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# Computational Corrosion Analysis for Protection of Naval Materials by Design

Presented at the Eighth Inter-Naval Corrosion Conference, 11-15 April 1988, Royal Naval Engineering College, Manadon, England

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## PREFACE

This document summarizes the development of computational corrosion analysis developed and applied at the Naval Underwater Systems Center since the mid-1970's. The paper was an invited presentation at the Eighth Inter-Naval Corrosion Conference held at the Royal Naval Engineering College, Manadon, England, 11-15 April 1988.

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A numerical method has been developed to predict corrosion states of wetted dissimilar metals in the electrolyte of a galvanic system. The method employs the finite element technique with computer implementation to solve for the potential distribution throughout the system of arbitrary geometry. The method fully accounts for the metals' nonlinear electrode kinetics and imposes charge conservation to agree with mixed potential theory.

Computational corrosion analysis is now a mature technology and has been used successfully in performing corrosion-resistant design and in addressing corrosion problems. This paper describes the theory behind this development, the uses of this method, an analysis problem already solved, and current research extending this method to microcorrosion problems. Keywords: computer simulation; electronics

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## INTRODUCTION

Interest in the quantitative prediction of electric current and potential distributions in conductive media has existed for at least five decades[1,2], with some background mathematics evident over a century ago.[3] Attempts to quantify these predictions for the specific discipline of electrochemistry are traceable back nearly as far,[4] the motivation being applications in corrosion prediction and protection, electrodeposition, and battery technology. The history of this problem depicts a slow development via analytical methods for thirty-five years until there was much more rapid advancement using numerical methods that began in the late 1970's. This paper describes the specific problem to be solved in terms of the partial differential equation describing electric fields in a conductive medium and the boundary conditions describing the nonlinear electrode kinetics (electrodics) involved. Subsequently, it outlines the formulation of the finite element scheme to solve the boundary value problem, provides a descriptive example, and indicates future work.

The problem considered herein is numerical prediction of the electric potential distribution in an electrolyte due to the presence of submerged dissimilar metals and/or externally-applied impressed currents (figure 1). The corresponding "applied" or net current density may be deduced from the electrochemical potential value adjacent to a wetted metal surface, using a potentiostatic polarization curve for that particular metal/electrolyte system. Further, depending on the proximity of other reactions, the predicted potential state of the metal surface may be indicative of the current density associated with metal dissolution, from which may be calculated the metal dissolution rate using Faraday's law. The method described herein uses existing numerical techniques to predict the electrochemical potential for a system of general geometry, involving several dissimilar wetted metals using physically significant analytical expressions; it incorporates the generally nonlinear electrode kinetics (polarization behavior) of the constituent metals; and it adheres to the principals of charge conservation and the modern mixed potential theory of electrode kinetics. The method is applicable to practical situations involving galvanic corrosion, sacrificial anode, and impressed current cathodic protection designs, electrodeposition, and battery technology.

The finite difference, finite element, and boundary integral element computational methods were examined. The application of each to the modeling of electrochemical phenomena and their particular advantages were considered. Since the finite element method was found to have more advantages,[5] it was pursued with earnest and is the only method treated in this paper.

ANALYSIS

## DIFFERENTIAL EQUATION

The Fourier-Ohm fundamental law of conduction governs flow in a conductive medium for any field problem. Figure 2 shows an infinitesimal element of conducting medium for which $\phi$ is the electric potential at the center of the element. For the conducting medium, conservation of charge is preserved in the steady state, i.e.,

$$\sum i \simeq \nabla \cdot i = \frac{\partial q}{\partial t} = 0 , \tag{1}$$

where   q is the charge in the element,
        $\sigma$ is the uniform electrical conductivity of the medium,
        $\phi$ is the electric potential at a point,
        x is one linear dimension, and
        t is time.

Considering a statement of Ohm's law, where $E = -\nabla \phi$,

$$i = \sigma(-\nabla \phi), \tag{2}$$

which allows conservation of charge to be represented in terms of potential

$$\nabla \cdot i = \nabla \cdot (-\sigma \nabla \phi) = -\sigma \nabla^2 \phi = 0$$

$$\nabla^2 \phi = 0, \tag{3}$$

the Laplace equation. Most electrochemical problems are considered to be quasi-steady state. It is important to note that this equation preserves conservation of charge, whereas the familiar Poisson equation does not. Therefore, the formulation of this method must be based on the Laplace equation, and any applied current density must be accounted for in the application of the boundary conditions.

