysis

TABLE IV

CORROSION CURRENT DENSITIES AND THEIR ERRORS FROM EACH OF THREE REPEATED POLARIZATION RESISTANCE MEASUREMENTS AT THREE DIFFERENT TEMPERATURES

Sample	Corrosion Current Density (nanoamps/cm^2)		
	1°C	15°C	25°C
Nb modified 70/30	8.39 ± 1.50	111.12 ± 11.57	154.10 ± 12.26
Copper Nickel Parent	30.99 ± 3.32	126.24 ± 9.43	210.05 ± 13.84
	9.52 ± 1.94	61.70 ± 5.98	236.46 ± 14.30
Cr modified 70/30	17.41 ± 2.31	89.29 ± 7.12	310.13 ± 17.85
Copper Nickel Parent	13.03 ± 2.42	67.98 ± 6.21	282.95 ± 21.20
	16.57 ± 3.92	132.58 ± 9.06	179.72 ± 10.88
Monel 67 Weld	15.16 ± 2.38	52.15 ± 5.69	129.21 ± 9.81
	32.80 ± 3.99	85.61 ± 7.62	228.00 ± 17.74
	30.98 ± 3.83	161.63 ± 10.51	266.78 ± 19.31
Nb modified	16.41 ± 2.10	101.48 ± 7.80	242.29 ± 15.55
Cuprotrode 521 Weld	44.54 ± 6.17	225.20 ± 10.20	375.28 ± 17.26
	35.49 ± 3.93	124.03 ± 9.72	220.05 ± 13.81
Cr modified	22.02 ± 3.63	35.06 ± 5.59	160.70 ± 11.93
Monel 451 Weld	31.53 ± 3.54	166.77 ± 9.92	239.53 ± 13.70
	18.61 ± 2.30	111.46 ± 9.58	139.92 ± 10.19
B61	25.74 ± 4.88	125.98 ± 9.11	123.40 ± 12.00
Leaded Tin Bronze	27.69 ± 4.89	75.84 ± 7.13	108.58 ± 9.98
	46.72 ± 4.38	78.12 ± 7.89	105.90 ± 11.20
90/10	29.77 ± 6.19	106.36 ± 19.03	42.62 ± 5.53
Copper Nickel	23.51 ± 3.42	85.52 ± 15.57	110.47 ± 1.69
	20.94 ± 3.23	49.99 ± 7.31	115.86 ± 13.14

TABLE V

AVERAGE CORROSION RATES AND THEIR STANDARD DEVIATIONS

Sample		Average Corrosion Current Density (nA/cm^2)	Density (g/cm^3)	Equivalent Weight (g/equiv)	Average Corrosion Rate (μm/year)
Nb modified 70/30	(1°C)	16.30 ± 12.70	8.94	52.9	0.32 ± 0.25
Copper Nickel	(15°C)	99.69 ± 33.75			1.93 ± 0.65
Parent	(25°C)	200.20 ± 42.05			3.87 ± 0.81
Cr modified 70/30	(1°C)	15.67 ± 2.32	8.94	52.3	0.30 ± 0.04
Copper Nickel	(15°C)	96.62 ± 32.92			1.85 ± 0.63
Parent	(25°C)	257.60 ± 68.80			4.93 ± 1.32
Monel 67 Weld	(1°C)	26.31 ± 9.70	8.94	52.7	0.51 ± 0.19
	(15°C)	99.80 ± 56.10			1.92 ± 1.08
	(25°C)	208.00 ± 70.93			4.01 ± 1.37
Nb modified	(1°C)	32.15 ± 14.36	8.94	52.8	0.62 ± 0.28
Cuprotrode 521	(15°C)	150.24 ± 65.89			2.90 ± 1.27
Weld	(25°C)	279.21 ± 83.94			5.39 ± 1.62
Cr modified	(1°C)	24.05 ± 6.70	8.94	52.4	0.46 ± 0.13
Monel 451	(15°C)	104.43 ± 66.14			2.00 ± 1.27
Weld	(25°C)	180.05 ± 52.55			3.45 ± 1.01
B61	(1°C)	33.38 ± 11.59	8.64	59.9	0.76 ± 0.26
Leaded Tin Bronze	(15°C)	93.31 ± 28.31			2.12 ± 0.64
	(25°C)	112.63 ± 9.43			2.55 ± 0.21
90/10	(1°C)	24.74 ± 4.54	8.94	59.3	0.54 ± 0.10
Copper Nickel	(15°C)	80.62 ± 28.50			1.75 ± 0.62
	(25°C)	89.65 ± 40.82			1.94 ± 0.89

