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Boundary element method in modeling of the galvanic corrosion cell of underground structures

Abstract. *In the analysis and design of galvanic corrosion protection systems the boundary element method (BEM) has been used most successfully, because of ease in the development of models, speed in the analysis and accuracy of the results. In this paper it is described the method of computation of current density field in bodies composed of materials of different conductivity and potential distribution on the boundary. The determination of current density distribution, its dependence on structure geometry is also considered. This enables us to apply adequate galvanic corrosion protecting system.*

Streszczenie. *W analizie i projektowaniu systemów ochrony przed korozją metoda elementów brzegowych (MEB) ma zastosowanie w modelowaniu ze względu na szybkość i dokładność analizy wyników. W artykule opisano metodę obliczania gęstości prądu w materiałach o różnej przewodności oraz rozkład potencjału na brzegu. Wyznaczenie rozkładu gęstości prądu, jego zależność od geometrii struktury są znane, co pozwala nam na zastosowanie odpowiedniego systemu ochrony przed korozją galwaniczną. (**Metoda elementów brzegowych w modelowaniu korozji galwanicznej w podziemnych strukturach**)*

Keywords: galvanic corrosion, boundary element method.
Słowa kluczowe: korozja galwaniczna, metoda elementów brzegowych.

Introduction

The economical importance of galvanic corrosion causes that large amounts of capital and engineering time be invested in the design and construction of protection systems such as cathodic and anodic protection.

Galvanic corrosion is the result of the electrochemical reaction between two dissimilar metals in electrochemical contact when they are in electrolyte. Cathodic protection is one of the more frequently used methods of corrosion prevention.

In the analysis and design of galvanic corrosion protection systems the boundary element method (BEM) has been used most successfully [1], because of ease in the development of models, speed in the analysis and accuracy of the results [2].

The whole surface of the protected structure can be considered as equipotential and distribution of the current in the volume of the structure has not to be calculated, because the protected structures are made of various kinds well conducting metals (or various kinds of steel) which conductivity is much higher than surrounding electrolyte. In order to be able to compute a distribution of the cathodic polarization on protected structure a calculation of the distribution of the current flow in the structure is necessary. The individual components of composite material have different polarized potentials what makes a design process much more complicated.

The distribution of the potential in homogeneous [3] and inhomogeneous [4] electrolyte between an anode and a cathode was investigated by some authors. The need for a BEM system which accounts for finite conductivities of protected structure is apparent.

This paper describes a calculation of the polarized potential by boundary element method on protected structure composed of materials of different conductivities. It is assumed that the value of the electrolyte conductivity is comparable with those of composed materials. Some illustrative examples at the end also will be given.

## Numerical model of the galvanic corrosion cell

Corrosion is the destruction of metals by interaction with environment. Material immersed in an electrolyte shell corrodes due to microscopic galvanic cells created on the material surface. In corrosion process there are two kinds of electrochemical reactions: the anodic and the cathodic reactions. At one surface can simultaneously occur both types of reactions [5]. The electrochemical potential between the anode and the cathode is the driving voltage source causing chemical reaction, and it is also the basic far cathodic protection. The most important cathodic reactions are:
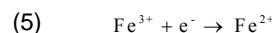
• evolution of H_2 from acid, neutral or alkaline solution

(1) $\qquad 2H^+ + 2e^- \rightarrow H_2 \qquad\qquad ph < 7$

(2) $\qquad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad ph \geq 7$
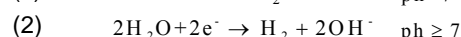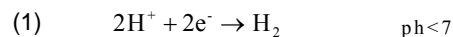
• reduction of dissolved oxygen in acid, neutral or alkaline solution

(3) $\qquad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad\qquad ph < 7$

(4) $\qquad O_2 + 2H_2O + 4e^- \rightarrow 4HO^- \qquad ph \geq 7$
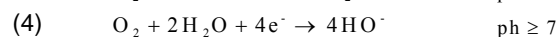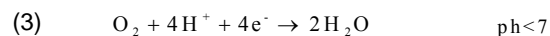
• reduction of dissolved oxidizer in a redox reaction such as reduction of ferric to ferrous ions

