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Abstract

Cathodic protection modelling often involves making assumptions about geometric features and material characteristics that directly impact accuracy of solutions. In the present paper, predictive power of the model using approximate uniform current boundary condition on the cathode is validated against the model using nonlinear cathode polarization curves representative of low-carbon steel structure of common geometry, buried in soil or immersed in seawater. In order to explore the worst case scenario, the present example deals with a large diameter pipeline ($\varnothing$ 2.1 m) and a wire anode ($\varnothing$ 0.05 m), separated by a distance d , both embedded in an infinite space of conductivity κ . The calculation is performed for the two sets of parameters – κ and limiting current density of oxygen reduction, i_l . For simulation of CP systems in seawater $\kappa = 4.79 \text{ S m}^{-1}$ and $i_l = -86 \text{ } \mu\text{A cm}^{-2}$ and for CP system in soil, $\kappa = 10^{-3} \text{ S m}^{-1}$ and $i_l = -1.1 \text{ } \mu\text{A cm}^{-2}$. The other physical parameters were identical for both systems (Tafel slopes $b_a = 60 \text{ mV dec}^{-1}$, $b_c = 120 \text{ mV dec}^{-1}$ and equilibrium potentials $\phi_a^e = -700 \text{ mV}$, $\phi_c^e = -800 \text{ mV}$). The results were visualized to best exemplify the general trends in potential and current distributions that appear upon switch between uniform and nonlinear cathodic boundary conditions.

1 Introduction

In order to find the corrosion rate at any point on a cathodically protected metallic structure submerged in an electrolyte (most frequently ground or seawater), a corrosion engineer needs to know the potential distribution over the electrolyte/structure interface. Today, the calculation of current and potential distribution is considered an indispensable means for study of cathodic protection (CP) systems and improvement of their reliability [1-25]. Traditional CP design methods are mostly based on simple empirical formulas that require the use of large safety factors and rely, to a great extent, on the engineer's experience. Modern CP design methods utilize explicit mathematical modelling. In general, the complexity of geometry and polarization behaviour of CP systems necessitates the use of numerical methods such as: the finite difference method (FDM) [1], finite element method (FEM) [2-5] and the boundary element method (BEM) [6-23]. Among these methods, BEM is the most suitable for CP problems for two reasons: (i) unlike FDM and FEM, BEM requires discretization only of the boundaries of the system and not of the space occupied by the electrolytic medium and (ii) in an infinite system, discretization of the boundary at infinity is avoided by assuming an unknown constant potential at that boundary and by imposing the conservation of current between the anodes and cathodes which insures that there is no loss of current to infinity [9].

In this work, BEM is applied to a simple two-dimensional CP geometry shown in Fig. 1, in order to study the influence of the nonlinearity of boundary conditions on the CP design. Due to its versatility, the investigated CP geometry has been considered previously in the works of *Newman* [24], *Kennelley* et al. [2], *Orazem* et al. [8, 10, 11] and *Rabiot* et al. [12]. *Newman* has developed analytical solution in the form of a Fourier series describing the potential distribution around the circumference of the pipe subject to impressed current CP with a wire anode placed in parallel and close to the pipe. The solution was obtained under the

assumption of the uniform current density on the cathode. However, this condition is only approximately satisfied in the region of electrode potentials in which cathodic process primarily comprises of the diffusion controlled oxygen reduction. *Kennelly et al.* [2] and *Orazem et al.* [8] used FEM in conjunction with a linear boundary condition on both, bare and coated cathode surfaces, to solve for the potential and current distribution. *Orazem et al.* [10, 11] used BEM along with a linear boundary condition on the coated and a nonlinear condition on bare cathode surface. The primary objective of the works of *Orazem et al.* and *Kennelly et al.* was to establish the influence of macroscopic coating defects on the efficiency of the CP system. *Yan et al.* [14] applied BEM to a CP system of similar geometry. Potential distribution on the circumference of the pipe protected by one or two sacrificial anodes of rectangular cross section was considered. A nonlinear polarization curve obtained for low carbon steel in artificial seawater was used as a cathode boundary condition.

