Inverse Analysis of Galvanic Corrosion Using Fuzzy A Priori Information

Kenji AMAYA**, Jun TOGASHI** and Shigeru AOKI**

A new method for estimating the galvanic corrosion rate is developed. In the case where the electrochemical polarization curves of metal in the electrolyte are available, the galvanic corrosion rate can be estimated by solving the Laplace equation with boundary conditions based on the polarization curves. The polarization curves, however, are not always available. In such a case, it is necessary to estimate the density of the current across the metal surfaces from the potential values measured at points far away from the metal surfaces. Since this inverse problem is ill-conditioned, direct application of the conventional method results in an oscillatory solution. To circumvent this problem, we formulate an inverse problem and employ the boundary element method to estimate the polarization curves. In addition, the estimation accuracy is improved by using a priori information which is expressed as fuzzy membership functions. Sample problems are also presented to demonstrate the effectiveness of this new method.

Key Words: Boundary Element Method, Fuzzy Set Theory, Inverse Problem, Galvanic Corrosion, Polarization Curve, A priori Information

1. Introduction

It is known that when a less noble metal is electrically connected to a noble metal in a corrosive environment, the less noble metal corrodes more rapidly than when it is unconnected. This phenomenon is called galvanic corrosion and is observed frequently in places such as chemical plants, underground structures and offshore structures.

In order to reduce economic loss due to this corrosion, it is necessary to estimate the distribution of corrosion rate along the surfaces of structures. Since the galvanic corrosion rate is proportional to the density of current across the surface of the anode, the estimation can be made by solving the Laplace equation. The corresponding boundary conditions are nonlinear and determined from experimentally measured electrochemical polarization curves. To approximate the solution, boundary element method

has become popular in this kind of analysis⁽¹⁾⁻⁽⁶⁾.

In many cases, however, the polarization curve is not available since direct measurements of potential and current are usually difficult (e.g., for underground structures). Under these conditions, we must solve inverse problems where the distribution of current densities is estimated from measurable information such as potentials at points far away from the structures (e.g., on the ground or sea surface). This problem usually yields an ill-conditioned system of linear equations. Therefore, direct application of conventional numerical procedures to the system of equations results in an oscillatory solution which is not physically meaningful⁽¹⁾. In order to avoid this difficulty, a boundary element method using fuzzy clustering techniques was developed in the previous paper⁽⁶⁾. However, this method requires time-consuming and laborious work since various currents must be impressed and measurements must be made at many points.

In this paper, a more effective procedure for estimating the distribution of current density is proposed. First, the parameters which characterize the polarization curve are estimated with a

* Received 25th March 1994. Japanese original: Trans. Jpn. Soc. Mech. Eng., Vol. 59, No 562, A (1993) pp. 1562-1567, (Received 29th October, 1992)

** Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152, Japan

conventional boundary element method. Then, the estimation accuracy is improved by using a priori information which is expressed as fuzzy membership functions. Sample problems are solved by the new procedure to demonstrate its accuracy.

2. Galvanic Corrosion Inverse Problem

We assume that the surface of the electrolyte domain Ω is $\Gamma (= \Gamma_d + \Gamma_n + \Gamma_m)$ as shown in Fig. 1, where the potential values and current densities are prescribed on Γ_d and Γ_n , respectively, while Γ_m is the metal surface. If we assume that the electrolyte is homogeneous and that there is no accumulation or loss of ions, the electropotential within the electrolyte, ϕ , obeys the Laplace equation

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

where κ denotes the electrical conductivity of the electrolyte. Boundary conditions can be represented as follows.

$$\phi = \phi_0 \quad \text{on } \Gamma_d \quad (2)$$

$$q \left(\equiv \kappa \frac{\partial \phi}{\partial n} \right) = q_0 \quad \text{on } \Gamma_n \quad (3)$$

$$\phi, q : \text{unknown} \quad \text{on } \Gamma_m \quad (4)$$

where q is the density of current across the boundary and $\partial/\partial n$ the outward normal derivative. We note that the electrical potential is defined with reference to the metal and its sign is opposite to that employed in corrosion science where the potential is defined with reference to an electrode such as a saturated calomel electrode (SCE). ϕ_0 and q_0 are the prescribed values of the potential and the current density, respectively.

