2012 Frank Newman Speller Award: Cathodic Protection of Offshore Structures—History and Current Status

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ABSTRACT

Categories of marine structures that use cathodic protection (CP) include port and harbor facilities, ships, coastal reinforced concrete bridges, pipelines, and those used for petroleum production. Primary focus of the present paper was on the last of these (offshore petroleum production structures) and CP theory and practice advances that have been made during the past several decades. Because of structure size, carbon or high-strength steel is the most common material of construction. The inception studies by Davy almost 200 years ago are reviewed briefly, followed by a review of subsequent CP evolvement and application. CP has been the primary corrosion control methodology for the submerged portion of offshore structures and pipelines for the past 60-plus years. Until the last several decades, however, improvements in marine CP design were incremental and based largely upon trial and error and empirical algorithms. These include the earlier single and subsequent triplicate design current density methods, which are reviewed. Also addressed are the recently developed first-principles-based slope parameter and unified design equation concepts, which require but a single design current density. Importance of the specified design current density, as affected by environmental conditions and calcareous deposits, is emphasized. Special topics, including deep water applications and design of retrofit systems, are discussed.

KEY WORDS: calcareous coating, cathodic protection, corrosion, deep water, dual nodes, galvanic anodes, retrofit, seawater, slope parameter, unified design equation

INTRODUCTION

History and Background

While the inception and early development of cathodic protection (CP) was based upon the remarkably insightful laboratory and field trials of Davy,1-3 the ensuing 100-plus years were uneventful. Basics of CP theory, however, were established in the 1930s at which time Hoar4 and Mears and Brown5 related the external applied current to affect cathodic polarization to the difference between the individual anodic and cathodic half-reaction currents, as graphically reflected by the Evans’ diagram. Also, the minimum potential for full protection was projected as that of the reversible anodic reaction. On the practical side, research and field studies conducted by the British, Canadian, and U.S. navies and the U.S. Bureau of Ships, as reviewed by Peterson,6 commenced in the 1940s and included both galvanic and impressed current systems with the former encompassing compositional evolution of magnesium, zinc, and aluminum anodes and the latter the transition from iron to Pb-Ag to Pt and more recently to mixed-metal oxide anodes. Presently, cathodic protection is the primary corrosion control methodology for buried and submerged components and marine structures7-8 and, to a lesser extent, for reinforcing steel in atmospherically exposed Cl−-contaminated concrete.9-11

Because of size, structural steel or reinforced concrete are the only economically viable materials of construction for offshore petroleum production structures. The early approach to cathodic protection design for steel structures, as detailed in the initial
version of NACE RP0176,\textsuperscript{12} was based upon application of sufficient current via either an impressed current or galvanic anode system such that polarization to –0.80 V vs. silver/silver chloride (Ag/AgCl) or more negative resulted from several months to a year. However, while the CP protection criterion is stated in terms of potential, design is necessarily based upon current density. Irrespective, polarization occurs in conjunction with the oxygen reduction reaction:

\[
\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-
\]

but under the early approach,\textsuperscript{12} the rate of calcareous deposit formation, which is discussed subsequently, and resultant oxygen concentration polarization occur somewhat slowly such that current density demand remains relatively high, even after steady state is achieved. Figure 1 schematically illustrates the long-term, steady-state polarization diagram for cathodically polarized steel based upon one or more galvanic anodes (identical and distributed in the multiple anode case). Therefore, potential of the former is shifted negatively from the native to the polarized value (\(\phi_{\text{CORR\(\text{(steel)}\)}}\)) to \(\phi_c\) and the latter positively from \(\phi_{\text{CORR\(\text{(anode)}\)}}\) to \(\phi_A\). Total circuit resistance is \(R_T\), and \(I_A\) is current output for a single anode. Except for conditions of high water movement, reaction kinetics for Equation (1) are under \(O_2\) concentration polarization control. Galvanic anodes, on the other hand, are alloyed to affect maximum current output per unit potential shift and, hence, are under activation control. The early CP design protocol for offshore structures using galvanic anodes\textsuperscript{12} involved determination of the current output per anode, \(I_A\), according to Ohm’s law:

\[
I_A = \frac{\phi_A - \phi_A}{R_A}
\]

where \(R_A\) is resistance of an individual anode. Application of this expression considers that \(R_A\) is the sole significant contributor to \(R_T\), as is normally the case for space-frame-type structures in a low-resistivity electrolyte such as seawater. From Equation (2), the number of anodes required for protection, \(N\), was determined from the relationship:

\[
N = \frac{i_C \cdot A_C}{I_A}
\]

where \(i_C\) is cathode current density for polarization and \(A_C\) is cathode surface area.