It was the aim of the present work to establish the influence of the form of the cathode boundary condition on polarization potential and current density at the protected surface in a CP system of common geometry. The results were obtained for a wide range of anode-to-cathode distances and for the two sets of physical parameters that most realistically describe the conditions prevailing in the CP systems containing either seawater or soil as an electrolytic medium. The model was verified by comparison to the results of *Newman* [24] and *Yan et al.* [14] for the same set of boundary conditions and geometric and physical parameters, as used by these authors. The results were visualized in 2D with the purpose of exemplifying the general trends in potential and current distributions that appear upon switch between constant and nonlinear cathodic boundary conditions.

2 Mathematical development

The governing equation for the distribution of potential ϕ , in a homogenous region of constant specific conductivity κ , surrounded by a boundary Γ is the Laplace equation [9, 15]:

$$\nabla^2 \phi = 0 \quad (1)$$

In a CP system with nonpolarizable anode, Equation (1) is subject to the boundary condition of the form:

$$\phi|_{\Gamma_a} = \text{const.} \quad (2a)$$

at the anode surface, Γ_a . Under the assumption of uniform current density, i_l , at the cathode surface, Γ_c , the boundary condition acquires the form:

$$\partial\phi/\partial n|_{\Gamma_c} = q = -i_l/\kappa \quad (2b)$$

where n is the unit normal to the cathode surface. Alternatively, the nonlinear boundary condition:

$$\partial\phi/\partial n|_{\Gamma_c} = q = -i(\phi)/\kappa \quad (2c)$$

is introduced, where the function $i(\phi)$ is given by the expression describing the polarisation characteristic of the protected structure [10,11,13, 14]:

$$i(\phi) = \text{Exp}\left[(\psi - \phi_a^e)/b_a\right] - i_l - \text{Exp}\left[-(\psi - \phi_c^e)/b_c\right] \quad (3)$$

where the first term denotes the partial current density of iron dissolution, the second term represents oxygen reduction, which is mass transfer limited, and the third term represents the hydrogen evolution. The parameters b_a and b_c are the Tafel slopes for iron dissolution and hydrogen evolution reactions and parameters ϕ_a^e , ϕ_c^e are the effective equilibrium potentials for the respective reactions that include the influence of the exchange current density.

The pipe itself, as well as the anode, is assumed to be an equipotential surface, thus, the electrode potential ψ at a point x , equals the potential of the electrode minus the potential of a reference electrode located in the adjacent electrolyte:

$$\psi(x) = \phi_{\text{pipe}} - \phi_0(x) \quad (4)$$

A boundary integral equation [25], equivalent to equations (1) and (2) can be written as:

$$c(\xi)\phi(\xi) + \int_{\Gamma} q^*(\xi, x)\phi(x)d\Gamma(x) = \int_{\Gamma} \phi^*(\xi, x)q(x)d\Gamma(x) + \phi' \quad (5)$$

where $c(\xi)$ depends on the boundary geometry at the source point ξ , $\phi^*(\xi, x)$ is the 2D free-space fundamental solution to Laplace equation, $q^*(\xi, x) = \partial\phi^*(\xi, x)/\partial n$ and $\Gamma = \Gamma_a + \Gamma_c$. ϕ' represents a constant potential which is equal to the actual potential at infinity. ϕ' is not a prescribed condition and an extra equation of the form [9]:

$$\int_{\Gamma} q(x)d\Gamma(x) = 0 \quad (6)$$

conveying the idea of conservation of current has to be employed for the complete problem solution.

Details of the BEM application to potential problems have been discussed extensively [25, 26]. The discretized versions of equation (5):

$$1/2\phi_i + \sum_{j=1}^N \left(\int_{\Gamma} q^* d\Gamma \right) \phi_j = \sum_{j=1}^N \left(\int_{\Gamma} \phi^* d\Gamma \right) q_j + \phi' \quad (7)$$

and equation (6)

$$\sum_{j=1}^N \left(\int_{\Gamma} d\Gamma \right) q_j = 0 \quad (8)$$

can be used, yielding a system of $N + 1$ linear equations, in case of the boundary condition equation (2b) and nonlinear equations in case of the boundary condition equation (2c).