## BOUNDARY CONDITIONS

Kasper[4] described a number of generic boundary conditions for the field problems represented by the Laplace equation. The three types of boundary value problems therein described have been used by several researchers[6,7,8] over the years to describe the electrochemical problem. Those mathematical descriptions are too primitive to describe such problems with real electrode metals over the general range of potentials to which they are exposed. The general case of electrodic polarization is a nonlinear Neumann boundary value problem and may be referred to as a fourth boundary value problem of the theory of the potential. This represents the general case of electrodic polarization behavior and is the primary aspect of the method described in this paper.

Bockris and Reddy[9] referred to the Butler-Volmer equation for the relationship between the electrochemical potential (overpotential) and the

net current density across the metal/electrolyte interfacial double layer. To develop this into a mathematically valid boundary condition for the electrochemical boundary value problem, the total electrochemical potential was used as the state variable, its value being the measured electrode potential difference using a reference electrode, herein denoted potential ($\phi$). This was previously discussed in full detail.[5] The experiments for these measurements are standard potentiostatic polarization tests.[10]

Electrodic polarization curves for metal in electrolytes are developed experimentally using (typically) potentiostatic polarization methods. The curves for most metals exhibit characteristic shapes with some anomalies. To fit experimental polarization curves to the theoretical model, it is desirable to transform the Butler-Volmer equation into the Tafel equation, in terms of the customary polarization parameters, for each participating reaction. Thus,

$$i_{net} = i_0 \{\exp(\eta/\overleftarrow{\beta}) - \exp(\eta/\overrightarrow{\beta})\}, \tag{4}$$

where    $i_0$    is the exchange current density,
         $\eta$    is the overpotential, $\eta \equiv \phi - \phi_{rev}$, and
         $\beta$    is the Tafel slope of the polarization curve, with the arrow
             ($\leftarrow$ or $\rightarrow$) indicating the direction of the reaction
             (reduction or oxidation),

and the sign of each $\eta$ and $\beta$ must be considered.

Figure 3 shows the total applied current polarization curved summed from the partial reactions shown in figure 4. The metal dissolution (anodic) behavior (M) is described by

$$\overrightarrow{\eta}_M = \overrightarrow{\beta}_M \log(i_0/i_{0_M}) , \tag{5}$$

which is easily inverted to give current as an explicit function of potential, i.e.,

$$i_M = i_{0_M} 10^{\overrightarrow{\eta}_M/\overrightarrow{\beta}_M} . \tag{6}$$

It will be noticed that the overpotential ($\eta$) is assigned a subscript to indicate which reaction and an arrow ($\leftarrow$ or $\rightarrow$) to indicate which partial of the reaction the partial current density is being calculated for, since the total applied current density on a polarization curve is herein being assembled as a sum of the current densities of the component partial reactions.

The combined activation-controlled and diffusion-controlled portions of the principal reduction (R) process (which for sea water is $O_2 + H_2O + 4e- \rightarrow 4OH-$) is described by Stern and Geary[11] as

$$\overrightarrow{\eta}_R = \overrightarrow{\beta}_R \log(i_R/i_{0_R}) + 2.3 (RT/nF) \log(1 - i_R/i_L) . \tag{7}$$

which is transcendental in nature and cannot be inverted to give current as an explicit function of potential. An expression that approximates this combined reduction behavior (both the Tafel and the diffusion-limited regions) in that it follows Tafel behavior for small overpotentials ($\eta$) but is asymptotic to the diffusion-limited current density ($i_L$) is

$$i_R = \frac{i_{o_R} 10^{\overleftarrow{\eta}_R / \beta_R}}{\left\{ 1 + \left[ \frac{i_{o_R} 10^{\overleftarrow{\eta}_R / \beta_R}}{i_L} \right]^{K_R} \right\}^{1/K_R}} \tag{8}$$

where $K_R$ is a constant affecting the curvature at the transition from Tafel to diffusion-limited behavior. This expression reduces to the Tafel behavior for current densities away from $i_L$ (denominator $\simeq 1$) but becomes asymptotic to $i_L$ with decreasing potential.