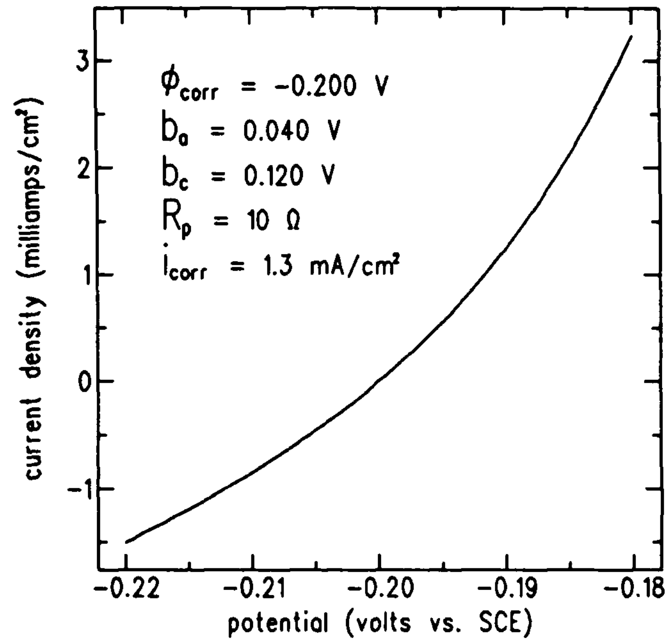
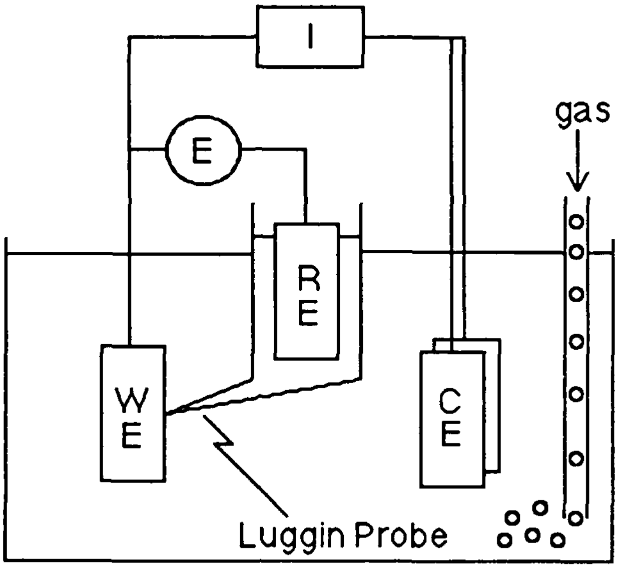


Figure 1 A polarization curve showing its nonlinearity at the corrosion potential



CE - graphite counter electrodes

WE - working electrode (sample)

RE - saturated calomel reference electrode

E - potentiometer

I - ammeter and power supply

Figure 2 Schematic of corrosion cell

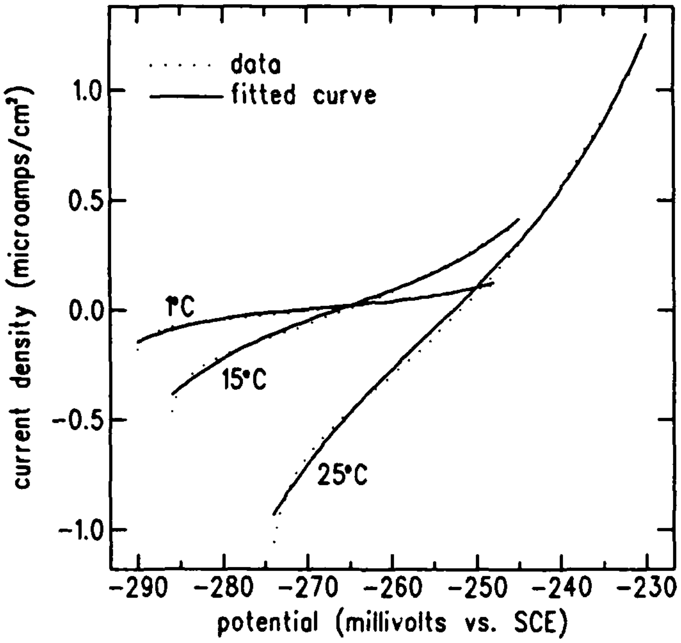


Figure 3 Polarization resistance data and fitted curves for one of three measurements at each of three temperatures on the chromium modified 70/30 copper nickel parent metal sample