$N = N_a + N_c$ is the total number of boundary elements.

Equations (7) and (8) were derived for “constant elements”, the simplest form of BEM, where the potential and current density are assumed to be uniform on each boundary element.

A six point Gauss quadrature formula was used in the present work for solving integrals in equations (7) and (8). The resulting system of equations was solved by an iterative

procedure based on the Newton-Raphson algorithm, implemented in the programming system *Mathematica* [27]. This algorithm was previously proved to be efficient for solving CP problems with nonlinear boundary conditions due to its second order convergence, which insures solution in a small number of iterations [16].

3 Result and discussion

The present example deals with a low carbon steel pipe of radius $r_c = 0.6$ m and a cylindrical anode of radius $r_a = 0.025$ m, separated by distance d , both embedded in an infinite space of conductivity κ . It is assumed that the CP system is dimensioned in such a way that the point on the cathode closest to the anode is polarized to -950 mV_{SCE}.

The boundaries of the anode and the cathode were discretized into 10 and 60 constant elements, respectively. The Laplace equation was solved under the assumption of uniform current density (UCD) and nonlinear current density (NLCD) on the cathode. Comparison of UCD solution with the known solution in the form of Fourier series, obtained by *Newman* [24] provides a useful test to gauge the performance of the numerical algorithm with respect to the number of boundary elements used. It is found that the present results obtained by boundary element method agree with those of Fourier series within 1.5 %.

The calculation is performed for the two sets of parameters κ and i_l , $\kappa = 4.79$ S m⁻¹ and $i_l = -86$ μ A cm⁻² for simulation of CP systems containing seawater and $\kappa = 10^{-3}$ S m⁻¹ and $i_l = -1.1$ μ A cm⁻² for systems containing soil as an electrolyte. The other physical parameters were identical for both systems ($b_a = 60$ mV dec⁻¹, $b_c = 120$ mV dec⁻¹, $\phi_a^e = -700$ mV, $\phi_c^e = -800$ mV). The parameters were chosen on the basis of the data available in literature [13, 14, 17, 28]. It was established previously by some authors [12, 14] that the geometrical parameters r_a and r_c , that were kept constant throughout the present calculation, exert lesser influence on the calculation results than κ and i_l . It is also reasonable to assume that the values

of r_a and r_c are constrained when a particular type of structure is considered. In that respect, the present calculation represents the worst case scenario of a large diameter pipeline ($\varnothing$ 2.4 m) protected by a wire anode ($\varnothing$ 0.05 m).

Another influential factor of CP design is the continuity and/or the efficiency of the pipe coating, if present. The pipe buried in soil was considered to be protected by a coating. To model the coating, a concept used by *Newman* [24] and also by *Mehdizadeh* et al. [29] was employed. This model describes natural coating microporosity but does not account for the macroscopic local defects. The coating reduces the metal surface area of the pipe in contact with the soil. A coefficient η is defined as a ratio between the electrochemically active surface and total surface area of the pipe yielding the apparent current density j_{app} equal to:

$$j_{app} = j\eta$$

In the present example, the coating is taken to highly damaged i.e. 90% effective ($\eta = 0.1$).

The maximum potential difference on the cathode can be defined as a difference between the point on the cathode nearest to the anode, polarized to the most negative value of the electrode potential, and the point furthest to the anode, polarized to the most positive value of the electrode potential. When the far side of the anode is unprotected, it is actually left at corrosion potential, E_{corr} . Taken that the near side is polarized to -950 mV_{SCE}, the maximum cathode potential difference can never exceed the value of -950 - E_{corr} . The calculated values of E_{corr} (for the given polarization parameters) in case of simulated CP systems in soil and seawater are -694.6 mV and -584.1 mV, respectively, yielding the maximum attainable potential differences on the cathode of -255.5 mV for seawater and -365.9 mV for soil. As seen from Figs. 2 (a) and (b), a maximum attainable potential difference is predicted only by the model taking into account the nonlinear boundary condition while for the model with uniform current condition, the predicted differences are unrealistically high below some value

of the anode-to-cathode distance (Fig. 2 (a)). Also, the discrepancy between UCD and NLCD model results is very high in case of CP in soil leading to the wrongful prediction of the minimum value of the anode-to-cathode distance for which the pipe is still well protected (7m for UCD as opposed to 0.4 m for NLCD).