Similar expressions for passivity, transpassivity, and water breakdown have been used[5] to complete a general expression for the electrodic polarization behavior metal-electrolyte systems. The partial current densities from the participating reactions are then summed to arrive at a total applied current density polarization curve and written into a boundary current density subroutine for the computation. As an example, figure 5 shows a polarization curve synthesized using the expressions above for elemental Fe in 3 percent NaCl solution at 25°C superimposed over the curve for Fe under the same conditions as measured by Bennett.[12]

Other researchers[13,14] have proposed alternate curve-fitting procedures following the expression presented by Stern and Geary.[11] These methods require intelligent first guesses for each appropriate electro-chemical parameter and each contributing reaction to calculate a first-trial polarization curve. The measured and simulated polarization curves are co-plotted to show the deviations of the simulated from the measured. The the electrochemical parameters are then massaged by trial-and-error or solved by numerical methods to minimize the deviations.

## FORMULATION OF THE FINITE ELEMENT METHOD

The finite element method involves discretizing the electrolyte continuum into a number of subdomains, or elements, and then formulating the potential solution in a piecewise manner over each element using one of several approaches to be described. The element formulations are then summed over the entire electrolyte domain, resulting in a system of simultaneous equations which may be solved by any of a number of methods for a steady-state potential distribution.

The finite element method grew out of extensions of matrix structural analysis techniques which existed for discrete-member structures (e.g., trusses) with a finite number of member interconnection points. Subsequent developments involved either combining pertinent energy forms of a system or transforming the elasticity equations into energy functionals to formulate

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the finite element equations. In application to electrochemical phenomena, these methods all fail, either by misrepresentation of the electrolyte continuum, assumption of thermodynamic equilibrium, or nonconservation of electrical charge.

A fourth approach to formulation of the element properties in the finite element method is the method of weighted residuals (MWR). This approach is more generalized in that it avoids those assumptions. This approach employs successive approximations by trial functions over the subdomain of the element of electrolyte. The special case of the MWR wherein the finite element interpolation functions are used for the weighting functions is the Galerkin method, formulated rigorously in reference 5 for the special case of the electrochemical problem. In this formulation, the important constraint of conservation of charge is introduced.

The set of equations formulated for the electrochemical problem shares two difficulties with that developed using the variational approach. First, the applied current density boundary condition ($i_p$) is a function of the local solution ($\emptyset$) itself. This situation requires an iteration of solutions until the boundary conditions ($i_p$) and the final solution $\{\emptyset\}$ are consistent according to polarization curve(s) of the electrode material(s). Secondly, the nature of electrochemical boundary conditions, that is, specified current densities, not specified potentials, gives a mathematically singular conductivity matrix for the electrolyte. Each of these apparent deficiencies may be overcome by performing a (pseudo-) transient solution[5] out to a long time period arriving at steady-state. It should be pointed out that this is not real time, simulating any effects of time on the state of the system. It is only performed to allow updating of the nonlinear electrodic boundary conditions ($i_p = i_c(\emptyset)$) and to use a transient solution scheme to solve the statically singular matrix.

The governing Laplace equation (3) may be subject to the Dirichlet boundary condition, i.e.,

$$\emptyset = \emptyset_B = \text{constant, on surface } S_1, \tag{9}$$

and the natural (Neumann) surface flux boundary condition, i.e.,

$$\sigma_{xx} \frac{\partial \emptyset}{\partial x} n_x + \sigma_{yy} \frac{\partial \emptyset}{\partial y} n_y + \sigma_{zz} \frac{\partial \emptyset}{\partial z} n_z + i_p = 0,$$
$$\text{on surface } S_2, \tag{10}$$

where $n_x$, $n_y$, and $n_z$ are the direction cosines of the vector normal to the surface $S_2$, and $i_p$ is the polarization current density. For no polarization current ($i_p=0$), the boundary condition prescribes $S_2$ as an insulated surface and equation (10) reduces to the homogeneous natural boundary condition. The desired solution (potential distribution) is that which satisfies the field (Laplace) equation subject to the $S_1$ and $S_2$ boundary conditions.