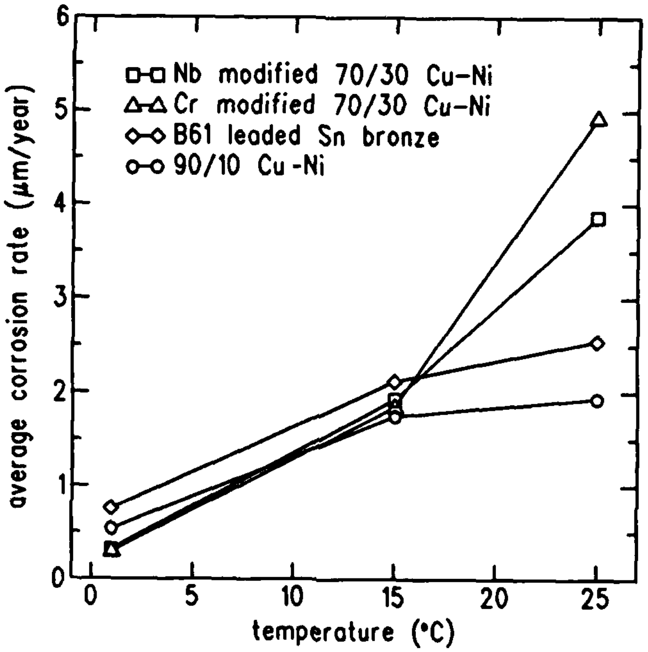


Figure 4 Average corrosion rates of the parent metal samples at three temperatures

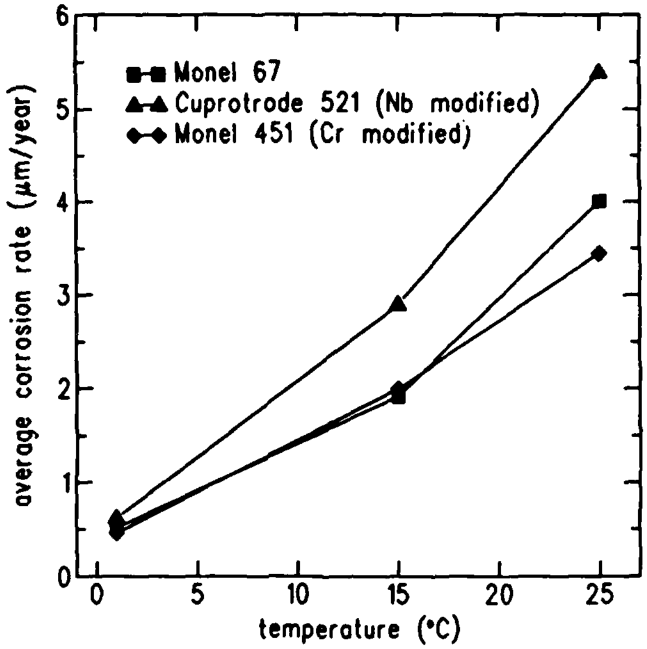
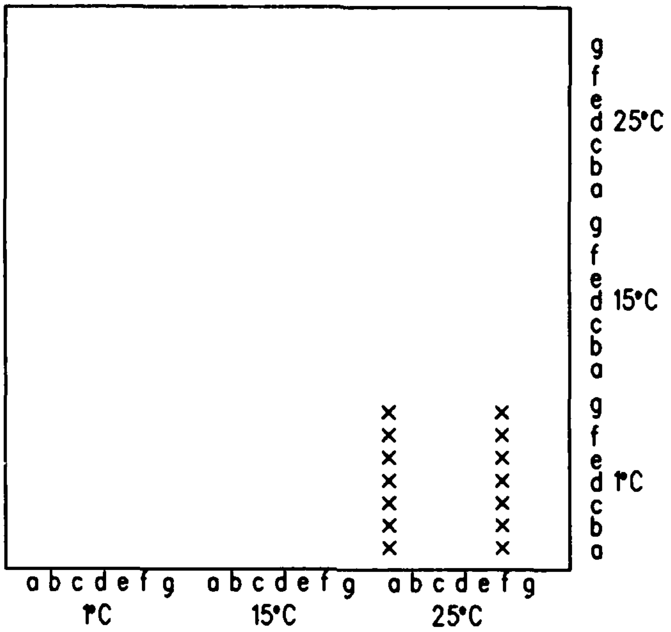
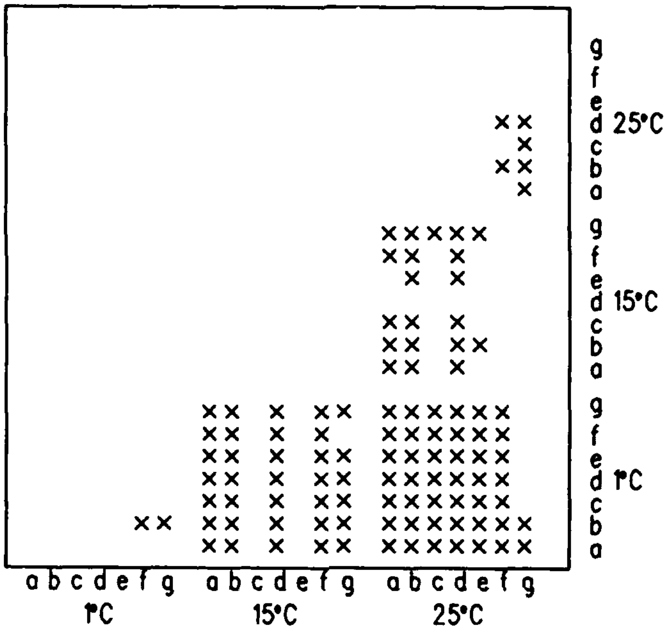