For CP in seawater, the results of the two models practically coincide for the anode-to-cathode distances greater than 0.4 m, (Fig. 2 (b)). The importance of providing the most accurate possible boundary condition was stressed by *Cicognani et al.* [17]. They have established that the inaccurate estimate of the boundary conditions can cause rough errors, up to 300 mV on potential, even in a high conductivity electrolyte, such as seawater. In the present example, a maximum error of 160 mV was observed in case of the cathode separated from the anode by 0.1 m. The predicted minimum distance of 0.9 m for which the cathode is still protected, falls within the range of distances in which the two models are in a good agreement, and is the same for both models.

The average current density on the structure in soil is shown in Fig. 3 as a function of the anode-to-cathode distance in soil. It is observed that the absolute value of average current density for NLCD model is more negative, for all anode-to-cathode distances, then the limiting current density of oxygen reduction (entered into the model equation (3) and also taken as a boundary condition of the UCD model). This is due to the nonlinearity of the condition equation (3) caused by the influence of the reaction of hydrogen evolution that is more pronounced in the systems with low i_l , such as coated steel surfaces in soil.

The average current density on the structure in seawater, shown in Fig. 4 as a function of the anode-to-cathode distance in seawater, is within $\pm 20\%$ of the value used in UCD calculation. The variation of the average current value may be clarified further, by inspection the spread of the calculated current density boundary values on the polarization curve for various values of the anode-to-cathode distances (Fig. 5). For close anode-to-cathode

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positions, the current density at 180° approaches the value of zero while the electrode potential approaches the corrosion potential, yielding underprotection of cathode areas furthest to the anode.

4 Conclusions

It was established by the present analysis that the simplified boundary condition of uniform current density on the cathode in a CP systems of low electrolyte conductivity and low limiting current density of oxygen reduction, such as soil, can lead to rough errors in predicted current and potential distributions in the CP system. For a given set of polarization parameters characteristic of soil, and for a moderate level of polarization (the most negative potential equals -950 mV), underestimate of the cathodic polarization magnitude at the point remotest to the anode was found to be $\sim 100\text{ mV}$.

Although being utterly simple, the investigated geometry bares resemblance to a number of real CP situations and the results of the presented calculation may serve as a guideline for initial estimate of the possibility of protection of a cylindrical structure by a single anode of significantly smaller diameter.

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RE

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TEXT OF FIGURES

Figure 1. Schematic representation of the investigated CP system.

Figure 2. Maximum potential difference on the cathode as a function of the anode-to-cathode distance for: (a) CP in soil and (b) CP in seawater. Shaded areas denote the interval of potential differences attainable in real systems.

Figure 3. Average current density on the cathode as a function of anode-to-cathode distance for CP in soil.

Figure 4. Average current density on the cathode as a function of anode-to-cathode distance for CP in seawater.

Figure 5. Spread of the calculated current density boundary values at the cathode, on the polarization curve that was entered as a nonlinear boundary condition of NLCD model of CP model in seawater.