If the electrochemical polarization curves (i.e., the relationships between ϕ and q on Γ_m) of the metals are given, the galvanic corrosion rate can be estimated by solving the Laplace equation directly. However, the corresponding electrochemical polarization curves are not always available and an inverse approach is necessary to determine the solution. In the inverse analysis, the boundary conditions are not completely given but the potential values ϕ are assumed to be known at several points in the electrolyte as

Fig. 1 Governing equation and boundary conditions

$$\phi = \bar{\phi} \quad \text{at several internal points.} \quad (5)$$

The above condition compensates for the lack of polarization curves.

3. Inverse Analysis Method

Since the quantities on the boundary of the electrolyte (i.e., potentials and current densities on the surface of materials) are important in corrosion problems, the boundary element method is ideal for such analysis. Thus, we employ the boundary element method to discretize the domain. By adopting the standard procedure for the boundary element, the following simultaneous equations are obtained.

$$\kappa[H]\phi - [G]q = 0 \quad (6)$$

Here, ϕ and q are the vectors whose components are nodal values of ϕ and q , respectively. Also $[G]$ and $[H]$ denote the matrices determined by the geometry of the boundary Γ .

Since the number of unknowns is greater than that of equations, this problem is indeterminate. To make the problem determinate, the potential values measured at several points in Eq. (5) are supplied as extra conditions. However, if we choose the unknowns as ϕ or q on Γ_m , the required number of measuring points becomes as large as that of elements on Γ_m . It follows that the solution is likely to oscillate enormously, because the condition number of coefficient matrices increases with the required number of measurement points. Although the oscillation of the solution may be suppressed if the measuring points are taken near the surface of metals, in practice, measurements can be made only on the surface of electrolytes (e.g., on the sea or ground surface). To overcome this difficulty, a new method which utilizes a fuzzy clustering technique was introduced in our previous paper⁽⁶⁾. In this method, the polarization curves are first estimated by a fuzzy clustering technique, and then ϕ or q on Γ_m are determined from the estimated polarization curves. However, this method is time-consuming and requires laborious work, because various currents must be applied and measurements must be made at many points.

Here, we introduce an efficient procedure which avoids the shortcomings of the fuzzy clustering method. The key point of this procedure is that the polarization curves of anode and cathode are represented by the following equations.

$$f_1(q) = \alpha_1 \sinh^{-1} q + \beta_1 \quad \text{for anode} \quad (7)$$

$$f_2(q) = \alpha_2 \sinh^{-1} q + \beta_2 \quad \text{for cathode} \quad (8)$$

where $\alpha_1, \beta_1, \alpha_2$ and β_2 are the parameters to be estimated by the inverse analysis. Examples of the polarization curves according to Eqs. (7) and (8) are shown in Fig. 2, where cast iron and stainless steel are modeled for the anode and cathode, respectively.

Fig. 2 Polarization curves

If the location of the interface of anode and cathode, x_0 , is not prescribed, x_0 must be included as a parameter to be estimated. By assuming appropriate initial values of the five unknown parameters $\alpha_1, \beta_1, \alpha_2, \beta_2$ and x_0 and solving the direct problem, all values of ϕ^n and q^n on Γ can be determined. Let ϕ_j and $\bar{\phi}_j$ denote the calculated and measured potential values at point j on the electrolyte surface, respectively. To obtain an estimate of polarization curves, we must minimize the following objective function $g(\alpha_1, \beta_1, \alpha_2, \beta_2, x_0)$

$$g(\alpha_i, \beta_i, x_0) = (\bar{\phi}_j - \phi_j)^2 \quad (i=1, 2 \quad j=1 \sim k) \quad (9)$$

where k is the total number of measuring points. A flow chart which illustrates the procedure of this analysis is shown in Fig. 3. In the analysis, iterations are performed until the value of function g becomes smaller than the tolerance ε as,

$$\varepsilon = k(\delta\bar{\phi})^2 \quad (10)$$

where $\delta\bar{\phi}$ represents the error of the measurement and ε is chosen as a small positive number. Once the convergence is achieved, the distribution of current density on the surface of metals can be determined by solving the direct problem with the estimated parameters.