Figure 5 Average corrosion rates of the weld metal samples at three temperatures



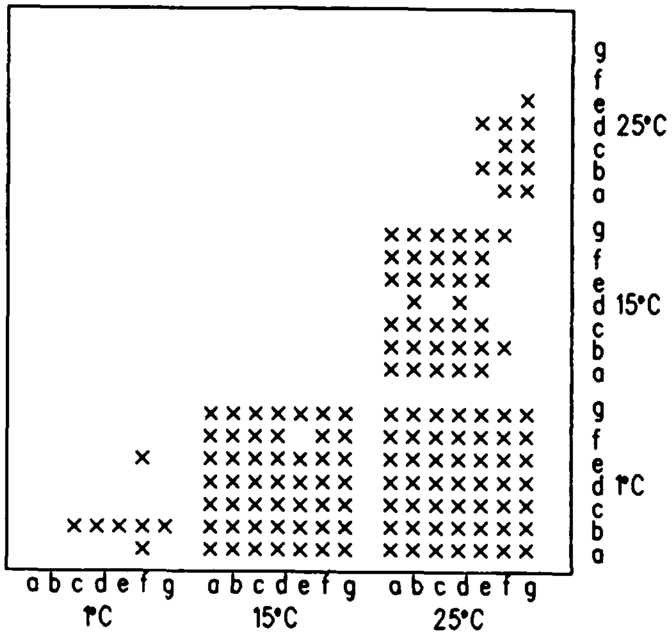
a	Niobium Modified 70/30 Copper Nickel Parent
b	Chromium Modified 70/30 Copper Nickel Parent
c	Monel 67 Weld
d	Niobium Modified Cuprotrode 521 Weld
e	Chromium Modified Monel 451 Weld
f	ASTM B61 Leaded Tin Bonze
g	90/10 Copper Nickel

Figure 6 Results of t test, with 99% confidence, showing pairs of populations which have a significant difference between their mean corrosion rates