The potential may be approximated within element (e) using the interpolation functions ($N_i$) for the element, i.e.,

$$\phi^{(e)} \approx \hat{\phi}(e) = \sum_{j=1}^{m} N_1(e)\ \phi(e) = [N]\ (e)\ \{\phi\}(e) \text{ , and}$$

$$\frac{\partial\phi}{\partial x}(e) = \left[\frac{\partial N}{\partial x}\right]\{\phi\}^{(e)} \quad , \tag{11}$$

where $\hat{\phi}(e)$ is the approximate potential at any point within an element, $N_i$, are the interpolation functions defined over the element, and $\{\phi\}^{(e)}$ is the vector of undetermined nodal values of the potential for all nodes of the element (e). The use of the element interpolation functions as the weighting functions is the special case of the MWR known as the Galerkin method.

Galerkin's criterion to minimize the residual (R) of a partial differential equation (P.D.E.) is

$$\int N_i(P.D.E.)dV = 0, \tag{12}$$

and as applied to the expanded Laplace differential equation is

$$\int_{V^{(e)}} N_i\ \sigma\ \left(\frac{\sigma^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2}\right)dV^{(e)} = R = 0. \tag{13}$$

To introduce the surface current density boundary condition (equation (10)), equation (13) is integrated by parts to reduce its order to that of equation (10) so that the $S_2$ boundary condition may be introduced. Performing this integration and incorporating the assumption that electrolyte conductivity is ($\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \sigma$), the governing equation becomes[5]

$$-\sigma\int_{V^{(e)}}\left(\frac{\partial\phi}{\partial x}^{(e)}\frac{\partial N_i}{\partial x} + \frac{\partial\phi}{\partial y}^{(e)}\frac{\partial N_i}{\partial y} + \frac{\partial\phi}{\partial z}^{(e)}\frac{\partial N_i}{\partial z}\right)dx\ dy\ dz$$

$$+\sigma\int_{S_2^{(e)}}\left(\frac{\partial\phi}{\partial x}^{(e)}n_s + \frac{\partial\phi}{\partial y}^{(e)}n_y + \frac{\partial\phi}{\partial z}^{(e)}n_z\right)N_i\ dS_2^{(e)} = 0. \tag{14}$$

where $dV^{(e)} = dx\ dy\ dz$ and $dy\ dz = n \cdot dS_2$. The second term allows introduction of the natural (surface current density) boundary condition of equation (10). Incorporating this, summing over all elements (e) of the electrolyte domain, and using the definitions of equation (11) results in

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$$-\sum_e \sigma \int_{V^{(e)}} \left[ \left[\frac{\partial N}{\partial x}\right] \{\phi\}^{(e)} \frac{\partial N_i}{\partial x} + \left[\frac{\partial N}{\partial y}\right] \{\phi\}^{(e)} \frac{\partial N_i}{\partial y} + \left[\frac{\partial N}{\partial z}\right] \{\phi\}^{(e)} \frac{\partial N_i}{\partial z} \right] dxdydz$$

$$+ \sum_e \int_{S^{(e)}} i_p N_i \, dS_2^{(e)} = 0 , \qquad (15)$$

which is a set of equations, one for each point in the electrolyte domain. Herein, the polarization flux has been introduced as an integral part of the P.D.E., rather than a load, preserving conservation of charge. Introduction of the fixed potential (Dirichlet) boundary condition (equation (9)) on surface $S_1$, if appropriate, is accomplished upon assembly of the element equations, by constraints on appropriate rows and columns of the equation matrices.

The solution of equation (15) for the vector of nodal potentials requires user input of conductivity ($\sigma$), current density boundary conditions ($i_p = i_p(\phi)$), fixed potential boundary conditions ($\phi = \phi_B$ = constant), when applicable, and, of course, the discretized geometry of the continuum. The interpolation functions are predefined for a particular element type (e.g., linear, parabolic, cubic, etc., functions of position within the element) and geometry. The method proceeds using a first approximation of potential distribution $\{\phi\}$, which is then recalculated as a solution to the boundary value problem with the updated surface fluxes $i_p$ until the solution changes less than a prescribed tolerance upon recalculation. The result is a vector of nodal potentials $\{\phi\}$ from which may be calculated interior potentials using the interpolation functions. Current fluxes may be calculated secondarily from the conductivity and the gradients of potential.