It was realized subsequently, however, that protection was more efficient; that is, \(i_C\) in the long-term was lower, upon providing an initially high current density, a concept referred to as rapid polarization. Consequently, more recent versions of RP0176 (presently designated SP0176-2007\textsuperscript{8}) have been based upon an initial \(i_0\), mean \(i_M\), and final \(i_F\) current density algorithm, where \(i_0\) is relatively large and affects polarization relatively fast, the second reflects the necessary anode mass to achieve protection for entirety of the design life, and the third is intended to assure that protection is maintained near the end of the design life in case of a depolarizing event such as a storm. Table 1 lists values for each of these design current densities from the above SP for several global waters. In this approach, the requisite anode mass is calculated according to each of three design current density criteria; the highest of the three is then

<table>
<thead>
<tr>
<th>Location</th>
<th>Water Resistance (\Omega \cdot m^2)</th>
<th>Water Temp. (^\circ)C</th>
<th>Wave Action</th>
<th>Lateral Action</th>
<th>Design (i_0) (mA/m(^2))</th>
<th>Design (i_M) (mA/m(^2))</th>
<th>Design (i_F) (mA/m(^2))</th>
<th>Design Slope (\Omega \cdot m^2)</th>
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specified. Consequently, the resultant CP system is overdesigned according to the other two. The last several revisions of RP0176/SP0176 have included an alternative design approach, known as the slope parameter method (last column in Table 1), which is first-principles-based as discussed below.

PROTECTION CRITERIA

As noted above, protection is generally recognized as being achieved upon polarization to \(-0.80 \text{ V}_{\text{Ag/AgCl}}\) or more negative,\(^7\)\(^8\) in which case there is no net anodic activity. The origin(s) of this criterion are unclear; however, \(-0.78 \text{ V}_{\text{SCE}}\) (\(-0.76 \text{ V}_{\text{Ag/AgCl}}\)) was stated as a generally recognized protection threshold as early as 1948.\(^13\) The \(-0.80 \text{ V}_{\text{Ag/AgCl}}\) value simply reflects a modest factor of safety relative to the earlier stated value (\(-0.78 \text{ V}_{\text{SCE}}\)). Several authors have indicated that with the presence of sulfate-reducing bacteria, an additional 0.10 V polarization is necessary (minimum protection potential \(-0.90 \text{ V}_{\text{Ag/AgCl}}\)).\(^14\)\(^16\) Also, while both theory and practice have indicated that corrosion remains mitigated at excessively negative potentials (\(\phi < -1.05 \text{ V}_{\text{Ag/AgCl}}\)), such over-protection results in a second cathodic reaction, water dissociation:

\[
\text{H}_2\text{O} + e^- \rightarrow \text{H} + \text{OH}^- \tag{4}
\]

and higher than necessary current and anode consumption rate, the possibility of hydrogen embrittlement, and damage to any protective coatings that might be present. Based upon the above, the appropriate potential range for protection would appear to be \(-0.80 \leq \phi_c \leq -1.05 \text{ V}_{\text{Ag/AgCl}}\); however, as subsequently indicated, an even narrower range is more appropriate.

Potentials of offshore structures are measured periodically to ensure protection is maintained.\(^17\) This can involve measurements taken either in conjunction with a reference electrode suspended from the platform or during which an electrode is traversed along structure members (or both). The former provides a global assessment and is applicable because seawater resistivity is relatively low such that voltage drop between the electrode and structure is generally negligible. However, areas of underprotection, such as can occur in locations of geometric constriction (conductor guides, for example), may go undetected.\(^18\) The latter, on the other hand, assesses protection level locally in the immediate electrode vicinity and so should address the entire structure. It has been reasoned that a global assessment may suffice using a minimum potential criterion of \(-0.90 \text{ V}_{\text{Ag/AgCl}}\), considering that seawater is unlikely to support more than a 100 mV potential drop, even in constricted areas.\(^19\)