4. Example of Numerical Analysis

Let us consider a two-dimensional galvanic field as shown in Fig. 4, where the potential values are given at five measuring points on the top surface of the electrolyte. The boundary is discretized into 120 constant elements as shown in Fig. 5. The conductivity of the electrolyte is assumed to be $\kappa=1.0$ [S/m]. First, a direct problem is solved by assuming the parameters characterizing the polarization curves of anode and cathode to be $\alpha_1=-0.1, \beta_1=0.7, \alpha_2=-1.0$ and $\beta_2=0.0$, and the position of the interface to be $x_0=0.0$. The computed values of potential at the five measuring points are rounded off to three significant figures to account for the measuring errors of a real electrometer. These values are used as the values of $\bar{\phi}_j$ in the following inverse analysis.

The aim of the inverse analysis is to estimate the

Fig. 3 Algorithm

Fig. 4 Example problem

Fig. 5 Boundary element discretization

distribution of the current density by minimizing the objective function g . In the minimization, the conjugate gradient method⁽⁸⁾ is employed with the convergence criterion, $g \leq 1.25 \times 10^{-6}$ [v²] or $\varepsilon = 1.25 \times 10^{-6}$ [v²] in Eq. (10). Figure 6 shows the calculated current density distribution on the metal surface, where the solid curves indicate the exact distribution (i. e., prescribed boundary condition in the direct problem) and white circles are the solution estimated by the inverse analysis. The figure shows a good estimate by the inverse analysis even though the number of measuring points is only five and they are on the electrolyte surface (far away from the metal surface). However, the estimated location of the interface, x_0 , is found to be slightly different from the exact location. The current density near the interface, which is critical in corrosion problems, also shows greater error.

Fig. 6 Current density distribution on metal surface

5. Application of Fuzzy A Priori Information

In this section, we present a method of improving the estimation accuracy. The mode of convergence in the inverse analysis of the previous section is shown in Fig. 7, where the horizontal and vertical axes indicate α_1 and g , respectively, and the arrow $\downarrow$ indicates the exact solution of α_1 . The figure shows that the iteration (see Fig. 8) has ended before the estimated value of α_1 approaches sufficiently close to the exact value. This occurs independently of the value of ε . Similar phenomena are also observed for the other parameters. Since the iteration does not converge, this implies that the solution depends on the initial values. The parameters which satisfy the following equation occupy a finite domain (see Fig. 8).

$$g(\alpha_i, \beta_i, x_0) < \varepsilon \quad (i=1, 2) \quad (11)$$

Hence, let us examine the Hessian matrix of the objective function g :

$$\begin{bmatrix} \frac{\partial^2 g}{\partial \alpha_1^2} & \frac{\partial^2 g}{\partial \alpha_1 \partial \beta_1} & \cdots & \frac{\partial^2 g}{\partial \alpha_1 \partial x_0} \\ \frac{\partial^2 g}{\partial \beta_1 \partial \alpha_1} & & & \vdots \\ \vdots & & & \vdots \\ \frac{\partial^2 g}{\partial x_0 \partial \alpha_1} & \cdots & \cdots & \frac{\partial^2 g}{\partial x_0^2} \end{bmatrix} \quad (12)$$

The eigenvalues of the Hessian matrix at a convergent point are calculated as follows.

$$\begin{Bmatrix} 0.00004282 \\ -0.006943 \\ 0.319 \\ -0.642 \\ 6.609 \end{Bmatrix} \quad (13)$$

It is seen that the eigenvalues are extremely small in two directions defined by the corresponding eigenvectors. Not only the gradient but also the change of gradient of g is extremely small in the two directions. This result suggests that the parameters which satisfy Eq. (11) occupy approximately a two-dimensional subdomain in the five-dimensional domain defined by the five parameters of the polariza-

Fig. 7 Mode of convergence of α_1 Fig. 8 Area for $g \leq \varepsilon$

tion curves. This is the reason why the minimization problem of g is indefinite.