(5) $\qquad Fe^{3+} + e^- \rightarrow Fe^{2+}$

The most important anodic reaction is oxidation of metal or alloy M liberating into solution a metal ion M^{n+} and into the metal electrons ne^-:

(6) $\qquad M \rightarrow M^{n+} + ne^-$

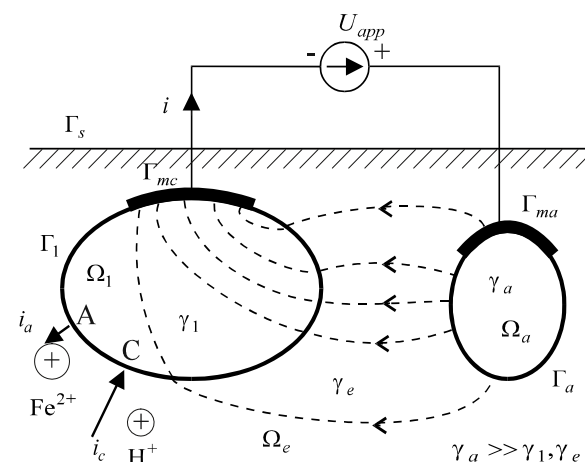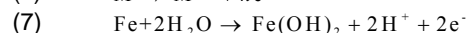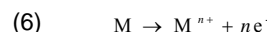(7) $\qquad Fe + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^-$

Fig. 1. Schematic cathodic protection system with a impressed current *i*. Description of the symbols in a text

The tendency of a metal to liberate electrons, and to go as ions into solution in an electrolyte and thus to become corroded, is related to the potential of the metal measured with reference to some other elements of construction. The potentials developed by electrode materials can be found tabulated in textbooks and handbooks. The electrochemical potential difference between the anode and the cathode is the driving voltage source causing chemical reaction, and it is also the basis for cathodic protection.

In analysis of the corrosion cells there are generally to do with two types of problems: with primary and secondary current density distribution calculations. In the first case the potential or current density on the boundary is prescribed and influence of nonlinearity caused by the relation between polarization and current density, as well as presence of concentration polarization is neglect. This type of analysis is usually the first step of the simulation. The secondary current density distribution in electrochemical cell is determined when, except of prescribed potentials, relation between polarization and current density is taken into account. In this publication only activation polarization is considered.

The net applied cathodic current is described by well-known Butler-Volmer equation [6]

$$(8) \qquad i(\eta) = i_0 \left[\exp\left(\frac{\eta}{\beta_a}\right) - \exp\left(\frac{-\eta}{\beta_c}\right) \right]$$

where:

$$(9) \qquad \beta_a = \frac{RT}{\alpha n F}$$

$$(10) \qquad \beta_c = \frac{RT}{(1-\alpha)nF}$$

i_0 – exchange current density in $\left[\frac{A}{m^2}\right]$, α – transfer coefficient usually equal 0.5, n – number of electrons in electrode reaction, F – Faraday constant, T – temperature in $[K]$, R – gas constant, i – current density on the surface, η – overpotential on the given electrode in $[V]$

$$(11) \qquad \eta = V_1 - E_o$$

where: V_1 is potential distribution on the corroding electrode and E_o is a potential of the electrode in equilibrium state, that is when anodic current is equal to the cathodic current and no net current i flows. Exact definitions of the above quantities together with adequate formulae can be found anywhere [7,8]. It is to point out, that above equations describe kinetics of the electrochemical reactions.

Boundary integral model
The aim of the analysis and modeling of cathodic protection system is to determine which parts of structure acts cathodically and which segments of structure acts anodically. The segment of a structure is said to be cathodically protected if in every point of this segment the applied potential is greater than potential difference that can exist on a metal surface caused by chemical reaction. Thus, the important quantity which must be calculated accurately for any successful cathodic protection scheme is the distribution of the potential and current density on the metal surface.

In regions Ω_1, Ω_2 and Ω_e we have following partial differential equations, respectively:

$$(12) \qquad \nabla(\gamma_1 \nabla V_1) = 0$$

$$(13) \qquad \nabla(\gamma_2 \nabla V_2) = 0$$

$$(14) \qquad \nabla(\gamma_e \nabla V_e) = 0$$

where Ω_1 and Ω_2 are compound material regions and Ω_e is region of electrolyte.