RAPID POLARIZATION AND CALCAREOUS DEPOSITS

Particularly important for affecting an optimized CP design is understanding the \(\phi_c\) trajectory with time toward steady state as polarization is affected. In this regard, early studies used potentiostatic polarization of steel specimens at a predetermined \(\phi_c\) and monitoring of the resultant \(i_c\) decay. However, such an approach does not capture behavior of field deployments for which polarization is invariably more gradual. Figure 2 shows an experimental arrangement for simulating such situations, where a steel specimen in natural seawater is polarized by a symmetrically positioned galvanic ring anode with an external resistor (\(R_x\)) in series between the two.\(^20\) In effect, the added resistance simulates a situation where the cathode has a larger surface area than is actually the case. Figure 3 illustrates results for nine different experiments, each with a different \(R_x\) based upon such an approach. The \(\phi_c-i_c\) decay for a given specimen is
approximately linear, albeit with increasing departure therefrom with decreasing $R_x$ for reasons explained later. The first number in the nomenclature is the $R_x$ value and the second is $R_x \cdot A_x$. Significance of the latter parameter is discussed below. The specific data points were recorded at 24, 120, 480, and 3,200 h exposure with the smoothed curve through the data at each of the four times extending generally from upper left to lower right. These indicate a progression with increasing time from modest to significant oxygen concentration polarization. However, a unique feature of such polarization in seawater is that, in the long term, the cathodic curve bends back upon itself in the $\phi_C$ range, −0.80 V$_{Ag/AgCl}$ to −1.00 V$_{Ag/AgCl}$. Figure 4 illustrates this long-term behavior in more detail for a greater number of specimens. Therefore, while protection is achieved by polarization to −0.80 V$_{Ag/AgCl}$, as noted above, $i_C$ in the long-term is about three times greater than that for polarization to the range near −1.00 V$_{Ag/AgCl}$. On this basis, the optimum potential range for protection is $−0.90 < \phi_C < −1.05$ V$_{Ag/AgCl}$.

The sigmoidal shape of the long-term $\phi_C$–$i_C$ trend in seawater (Figures 3 and 4) resulted because of the unique chemistry of seawater and precipitation of calcareous deposits upon cathodic surfaces. Therefore, calcium carbonate (CaCO$_3$) is supersaturated in temporal, near-surface waters, such that a driving force exists for its precipitation. This does not normally occur under ambient conditions, however, because of kinetic factors (blockage at potential nucleation sites by adsorbed species, Mg$^{2+}$ and dissolved organics$^{21,23,27}$ in particular) but does proceed given greater driving force, as affected by sufficient cathodic polarization and generation of OH$^-$ at cathodic sites. A second potential precipitant, magnesium hydroxide (Mg(OH)$_2$), is undersaturated in seawater at ambient conditions but becomes saturated once cathodic polarization raises electrolyte pH at the interface to about 9.3. In either case, precipitation proceeds as a consequence of the OH$^-$ product from Reactions (1) and (4), displacing the inorganic carbon equilibria, expressed by:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$$  \hspace{1cm} (5)
$$\text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+$$  \hspace{1cm} (6)
$$\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+$$  \hspace{1cm} (7)

to the right such that pH in the vicinity of the cathode is increased and calcium- and magnesium-rich precipitates form according to:

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3$$  \hspace{1cm} (8)
$$\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2$$  \hspace{1cm} (9)

The finding that the optimum potential range for protection is $−0.90$ V$_{Ag/AgCl}$ to $−1.05$ V$_{Ag/AgCl}$ results because of limited reaction kinetics for CaCO$_3$ precipitation at more positive potentials and because deposits formed at more negative potentials are relatively porous and dislodged by hydrogen gas generation (Reaction 4). Precipitation kinetics for Mg(OH)$_2$, on the other hand, are much more rapid.

As noted above, emphasis for the past several decades has been upon what are termed free-running experiments, as illustrated in Figures 2 through 4, rather than ones involving potentiostatic polarization. However, the latter has had utility for studying calcareous deposits. In this regard, Figure 5 shows an $i_C$ vs. time plot for a 1018 steel specimen (UNS K01800)$^{28}$ polarized in seawater at a constant cathodic potential of $−0.880$ V$_{Ag/AgCl}$. The general trend is one where $i_C$ remained in the 400 mA/m$^2$ to 450 mA/m$^2$ range for the initial 35 h of exposure but subsequently decayed slowly to a steady-state value near 20 mA/m$^2$ after about 100 h. Figure 6 shows the initial (20 min) $i_C$ decay trend for two steel specimens.
both polarized potentiostatically to this same potential \((-0.880 \text{ V}_{\text{Ag/AgCl}})\), where one was exposed in natural seawater and the second in a 3.5 wt% sodium chloride (NaCl) solution. The two data sets both exhibit a sharp current drop within the first minute because of \(O_2\) concentration polarization with \(i_c\) being relatively invariant thereafter. However, the steady-state \(i_c\) for the specimen in seawater is approximately half that for the NaCl solution. This reduced \(i_c\) resulted because Mg(OH)\(_2\) precipitated in the former case as a consequence of its concentration being relatively high in seawater and reaction kinetics rapid such that a thin film of this phase formed within the first minute of exposure. Figure 7 shows a micrograph of such a film (partially disbonded) that formed on a cathodically polarized specimen that had been exposed for 15 min. \(^{28}\) Thickness of the film was estimated as \(10^{-2} \text{ µm}\). The initial \(i_c\) drop in Figure 6 is not apparent in Figure 5 because of the difference in time scales; however, the Mg(OH)\(_2\) film accounts for the upper plateau \(i_c\) in Figure 5, the duration of which was an incubation period for the onset of CaCO\(_3\) precipitation. Reduced current density to affect polarization in seawater relative to NaCl solutions also has been reported in the long term and attributed to calcareous deposits. \(^{25,29-31}\)