In order to identify this subdomain quantitatively, we fix α_1 and α_2 while the other three parameters are considered as independent variables. Then we carry out minimization of function g for 25 combinations ($= 5 \times 5$) of fixed α_1 and α_2 . Although it is obvious that the exact solution exists in this subdomain, it is impossible to focus it better by just the information on the measured values of ϕ .

Here, we consider fuzzy a priori information such as "the structure is made of copper and cast iron" and "the location of the interface is about here". Membership functions which represent this fuzzy a priori information⁽⁹⁾ are shown in Fig. 9, where $\mu_i (i=1 \sim n)$ denote the membership functions and n is the total number of information items.

Let B_i denote fuzzy sets of parameters and A the crisp set of parameters which satisfy Eq. (11). The solution can be obtained by the following procedure (see Fig. 10).

1. Define C as $C = A \cap B_1 \cap B_2 \cdots \cap B_n$.
2. Take the center of gravity of C as the solution.

The obtained current density distributions for the example problem in the previous section are shown in Fig. 11, where $\bullet$ and $\circ$ represent the values estimated with and without a priori information, respectively. It is found that the accuracy of the solution has been improved by taking account of a priori information. The membership functions shown in Fig. 9 were used

Fig. 9 Membership functions

Fig. 10 Fuzzy sets on parameter space

Fig. 11 Improvement of estimation accuracy using fuzzy a priori informations

for this problem.

In order to demonstrate the applicability of the method using fuzzy a priori information to practical problems, we consider two more example problems. In the first, the electrolyte is sea water with conductivity, k [S/m], equal to 4.6 and all other conditions are

Fig. 12 Potential distribution on the surface of metal in sea water

Fig. 13 Current density distribution on the surface of metal in sea water

Fig. 14 Potential distribution on the surface of metal of an underground structure

the same as those given in the previous example. Because of the high conductivity, the potential values on the electrolyte surface change only slightly. This means that the problem is ill-conditioned. Figures 12 and 13 show the estimated distributions of potential and current density, respectively. We observe excellent agreement between the estimated and exact solutions.

The last example concerns an underground structure. The conductivity of the electrolyte is equal to 0.05 [S/m]. Because a limited part of the anode near the interface corrodes, there is only a small effect on the electrolyte surface. This makes the problem

Fig. 15 Current density distribution on the surface of metal of an underground structure

ill-conditioned. The location of the interface is $x_0 = 0.3$ [m] and the other conditions are the same as in the previous example. Figures 14 and 15 show the estimated potential and current density distributions, respectively. It is seen that a good estimation has been obtained.

6. Conclusion

A new inverse analysis method for estimation of the galvanic corrosion rate is developed. The procedures of this method can be summarized as follows.

- (1) Assume that polarization curves are represented by appropriate model functions.
- (2) Take the coefficients of the functions as unknown parameters.
- (3) Define the objective function g to be the square norm of residuals between measured values and analyzed values.
- (4) Determine the set of parameters which satisfy $g < \varepsilon$, where ε is tolerance.
- (5) Represent fuzzy a priori information with membership functions.
- (6) Determine the values of parameters by fuzzy

reasoning from the results of procedures (4) and (5).

- (7) Calculate current densities using the polarization curves with the obtained parameters.

We have solved a few example problems using this method in order to demonstrate the estimation accuracy. This method can be applied to many problems which require inverse analysis. In noncorrosion problems the polarization curves are simply exchanged with the relationship between physical quantities in boundary conditions.

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