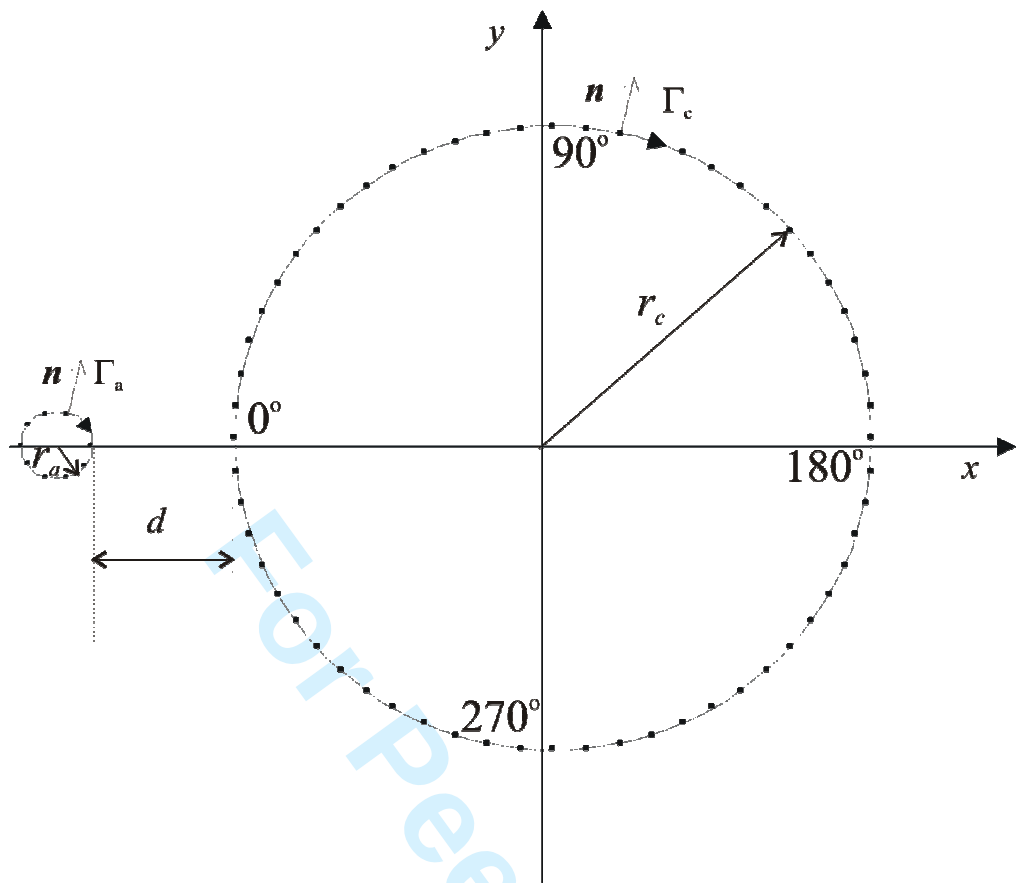


Figure 1.
Martinez S., Evaluation of the Uniform Current Density Assumption in Cathodic Protection
Systems with Close Anode-to-Cathode Arrangement