Because \([\text{Mg}^{2+}]\) in seawater is relatively high and reaction kinetics rapid, precipitation of Mg(OH)\(_2\) is under [OH\(^-\)] control. Consequently, pH immediate to the metal-electrolyte interface is buffered and should rise only slightly above the value corresponding to the Mg(OH)\(_2\) solubility limit \((-9.3)\); and \([\text{Mg}^{2+}]\) here should not be significantly different from the saturation value at that pH. Although precipitation of the Mg-rich film occurs readily during the initial few seconds of exposure, its subsequent development is normally limited because of the modest electrolyte layer thickness within which pH is such that \([\text{Mg}^{2+}][\text{OH}^-]^2 > K_{sp}\). Thicker Mg(OH)\(_2\) deposits can occur in relatively cold seawater (deep ocean or northern latitudes), where CaCO\(_3\) solubility is greater; however, the former are not as protective as the latter. \(^{32}\)

SLOPE PARAMETER-BASED CATHODIC PROTECTION DESIGN

As for the three CP design current density algorithms described above, the slope parameter, \(S\), approach affects rapid polarization; this method also is based upon Ohm’s law expressed as Equation (2) and illustrated graphically in Figure 1. It was noted above that \(R_A\) is the sole significant contributor to \(R_T\) for space-frame structures in seawater protected by galvanic anodes; so, assuming \(N\) identical, distributed anodes are at issue:

\[
R_T = \frac{R_A}{N} \quad (10)
\]

The slope parameter, \(S\), is then defined as:

\[
S = \frac{\phi_C - \phi_A}{i_c} = R_T \cdot A_c = \frac{R_A \cdot A_c}{N} \quad (12)
\]

Note that values for \(S\) are listed in Table 1 and in the Figure 3 nomenclature as \(R_T \cdot A_c\). Therefore, Equation (11) projects a linear interdependence between \(\phi_C\) and \(i_c\) with slope \(R_T \cdot A_c\) and vertical intercept \(\phi_A\) provided \(R_T\), \(A_c\), and \(\phi_A\) are constant for the time span to which the \(\phi_C\) and \(i_c\) data pertain. Also assumed is that \(\phi_C\) is spatially invariant.

One aspect of \(S\) applicability for data analysis is realized by considering results reported by Kennelley and Mateer \(^{34}\) for a production jacket in 162 m Gulf of Mexico water. The CP system consisted of 265 Al-Zn-
In anodes, each weighing 330 kg, with ones at the –37 m and –105 m depths being instrumented such that $\phi_C$ and $i_C$ were recorded (calculated from voltage drop measurements in the $i_C$ case) for the initial 7,000 h of deployment. Figure 8 presents the resulting data. Also shown are data for a cylindrical API Grade 42 (UNS K12037) steel specimen (AC = 41 cm$^2$) polarized in quiescent natural seawater using a single, small Al-Zn-Hg ring anode (Figure 2) with $R_x = 450 \, \Omega$. This resistor size was selected such that $RT \cdot AC$ was the same as for the above structure. Both sets of data transcend with time from upper right to lower left, such that initial structure potential and current density were approximately $-0.64 \, V_{Ag/AgCl}$ and 245 mA/m$^2$, respectively, and after 7,000 h, $-0.98 \, V_{Ag/AgCl}$ and 50 mA/m$^2$. For the Kennelley and Mateer data, Equation (12) indicates $S = 1.79 \, \Omega \cdot m^2$. The graphically measured slope for the laboratory specimen data, on the other hand, is $S = 1.75 \, \Omega \cdot m^2$. Note also that both sets of data extrapolate to what is a reasonable value of $\phi_A$ for an Al-Zn-Hg anode ($\sim -1.08 \, V_{Ag/AgCl}$). Therefore, it was demonstrated that two sets of data representing vastly different size and geometry can be normalized with respect to one another using the slope parameter.