To enhance this matrix equation with an iterative capability to update the boundary fluxes ($i_p$) consistent with the adjacent potential values ($\phi$), a pseudo-transient solution scheme is used with time as a dummy iteration parameter. In this scheme, a term analogous to a heat storage term is added to equation (15). With generalization of the second term,

$$\left[ \sum_e \int_{V^{(e)}} NT \, \rho \, c \, N \, dV \right] \{\dot{\phi}\}^{(e)} + \left[ \sum_e \sigma \int_{V^{(e)}} \left[\frac{\partial N}{\partial x}\right] \frac{\partial N_i}{\partial x} + \ldots dV \right] \{\phi\}^{(e)}$$

$$= + \left\{ \sum_e \int_{S_2^{(e)}} i_p N_i \, dS_2^{(e)} \right\}. \qquad (16)$$

Herein, the first term is the storage matrix [M], the second term is the conductivity matrix [K], and the third is the flux vector {Q}. With the Galerkin approximation given for a point in (pseudo-) time (equation (16)), what remains to be developed is a scheme to iterate to a solution using pseudo-time as the iteration parameter.

The central finite difference (or Lee's) operation is one method of progressing in time allowing determination of the nodal potential distribution $\{\phi\}$ in terms of the potential history $\{\phi_t\}$, $\{\phi_{t+\Delta t}\}$, the mass [M] and conductivity [K] matrices, and the flux vector $\{Q\}$, all of which are evaluated at time t. This allows solution of these equations without iteration.

It should be noted at this point that the "operator" matrix, which includes the first two terms of equation (16), must be non-singular in order for the solution to be performed; that is, either [M] of [K] must be non-zero. If no Dirichlet (fixed potential) boundary conditions are present (as generally true for electrochemical problems), then [K] is singular relative to a reference potential level; the particular polarization behavior that provides for a unique solution is not manifested in [K] (or [M]), so the polarization condition does not overcome any possible singularity in the operator matrix. Since [K] is usually singular in electrochemical problems, a non-singular [M] matrix must be introduced, so that the effective operator matrix becomes:

$$\left[\frac{1}{2\Delta t}\,[M]\right] = \left[\frac{1}{2\Delta t}\,\sum_e \int_{V^{(e)}} N^T \rho\, c\, N\, dV(e)\right], \tag{17}$$

with the mass density ($\rho$), the specific capacity (or capacitivity, c), and the time step ($\Delta t$) being non-zero.

In equation (16), the current density boundary conditions are incorporated in the right-hand side as a flux vector $\{Q\}$. The components of the flux,

$$\{Q\} = \{Q_1,\ \ldots\ Q_i,\ \ldots\ Q_E\}, \qquad i = 1(1)E, \tag{18}$$

are calculated individually for each element surface on a metal boundary of the electrolyte, according to the relationship developed in Reference 5, and the appropriate polarization parameters determined for each element's metal/electrolyte system.

Much of the previous discussion regarding formulation of the finite element analysis of electrochemical phenomena has referred to the interpolation functions [N] which describe the relationship between the potential at any point within an element $\phi^{(e)}$ and the potentials at ' ` nodes of the element $\{\phi\}^{(e)}$ (equations (11)). Indeed, these interpolation functions are used as the weighting functions in the Galerkin weighted residual approach to generating the finite element equations. The choice of element type (i.e., geometrical shape and interpolation function) is extremely problem-dependent, both to model the geometry of the problem and to accommodate the accuracy of the expected solution. Reference 5 depicts a number of finite element types derived thus far and tabulates the interpolation functions for them.

DESCRIPTIVE EXAMPLE:  SHIPBOARD SEA WATER TANK

The preceding sections have described the development, formulation, and implementation of a method for electrochemical analysis using the finite element method.  This section will briefly describe an example of the application of this method, with correlation to the measured solution to the problem (the problem and solution are detailed in reference 15).

STATEMENT OF THE PROBLEM

On most seagoing ships there are sea chest cavities and internal sea water tanks that are subject to the corrosive effects of sea water on the wetted metallic surfaces.  Cathodic protection of these cavities is usually afforded by an array of zinc sacrificial anodes attached to their inside surfaces, the amount and locations of zincs chosen by design tradition, experience, and rules-of-thumb rather than by rigorous design.