On boundaries Γ_{1e} and Γ_{2e} between compound material and electrolyte we have following Neuman's boundary conditions given by relation (8)

$$(15) \qquad \frac{\partial V_1}{\partial n} = -\mathbf{E} \cdot \mathbf{n} = -\frac{1}{\gamma_1} \mathbf{i}_1 \cdot \mathbf{n} = -\frac{1}{\gamma_1} i_{1n}$$

$$(16) \qquad \frac{\partial V_2}{\partial n} = -\mathbf{E} \cdot \mathbf{n} = -\frac{1}{\gamma_2} \mathbf{i}_2 \cdot \mathbf{n} = -\frac{1}{\gamma_2} i_{2n}$$

where $\mathbf{n}$ is the normal outward unit vector to the boundary.

All potentials have to fulfill Neuman's and Dirichlet's boundary conditions on all boundaries. Dirichlet's boundary conditions on boundaries Γ_{1e}, Γ_{12} and Γ_{2e} are given by relations [9]:

$$(17) \qquad V_1 = V_e = V_{1e} = V_{e1} \qquad \text{for } \mathbf{y} \in \Gamma_{1e}$$

$$(18) \qquad V_1 = V_2 = V_{12} = V_{21} \qquad \text{for } \mathbf{y} \in \Gamma_{12}$$

$$(19) \qquad V_2 = V_e = V_{2e} = V_{e2} \qquad \text{for } \mathbf{y} \in \Gamma_{2e}$$

Continuity condition of the normal component of the current density vector on each boundary yields Dirichlet's boundary conditions:

$$(20) \qquad \gamma_1 \frac{\partial V_1}{\partial n} = \gamma_e \frac{\partial V_e}{\partial n} \quad \text{on } \mathbf{y} \in \Gamma_{1e}$$

$$(21) \qquad \gamma_1 \frac{\partial V_1}{\partial n} = \gamma_2 \frac{\partial V_2}{\partial n} \quad \text{on } \mathbf{y} \in \Gamma_{12}$$

$$(22) \qquad \gamma_2 \frac{\partial V_2}{\partial n} = \gamma_e \frac{\partial V_e}{\partial n} \quad \text{on } \mathbf{y} \in \Gamma_{2e}$$

For homogeneous part Ω_1 the equation (12) becomes the Laplace equation, and the boundary integral equation associated with it may be derived after twice integrating it by parts [10]. For each of equations (12), (13) and (14) we can derive appropriate boundary integral equation:

(23)
$$\left.\begin{array}{l} c_{1e}V_{1e} \quad \mathbf{y} \in \Gamma_{1e} \\ c_{12}V_{12} \quad \mathbf{y} \in \Gamma_{12} \end{array}\right\} + \int_{\Gamma_{1e}} \frac{\partial G}{\partial n_{1e}} V_{1e} d\Gamma +$$
$$+ \int_{\Gamma_{12}} \frac{\partial G}{\partial n_{12}} V_{12} d\Gamma = \int_{\Gamma_{1e}} G \frac{\partial V_{1e}}{\partial n_{1e}} d\Gamma + \int_{\Gamma_{12}} G \frac{\partial V_{12}}{\partial n_{12}} d\Gamma$$

(24)
$$\left.\begin{array}{l} c_{21}V_{21} \quad \mathbf{y} \in \Gamma_{21} \\ c_{2}V_{2e} \quad \mathbf{y} \in \Gamma_{2e} \end{array}\right\} + \int_{\Gamma_{21}} \frac{\partial G}{\partial n_{21}} V_{21} d\Gamma +$$
$$+ \int_{\Gamma_{2e}} \frac{\partial G}{\partial n_{2e}} V_{2e} d\Gamma = \int_{\Gamma_{21}} G \frac{\partial V_{21}}{\partial n_{21}} d\Gamma + \int_{\Gamma_{2e}} G \frac{\partial V_{2e}}{\partial n_{1e}} d\Gamma$$