In some cases, departure of the $\phi_{C-i_C}$ trend from linearity is apparent, particularly near the beginning and end of the experiments. This is seen for the low $R_x$ specimen data in Figure 3 and, to a lesser extent, the long-term laboratory specimen results in Figure 8. Figure 9 shows another example involving a more complete set of data, also for an API-Grade 42 (UNS K12037) steel specimen tested according to the experimental arrangement in Figure 2. Arrows indicate the trend with time. Therefore, while a majority of the $\phi_{C-i_C}$ history conforms to a linear trend, the initial and long-term data do not. The departure at the most positive potential reflects anode activation and a time period during which $\phi_A$ shifted to more negative values. Three possible causes for the shift to more positive potentials at long term have been identified as follows:

- anode resistance increase with time as a result of corrosion product accumulation
- cathode resistance increase with time because of calcareous deposits
- partial anode passivation resulting from reduced current output

The first of these is discounted in the case of laboratory specimens, since anode current density was low and corrosion occurred mostly as isolated pitting; however, this could be a factor in the long term for anodes on actual structures. The second possibility is not considered realistic for structures since voltage drop increase associated with calcareous deposit formation on large structures should be small compared to that which develops at anodes. This leaves the third cause as the most plausible, and the progressive concavity of the long-term data in Figure 3 for specimens with $R_x \leq 1,000 \, \Omega$ is attributed to this.

**UNIFIED DESIGN EQUATION**

Combining Equation (12) with the modified Faraday’s law expression for design of galvanic CP systems based upon $i_M$:

$$N = \frac{i_M \cdot A_C \cdot T}{u \cdot C \cdot w}$$

where $T$ is design life, $u$ is an anode utilization factor, $C$ is anode current capacity, and $w$ is weight of an individual anode, yielding what has been termed the unified design equation:

$$R_A \cdot w = i_M \cdot T \cdot K \cdot S$$

where $K$ is anode consumption rate (inverse of $C$). For simplicity, $u$ has not been included in the latter expression. Of the parameters on the right side of this equation, $i_M$, $S$, and $T$ are design choices with the first
two being determined by nature of the exposure and K being a material property.\(^{(2)}\) Consequently, the value for the right side is defined; so, the CP design process reduces to selecting or designing an optimized anode such that the product of \(R_A\) and \(w\) is the same. This may be accomplished by anodes of standard dimensions or, alternatively, by elongated anodes or by dual nodes;\(^{(36-39)}\) that is, conventional Al anodes with a Mg layer cast onto one face. As an example,\(^{(35)}\) if anode resistance is expressed in terms of a modified form of Dwight’s equation:\(^{(40)}\)

\[
R_A = \frac{\rho}{2\pi L} \ln \left(\frac{4L}{r}\right) - 1
\]  

(15)

where \(\rho\) is electrolyte resistivity, \(L\) is anode length, \(r\) is effective anode radius. Then, the left side of Equation (14) becomes:

\[
R_A \cdot w = \frac{\rho'}{2} \cdot r^2 \cdot v \ln \left(\frac{4L}{r}\right) - 1
\]  

(16)

where \(\rho'\) is anode density and \(v\) is volume fraction of the anode that is galvanic metal as opposed to core.

Values for \(r\) and \(L\) can then be selected and the required number of anodes calculated from Equation (12). The advantage of this method over the three current densities algorithm is that Equation (14) is first-principles-based and includes both \(i_0\) and \(i_M\), the former implicitly within \(S\) (Equation [12]) and the latter explicitly. As such, design can be optimized in terms of two current densities instead of just one. An alternative view is that, of the two terms on the left side of Equation (14), \(R_A\) determines \(i_0\) while \(w\) is governed by \(i_M\). It has been shown that CP design according to the Equation (14) protocol results in approximately one-third less anode mass compared to the three design current densities algorithm.\(^{(35)}\)

Figure 10 schematically illustrates this approach to CP design considering four design \(S\) alternatives and how each relates to both the dynamic and long-term, steady-state polarization curves (Figures 3 and 4). Therefore, design according to \(S_1\) results in underprotection and \(S_2\) in protection but at a relatively high \(i_C\). Designs in the range \(S_3\)–\(S_4\), on the other hand, are optimum in that protection is achieved and \(i_C\) minimum.