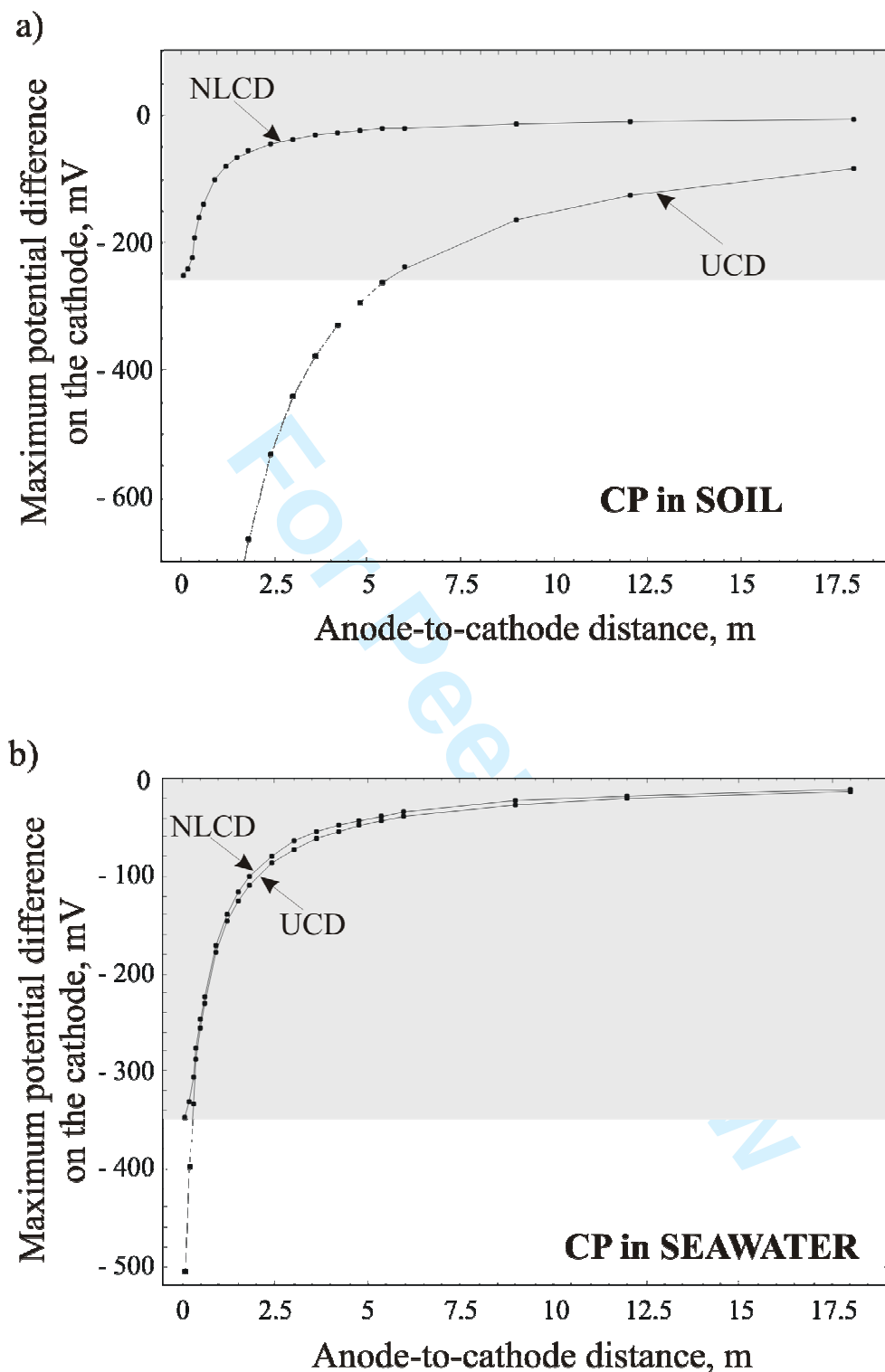


Figure 2.

Martinez S., Evaluation of the Uniform Current Density Assumption in Cathodic Protection Systems with Close Anode-to-Cathode Arrangement