(25)
$$\left.\begin{array}{l} c_{e1}V_{e1} \quad \mathbf{y} \in \Gamma_{e1} \\ c_{e2}V_{e2} \quad \mathbf{y} \in \Gamma_{e2} \\ c_{as}V_{as} \quad \mathbf{y} \in \Gamma_a \cup \Gamma_s \end{array}\right\} + \int_{\Gamma_{e1}} \frac{\partial G}{\partial n_{e1}} V_{e1} d\Gamma + \int_{\Gamma_{e2}} \frac{\partial G}{\partial n_{e2}} V_{e2} d\Gamma +$$
$$+ \int_{\Gamma_a \cup \Gamma_s} \frac{\partial G}{\partial n} V d\Gamma = \int_{\Gamma_{e1}} G \frac{\partial V_{e1}}{\partial n_{e1}} d\Gamma + \int_{\Gamma_{e2}} G \frac{\partial V_{e2}}{\partial n_{e2}} d\Gamma + \int_{\Gamma_a \cup \Gamma_s} G \frac{\partial V}{\partial n} d\Gamma$$

where: $c_{1e} = c_{1e}(\mathbf{y})$ is a constant determined from the Cauchy's principal value integration of the Green's function singularity, $\mathbf{y}$ and $\mathbf{x}$ are the observation and integration points respectively, $\mathbf{n}_{1e}$ is a unit vector normal to the boundary and directed outside domain Ω_1. One has to remember that when normal vector is directed in opposite direction following formulae has to be fulfilled: $c_{2e} = 1 - c_{1e}$. Other constants are defined in similar way. Function $G(\mathbf{y},\mathbf{x})$ is the free space Green's function of the Laplace equation. For two dimensional problems it has a value

$$(26) \qquad G(\mathbf{y},\mathbf{x}) = -\frac{1}{2\pi} \ln |\mathbf{y} - \mathbf{x}|$$

To get final boundary integral equation relating only potentials on the problem and interzonal boundaries we have to multiply equation (12) by γ_1, equation (13) by γ_2, equation (14) by γ_e, to add them together and to utilize boundary conditions (17) - (22). In the resulting integral equation there are not partial normal derivatives of potentials on structure boundaries. This makes formulations of algebraic equation set easier and reduces of total number of these equations [11].

(27)

$$\left.\begin{array}{ll} [\gamma_1 c_{1e} + \gamma_e(1-c_{1e})]V_{1e} & \mathbf{y} \in \Gamma_{1e} \\ [\gamma_1 c_{12} + \gamma_2(1-c_{12})]V_{12} & \mathbf{y} \in \Gamma_{12} \\ [\gamma_2 c_{2e} + \gamma_e(1-c_{2e})]V_{2e} & \mathbf{y} \in \Gamma_{2e} \\ c_{as}V_{as} & \mathbf{y} \in \Gamma_a \cup \Gamma_s \end{array}\right\} +$$

$$+ (\gamma_1 - \gamma_e) \int_{\Gamma_{1e}} \frac{\partial G}{\partial n_{1e}} V_{1e} d\Gamma +$$

$$+ (\gamma_1 - \gamma_2) \int_{\Gamma_{12}} \frac{\partial G}{\partial n_{12}} V_{12} d\Gamma + (\gamma_2 - \gamma_e) \int_{\Gamma_{2e}} \frac{\partial G}{\partial n_{2e}} V_{2e} d\Gamma +$$

$$+ \int_{\Gamma_s} \frac{\partial G}{\partial n} V_s d\Gamma = \int_{\Gamma_a} \frac{\partial G}{\partial n} U_{app} d\Gamma + \int_{\Gamma_a} G \frac{\partial V_a}{\partial n} d\Gamma$$

In the above it was taken into consideration that the value of potential on Γ_a is equal U_{app} and current density normal to the boundary Γ_s is equal zero.

The boundary $\Gamma = \Gamma_1 \cup \Gamma_s \cup \Gamma_a$ is discretized into boundary elements, and values of V and i are approximated in terms of interpolation functions and nodal values. By adopting standard procedure of the boundary element method [12,13] we obtain the following simultaneous equations:

$$(28) \qquad [A]\begin{Bmatrix} V_i \\ i_i \end{Bmatrix} = [B]\begin{Bmatrix} b_i \\ d_i i(V_{ei} - E_o) \end{Bmatrix}$$

The above equation is solved by using usual Newton-Raphson iterative numerical procedure.