**IMMERSED CURRENT CATHODIC PROTECTION SYSTEMS**

The \(S\) approach also can be applied to immersed current CP design by using the relationship:

\[
\phi_C = S \cdot i_C + \phi_A\text{[eq]}
\]  

(17)

\(^{(3)}\) \(K\) may also be viewed as a design choice considering that different anode types are available.

\[\text{FIGURE 10. Schematic illustration of four design} \ S \text{ choices in perspective to the dynamic and steady-state} \phi_C-i_C \text{ trends.}\]
parameter decayed with time according to a power law expression of the form:

\[ i_{\text{MAINT}} = 10^{a + k \sigma} \cdot T^b \]  

(19)

where \( T \) is exposure time, \( a \) and \( b \) are constants, \( \sigma \) is the standard deviation for \( i_{\text{MAINT}} \) (actually, for the constant \( a \)), and \( k \) is a multiple upon \( \sigma \) (for the mean curve, \( k = 0 \)).

Trend lines corresponding to \( \pm 1 \sigma \) and \( \pm 2 \sigma \) are also indicated. Table 2 lists values of \( a \), \( b \), \( \sigma \), and for both the warm and cold seawater cases. Integrating Equation (19) over a \( T \) of interest and dividing by that \( T \) yields an expression for \( i_M \) as:

\[ i_M = \frac{10^{(a + k \sigma)} \cdot T^b}{b + 1} \]  

(20)

It was proposed that this expression serves as the basis whereby values for \( i_M \) are specified in design. The choice of \( k \) can vary depending upon the degree of conservatism that is considered appropriate or the extent to which data exist for the specific site in question (\( k \) need not be a whole number). Also, by this procedure, \( i_M \) is a function of design life. Table 3 tabulates \( i_M \) values for different design lives, and Table 4 lists, first, \( i_M \) for the specific case of \( T = 20 \) years according to three levels of conservatism and, second, the percent difference between these \( i_M \) and presently recommended values. Therefore, the proposed mean+2\( \sigma \) value for \( i_M \) (high level of conservatism, \( k = 2 \)) is about 15% less than the recommended Gulf of Mexico value (47 \( \text{mA/m}^2 \) compared to 55 \( \text{mA/m}^2 \)), while the mean+1\( \sigma \) value (intermediate conservatism, \( k = 1 \)) is about one-half of this. The mean itself, on the other hand, is 71% less than the presently recommended value. In the cold water case, these same values range from 77% greater to about the same to 38% below the present North Sea design \( i_M \) (90 \( \text{mA/m}^2 \) for the same three degrees of conservatism (mean+2\( \sigma \), mean+1\( \sigma \), and mean, respectively). It was considered based upon this that the presently recommended North Sea design \( i_M \) appears to be an appropriate level of conservatism for a 20-year life, while the Gulf of

### Table 2

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<tr>
<th></th>
<th>Warm/Shallow Water</th>
<th>Cold/Deep Water</th>
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<td>( b )</td>
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### Table 3

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<th>Time (Years)</th>
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<td>14</td>
<td>86</td>
<td>23</td>
<td>145</td>
<td>40</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Degree of Conservatism(( a ))</th>
<th>Warm Water ( i_M ) (( \text{mA/m}^2 ))</th>
<th>Percent Difference to SP ( i_M ) (( \text{mA/m}^2 ))</th>
<th>Cold Water ( i_M ) (( \text{mA/m}^2 ))</th>
<th>Percent Difference to SP ( i_M ) (( \text{mA/m}^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (( k = 0 ))</td>
<td>16</td>
<td>-71</td>
<td>56</td>
<td>-38</td>
</tr>
<tr>
<td>Intermediate (( k = 1 ))</td>
<td>28</td>
<td>-49</td>
<td>94</td>
<td>4</td>
</tr>
<tr>
<td>High (( k = 2 ))</td>
<td>46</td>
<td>-15</td>
<td>159</td>
<td>77</td>
</tr>
</tbody>
</table>

(\( a \)) A positive percent difference indicates that \( i_M \) for the present method exceeds that from the SP.
Mexico one constitutes over-design by about a factor of two. However, these analyses do not take into account the possibility that anode C may decrease at relatively low \( I_a \), as explained subsequently. Irrespective, such projections are important because, first, Equation (14) indicates a direct proportionality between \( i_M \) and \( w \) and, second, the value for \( i_{M\text{AINT}} \) influences design of retrofit CP systems, as discussed below.