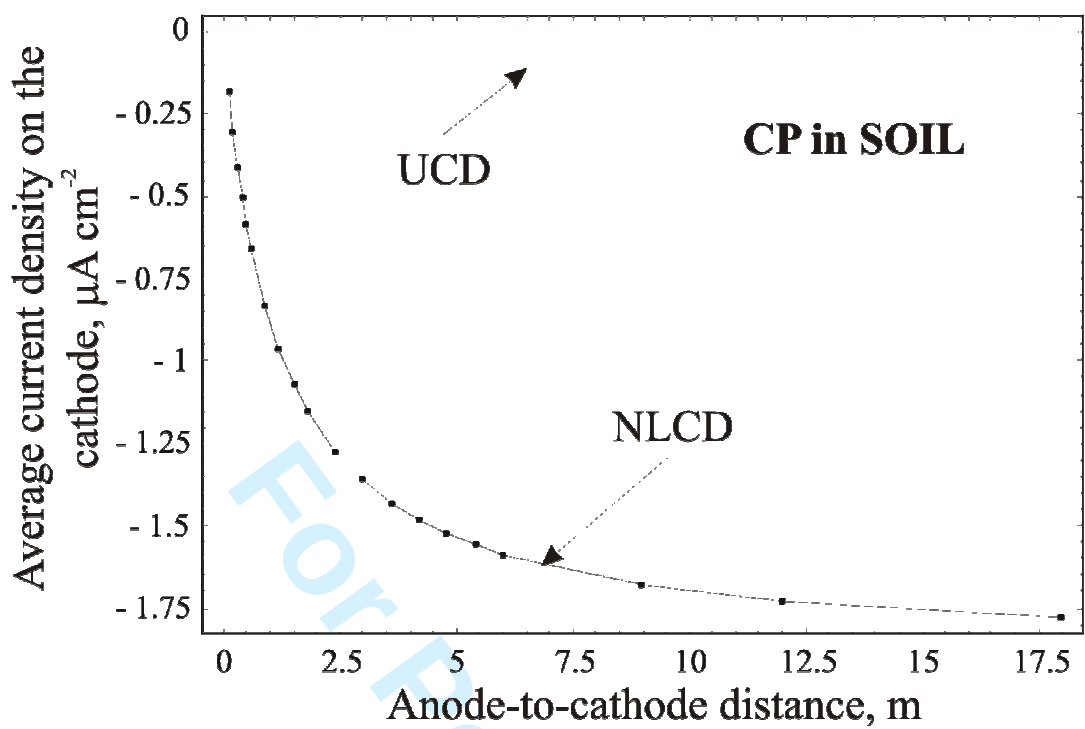


Figure 3.
Martinez S., Evaluation of the Uniform Current Density Assumption in Cathodic Protection
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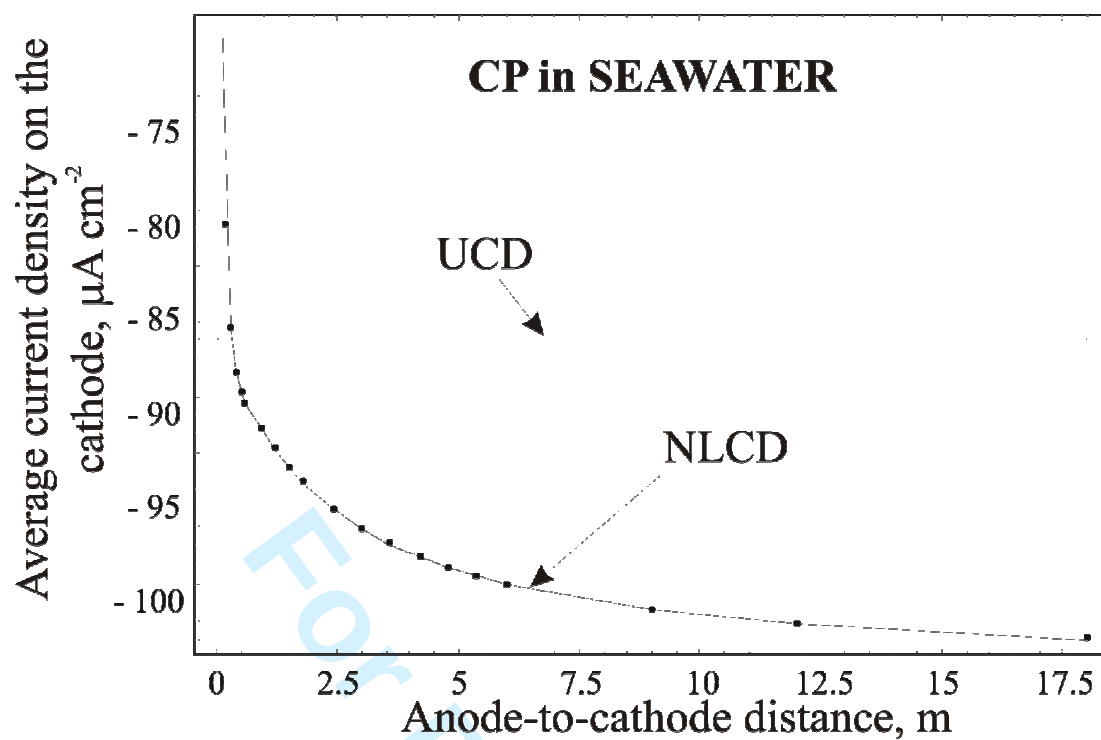


Figure 4.