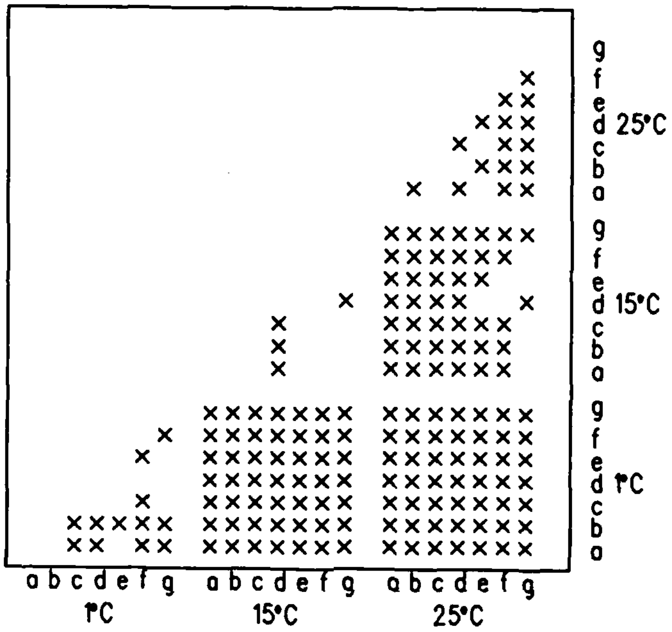
a Niobium Modified 70/30 Copper Nickel Parent
b Chromium Modified 70/30 Copper Nickel Parent
c Monel 67 Weld
d Niobium Modified Cuprotrode 521 Weld
e Chromium Modified Monel 451 Weld
f ASTM B61 Leaded Tin Bonze
g 90/10 Copper Nickel

Figure 7 Results of t test, with 95% confidence, showing pairs of populations which have a significant difference between their mean corrosion rates



a	Niobium Modified 70/30 Copper Nickel Parent
b	Chromium Modified 70/30 Copper Nickel Parent
c	Monel 67 Weld
d	Niobium Modified Cuprotrode 521 Weld
e	Chromium Modified Monel 451 Weld
f	ASTM B61 Leaded Tin Bonze
g	90/10 Copper Nickel

Figure 8 Results of t test, with 90% confidence, showing pairs of populations which have a significant difference between their mean corrosion rates



a Niobium Modified 70/30 Copper Nickel Parent
b Chromium Modified 70/30 Copper Nickel Parent
c Monel 67 Weld
d Niobium Modified Cuprotrode 521 Weld
e Chromium Modified Monel 451 Weld
f ASTM B61 Leaded Tin Bonze
g 90/10 Copper Nickel

Figure 9 Results of t test, with 80% confidence, showing pairs of populations which have a significant difference between their mean corrosion rates

REFERENCES

1. Hanham, C.M. and Hollingshead, R.S., "Erosion Corrosion Resistance of Chromium and Niobium Modified 70/30 Copper Nickel Alloys for Seawater Piping Systems", Defence Research Establishment Atlantic Technical Memorandum 84/I, May 1984.

2. Hanham, C.M., Sahoo, M. and Hollingshead, R.S., "Copper Nickel Casting Alloys for Seawater Piping Systems", ASM Metals Congress, Philadelphia, October 1983, Metals/Materials Technology Series #8305-022, American Society For Metals, Metals Park, Ohio, 1983.

3. Wang, K.C., Sahoo, M. and Edwards, J.O., "Summary of High-Strength Cupro-Nickel Casting Alloys - Part I: Foundry Characteristics and Mechanical Properties of Niobium-Modified 70/30 Cupro-Nickel", Division Report MRP/PMRL 78-3 (TR); CANMET, Energy, Mines and Resources Canada, 1978.

4. Sahoo, M., Wang, K.C. and Edwards, J.O., "Summary of High-Strength Cupro-Nickel Casting Alloys - Part II: Foundry Characteristics and Mechanical Properties of Chromium-Modified 70/30 Cupro-Nickel", Division Report MRP/PMRL 78-11 (TR); CANMET, Energy, Mines and Resources Canada, 1978.

5. Campbell, W.P. and Sahoo, M., "Summary of High-Strength Cupro-Nickel Casting Alloys - Part III: Weldability of Niobium-Modified 70/30 Cupro-Nickel", Division Report MRP/PMRL 79-24 (TR); CANMET, Energy, Mines and Resources Canada, 1979.

6. Sahoo, M. and Edwards, J.O., "High Integrity Cu-Ni Castings for Technology Demonstration and Seawater Service Evaluation", Division Report MRP/PMRL 80-61 (TR); CANMET, Energy, Mines and Resources Canada, 1980.

7. Wagner, C.W. and Traud, W., "Concerning the Evaluation of Corrosion Reactions by Superposition of Electrochemical Partial Reactions and Concerning the Potential Formation on Mixed Electrodes", Z. Elektrochem, 44, p. 391, 1938.

8. Oldham, K. and Mansfeld, F., "On the So-Called Linear Polarization Method for Measurement of Corrosion Rates", Corrosion, 27, p. 434, 1971.