### SPECIAL TOPICS

**Deep Water Cathodic Protection**

Some 30 years ago, an industry shift began where a series of technology breakthroughs resulted in petroleum production in progressively deeper Gulf of Mexico and other waters. However, this raised concerns regarding CP design criteria because, first, current density demand was known to be greater than for warmer, near-surface waters, and, second, retrofits here, if required, are more costly than in relatively shallow locations. In response to this, a Joint Industry Project was initiated to better define deep water CP design criteria. The program consisted in part of a 405-day Gulf of Mexico deployment of instrumented specimens at 900 m depth and a location for which water properties were known, as listed in Table 5.

Companion laboratory experiments in natural seawater for which temperature, pressure, [O2], and pH mirrored those at the deep water site were also performed. Figure 13 schematically illustrates the experimental arrangement of individual cells, which included:

- 20 cm², 1.6 mm thick, low-carbon steel (UNS G10060) plate (coated on the back side)
- 38 mm diameter by 32 mm long Al-Zn-Hg anode machined from the same casting as for the experiments reflected in Figures 3 and 4 (anode-cathode surface area ratio: 0.12)
- Ag/AgCl reference electrode
- Pressure-compensated wiring junction box
- Pressure vessel housed data logger

A limited number of cylindrical cathode assemblies according to Figure 2 also were included so that results from the plate cathodes could be normalized to that for the laboratory specimen geometry. Figure 14 shows a schematic illustration of specimen assemblies and an exposure test frame, whereas Figure 15 provides a photograph of the three frames subsequent to recovery. Resultant deep water \( \phi_C-I_C \) data after

| Water Property Data at the Deep Water Exposure Site |
|----------------------------------|------------------|
| Location                         | GOM, Miss. Canyon Block 807 |
| Depth (m)                        | 899               |
| Temperature (°C)                 | 5.1               |
| Resistivity (Ω·cm)               | 29.4              |
| Average water velocity (cm/s)    | 5                 |
| Pressure (MPa)                   | 8.96              |

![Figure 13. Schematic illustration of the deep water deployment electrodes and data acquisition hardware.](image)

![Figure 14. Schematic illustration of the deep water test frame, electrodes, and instrumentation.](image)

![Figure 15. Photograph of the three test frames subsequent to recovery.](image)
3,000 h to 4,000 h deployment are shown in Figure 16 in comparison to:
— laboratory ambient temperature/pressure results (Figure 4, Phase I)
— 5°C ambient pressure data with no pH or \([O_2]\) control (Phase II)
— 5°C ambient pressure data with pH and \([O_2]\) controlled to the same values as for the deep water site (Table 5, Phase II’)
— 8.96 MPa, 5°C data with pH and \([O_2]\) controlled to the same values as for the deep water site (Phase III’)

Seawater for the high-pressure experiments was recirculated via a high-pressure pump and damper with partial replenishment. Within the context of data scatter, no effect of pressure, pH, or \([O_2]\) distinctions is apparent for the laboratory results; however, the latter failed non-conservatively to reproduce the deep water results by more than a factor of about two. If the deep water data were corrected for specimen geometry distinctions relative to the laboratory results (plate vs. cylindrical cathodes), this difference would be even greater. Also, little or no indication is apparent of a sigmoidal trend for the Phases II, II’, III’, and deep water \(\phi-i\) data, as occurred for the Phase I results. These distinctions were projected to be a consequence of differences in calcareous deposits, with aragonite being predominant at ambient temperature (Phase I), an inner brucite and outer aragonite layer with some gaps in the latter being predominant for the 5°C laboratory specimens, and brucite and calcite occurring on the deep water specimens. Figure 17 reproduces Figure 16 but with scanning electron microscopy (SEM) micrographs added that show deposit morphology for different exposure conditions and steady-state potentials. A possible compounding factor of influence for the laboratory vs. field data is an effect of biofilms on calcareous deposits and current density demand. Such films are invariably present for marine exposures; however, the seawater supplied for the above laboratory experiments was acquired through a near shore well point that was buried in sand that filtered out most species. Several authors have reported that calcareous deposit formation either can be enhanced or reduced depending upon current density; however, biofilms apparently serve as a cathodic depolarizer at current densities that are in the range of most CP systems, including those for the present experiments.48-49