Martinez S., Evaluation of the Uniform Current Density Assumption in Cathodic Protection Systems with Close Anode-to-Cathode Arrangement

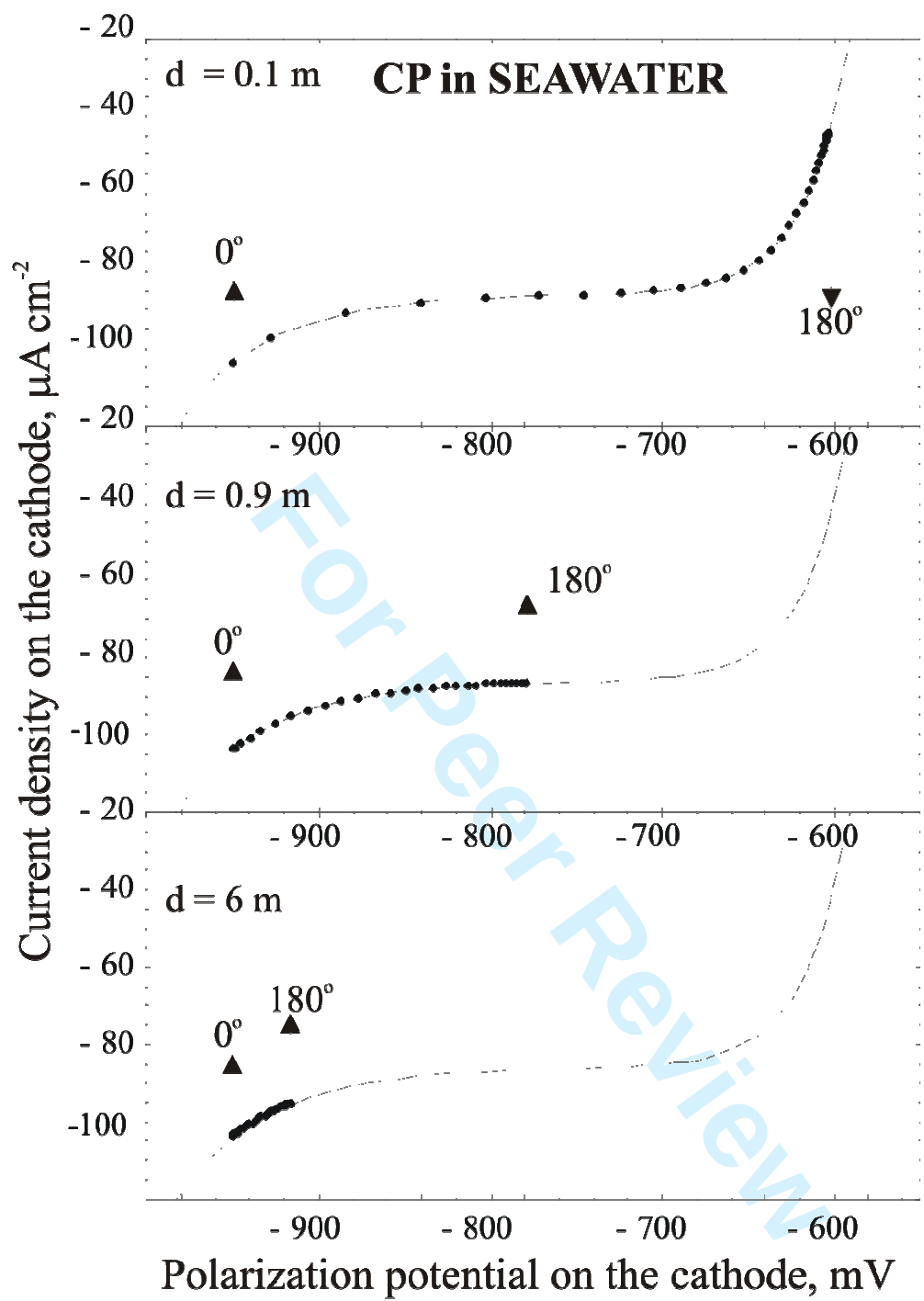


Figure 5.
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