9. Mansfeld, F. and Oldham, K., "A Modification of the Stern-Geary Linear Polarization Equation", Corrosion Science, 11, p. 787, 1971.

10. Bonhoeffer, K.F. and Jena, W., "On The Electrochemical Behavior of Iron", Z. Elektrochem., 55, p. 151, 1951.

11. Stern, M. and Roth, R.M., "Anodic Behavior of Iron in Acid Solutions", J. Electrochem. Soc., 104, p. 390, 1957.

12. Stern, M., "A Method for Determining Corrosion Rates from Linear Polarization Data", Corrosion, 14, p. 440t, 1958.

13. Palombarini, G., Felloni, L. and Cammarota, G.P., "On the Shape of Some Polarization Curves in the Vicinity of the Corrosion Potential", Corrosion, 29, p. 245, 1973.

14. Stern, M. and Geary, A.L., "Electrochemical Polarization I. A Theoretical Analysis of the Shape of Polarization Curves", J. Electrochem. Soc., 104, p. 56, 1957.

15. Mansfeld, F., "Tafel Slopes and Corrosion Rates from Polarization Resistance Measurements", Corrosion, 29, p. 397, 1973.

16. Mansfeld, F., "Simultaneous Determination of Instantaneous Corrosion Rates and Tafel Slopes from Polarization Resistance Measurements", J. Electrochem. Soc., 120, p. 515, 1973.

17. Mansfeld, F., "Some Errors in Linear Polarization Measurements and Their Correction", Corrosion, 30, p. 92, 1974.

18. Mansfeld, F., "On the Shape of Some Polarization Curves in the Vicinity of the Corrosion Potential", Corrosion, 30, p. 320, 1974.

19. Jones, D.A., "Discussion On the So-Called Polarization Method for Measurement of Corrosion Rates", Corrosion, 28, p. 180, 1972.

20. Leroy, R.L., "The Range of Validity of the Linear Polarization Method for Measurement of Corrosion Rates", Corrosion, 29, p. 272, 1973.

21. Jankowski, J. and Juchniewicz, R., "A Four-Point Method for Corrosion Rate Determination", Corrosion Science, 20, p. 841, 1980.

22. Hoar, T.P., "On The Relation Between Corrosion Rate And Polarization Resistance", Corrosion Science, 7, p. 455, 1967.

23. Oldham, K.B. and Mansfeld, F., "Corrosion Rates From Polarization Curves: A New Method", Corrosion Science, 13, p. 813, 1973.

24. Gerchakov, S.M., Udey, L.R. and Mansfeld, F., "An Improved Method for Analysis of Polarization Resistance Data", Corrosion, 37, p. 696, 1981.

25. Peterson, W.M. and Siegerman, Howard, "A Microprocessor-Based Corrosion Measurement System", Electrochemical Corrosion Testing, ASTM STP 727, Florian Mansfeld and Ugo Bertocci, editors, American Society for Testing and Materials, p. 390, 1981.

26. 1983 Annual Book of ASTM Standards, Section 3: Metals Test Methods and Analytical Procedures, Volume 03.02: Metal Corrosion, Erosion, and Wear, G5-82, American Society for Testing and Materials, Philadelphia, PA., p. 122, 1983.

27. Hanham, C.M. and Gallagher, P., "CORROS: A Computer Program for Analyzing Polarization Resistance Data", DREA Technical Communication, (in edit), 1985.

28. "Basics of Corrosion Measurements", Application Note CORR1, Applied Instruments Group, EG&G Princeton Applied Research, p. 7, 1982.

29. Gore, W.L., Statistical Methods for Chemical Experimentation, Interscience, New York, p. 32, 1959.

30. Dixon, W.J. and Massey, Jr., F.J., Introduction to Statistical Analysis, Third Edition, McGraw-Hill Book Company, New York, p. 464, 1969.

31. Callow, L.M., Richardson, J.A. and Dawson, J.L., "Corrosion Monitoring Using Polarisation Resistance Measurements II. Sources of Error", British Corrosion Journal, 11, p. 132, 1976.

32. MacDonald, D.D., Syrett, B.C. and Wing, S.S., "The Corrosion of Copper-Nickel Alloys 706 and 715 in Flowing Sea Water. I - Effect of Oxygen", Corrosion, 34, p. 289, 1978.

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