**Cathodic Protection Retrofits**

A need for CP system retrofitting can arise for a number of reasons, including:
Irrespective of the first three causes, retrofitting becomes invariably necessary with structure age, assuming the field does not become depleted first. As depolarization occurs, the $\phi$–$i$ path does not retrace the linear trend of initial polarization, since a calcareous film is already present and presumably remains intact, at least for some period. Instead, $i_c$ progressively decreases as $\phi$ increases. Also, experiments have been performed that bear upon the $i_C$ that results from polarization of underprotected steel. In these, four individual specimens were initially polarized with $R_x = 1,437, 2,874, 3,784$, and $5,750$, respectively ($S = 5.75, 11.50, 15.14$, and $23.00 \ \Omega\cdot m^2$) for approximately 7,000 h (Phase I). Subsequently, $R_x$ was decreased from 75 $\Omega$ to 340 $\Omega$ ($S = 0.30$ to $1.36 \ \Omega\cdot m^2$, respectively) to polarize each specimen to $-1.00 \ \text{V}_{\text{AgAgCl}}$ (Phase II), thereby simulating a CP retrofit; exposure then was continued for approximately 14,000 additional hours. Figure 18 shows the steady-state $\phi$–$i_c$ data for each of the four exposures in perspective to the sigmoidal $\phi$–$i$ curve in Figure 4. The results indicate that $i_c$ upon full protection was higher the greater the amount of corrosion that occurred during the time of partial CP, considering that corrosion during the initial exposure was greater the higher $R_x$.

Critical parameters that determine remaining CP system life and, hence, appropriate timing for intervention prior to depolarization are:

- $i_{\text{MAINT}}$
- remaining anode mass
- residual anode current capacity

An approach for estimating $i_{\text{MAINT}}$ involves acquisition of potential data immediate to anodes and for adjacent structural members, example potential survey results being as shown in Figure 19. From this, Equation (11) can be solved for $i_c$ as $i_{\text{MAINT}}$ with $R_x$ determined from Equation (15), assuming $R_c = R_x/N$. Accuracy limitations arise, however, in conjunction with knowing resistivity of any anode corrosion products or fouling, anode geometry estimations, an appropriate choice for $\phi_c$, and the possibility that $\phi_c$ is influenced by multiple anodes. Table 6 compares $I_A$ values as determined for six anodes by the above protocol with Gauss meter measurements made at the exposed core at each anode end. While differences between the two methods approach 70% for an individual anode, the average difference overall is only 11%.

It is generally recognized that anode current capacity decreases once $I_A$ falls below a certain value. Such a decrease may occur if $I_A$ is relatively low. Maintenance anode current capacity, $C_{\text{MAINT}}$, can be estimated from results for two structure surveys using the expression:

$$C_{\text{MAINT}} = \frac{i_{\text{MAINT}} \cdot A_c \cdot \Delta T}{\Delta w}$$

(21)

where $\Delta T$ is the time between the two surveys and $\Delta w$ is the corresponding anode weight loss as estimated from dimensional changes.

**Dual Nodes**

An underutilized concept and technology is that of dual nodes, that is, of galvanic Al anodes with
pared to Al-Zn-Hg anodes, polarization is affected more rapidly with the former. Experiments that demonstrate the advantage of dual nodes used the same anode, cathode, and reference electrode sizes and configuration as in Figure 13 but with a 38 mm diameter by 1.6 mm thick 99.99 wt% Mg disc mechanically fastened to the outward face of the Al-Zn-Hg anode.\textsuperscript{51} Figures 20 through 22 show experimental results for an Al-only and the above dual node as potential-time, current density-time, and potential-current density plots, respectively, with $R_x = 55$ $\Omega$ ($S = 2.66$ $\Omega \cdot m^2$) in both cases. These show that, first, initial polarization was more rapid in the dual node case but with the Mg expired after about 480 h and, second, and more important, the average steady-state $i_C$ for the steel polarized by the dual node was approximately three times lower than for the Al-Zn-Hg anode-only case (10.3 mA/m$^2$ compared to 33.5 mA/m$^2$). Presumably, this was a consequence of the formation of a thicker, more protective calcareous deposit during the initial exposure period for the steel polarized by the dual node.

**CONCLUSIONS**

The theory and practice of offshore structure cathodic protection has evolved with time from being mostly trial and error to first-principles-based. Specific noteworthy accomplishments include recognition of the importance of design based upon, first, rapid polarization and, second, the slope parameter and unified design equation. Implicit to each of these is calcareous deposit formation, an understanding of which remains incomplete.

**REFERENCES**