An illustrative example

As an illustrative example let us consider the distribution of the current density in two dimensions in the electrolyte and in conducting cathode composed of two different materials in situation depicted in fig. 2. The anode is assumed to be perfect conductor so distribution of the current inside it needs not to be calculated. The soil is simulated as rectangle and it is assumed to be sufficient large to have the current density parallel to the boundary. The conductivity of the soil is assumed $\gamma_e = 0.1$ S and that of the cathode $\gamma_1 = 1$ S and $\gamma_2 = 0.01$ S, respectively.
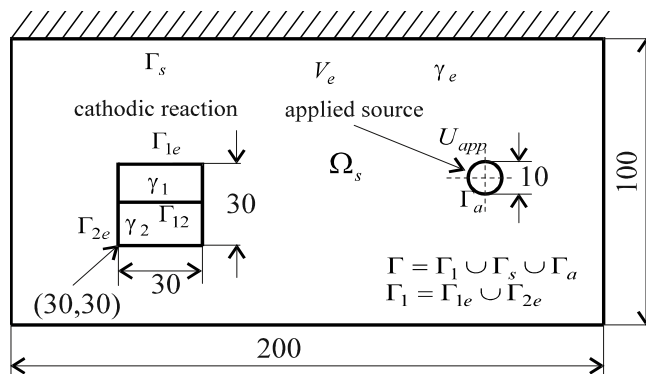

Fig. 2. Representation of the cell used to numerically simulate a secondary current distribution

Potential of the electrode in equilibrium state for an iron is equal $E_o = -0.8$ V and is assumed to be the some for both materials. Cathodic electrode kinetic parameters for $T = 20\ ^{\circ}C$ are taken from [11], table 3.2 and there are

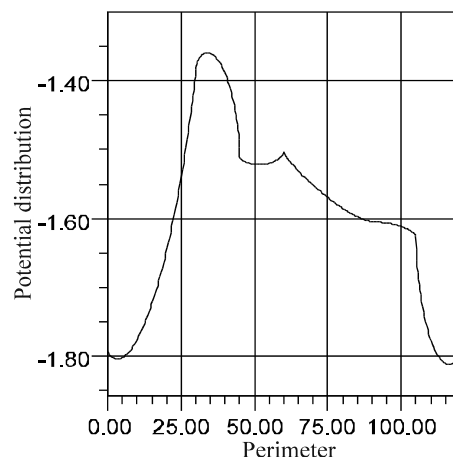$$(29) \qquad i_o = 10^{-3}\left[\frac{A}{m^2}\right], \qquad \beta_c = \beta_a = 1[V]\ .$$

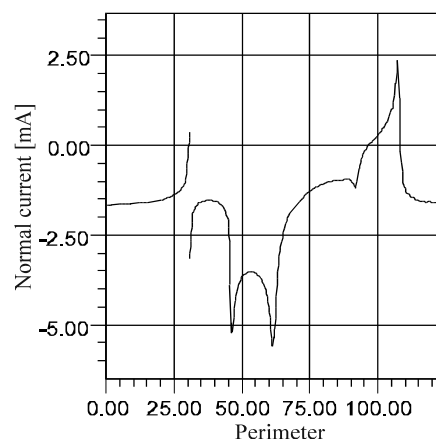Fig. 3. Potential distribution in volts along boundary Γ_1

Fig. 4. Current density distribution along boundary Γ_1

It is assumed that only activation polarization is present on the cathodic surface and contraction polarization effects are discarded. For these data the equation (28) has been solved. The potential and current density normal to the boundary along perimeter of the cathode is shown on Fig. 3 and Fig. 4, respectively.

The applied voltage $U_{app} = 1$ V. The total current supplied to the structure can be computed as

(30)
$$I = \oint_{\Gamma_1} \mathbf{i} \cdot \mathbf{n} \, d\Gamma = -\oint_{\Gamma_1} \gamma_e \frac{\partial V_e}{\partial n_1} \cos(\mathbf{i}, \mathbf{n}) d\Gamma$$

For our example $I = 0.1943$ mA.
Extension of the above procedure to taken into account concentration polarization is also possible.

Conclusions

In the case when protected cathode is made of a composed material, that is when the structure consist of more then one material of different conductivity and electro-chemical properties, the presented procedure is applicable without changes. The potential along boundaries between different mediums are to be defined and additional boundary conditions have to be written. The only problem which can be met is the convergence problem in Newton-Raphson iterative procedure, caused by highly non-linear dependence between current density an polarization.

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