One such tank on a class of seagoing ships (figure 6) experienced internal fouling with visible paint chips and calcareous deposits lining the tank bottom after only several months of service.  Further inspection revealed that the zinc anodes in the tank were in virtually new condition, whereas the zincs in other cavities showed signs of significant dissolution.

This evidence founded speculation that perhaps the amount of zinc used was excessive for the protection it was required to afford, especially in light of the common belief that Monel does not have a galvanic effect on steel as detrimental as might be inferred from their relative open-circuit corrosion potentials.  The peeled paint could have been caused by poor application procedures and/or by the presence of significant cathodic reaction ($O_2 + 2H_2O + 4e- \rightarrow 4OH-$) at the interface between the paint and the substrate metal.  The products of this reaction can couple with those of the carbon dioxide system in sea water ($CO_2 + H_2O \rightarrow 2H^+ + CO_3^{2}$) and with the calcium ions in sea water ($Ca^{+2} + 2OH- + 2H^+ + CO_3^{2} \rightarrow 2H_2O + CaCO_3(ppt)$) to form calcareous deposits, often an indication of excessive cathodic oxygen reduction reaction.  The lack of zinc degradation indicates a low degree of oxidation (dissolution) reaction on the zinc surface, perhaps explained by an overly-large anode/cathode area ratio.

APPROACH

The overprotection hypothesis was evaluated by a coordinated test and analysis program. The electrochemical potentials at representative locations throughout the tank were measured over a three-day period while the tank was flooded with sea water;[15] these potentials were then related back to the materials' polarization curves to ascertain the electrochemical state throughout the tank.  Analytically, the computational electrochemical analysis method developed herein was applied to draw a correlation with the measurement test and predict the effects of candidate corrective measures.

MATERIAL MEASUREMENTS

The electrochemical behaviors of the components in sea water under these particular conditions (temperature, exposure time, velocity, etc.)

were completely described by their potentiostatic polarization curves developed under those conditions for the constituent metals in this system: steel (painted and unpainted), nickel-aluminum bronze, Monel, and zinc. These tests were performed in a laboratory using a digital potentiostat and a standard ASTM polarization cell with fresh sea water of conductivity 0.035 mho/cm at 15°C, after several days' pre-exposure. The polarization curves developed from the first two of these tests are shown in figures 7 and 8 as potential ($\phi$, mV vs. a Ag-AgCl reference electrode) versus applied current density (i, mA/cm$^2$).

ANALYSIS

A finite element galvanic analysis was performed using the theory and the development of this computational method described herein. A finite element model of a repeated section of the cavity (electrolyte) was modeled as an axisymmetric conductive medium. Border element faces were given applied current density boundary conditions, which varied as a function of potential according to the measure polarization curves. The problem was solved with a pseudo-transient iterative solution to update the nonlinear polarization function to correspond to the interim distribution of potentials. Convergence occurred when the residuals in the numerical solution reduced to less than a prescribed 10 mV tolerance throughout (i.e., steady state). The finite element analysis used the MARC finite element computer program,[16] heat option, modified for electroconductive analysis. The analysis was performed on a VAX 11/782 computer at the Naval Underwater Systems Center with a run time of approximately two and one-half hours.

RESULTS AND RECOMMENDATIONS

The steady-state potential distribution resulting from this analysis with the material properties of figures 7 and 8 is shown in figure 9 as isopotential contour lines over the electrolyte region (in mV vs. AgAgCl). A further analysis was made with a reduced number of zinc anodes -- two versus the five in existence. The results of the analysis with the final choice of anode location is given in figure 10.

The potentiostatic polarization curves developed for the constituent materials of this problem showed familiar behavior. The shape of the polarization curve for painted steel is atypical, but reasonable; the high-resistance paint layer allows polarization of the surfaces with extremely low applied current densities. This implies that painted and unpainted steels behave as different metals in this electrolyte. These curves allow a determination of electrochemical state from the potentials measured in the field test.

The measured electrochemical potentials inside the tank are consistent with intuitive qualitative predictions, based on the metals and the amounts present. Potentials on the cathodic side for Monel (on the order of -600 mV vs. Ag-AgCl) are clearly prevalent in the left-hand (smaller diameter) portion of the cavity. In the large diameter portion of the tank, the potentials are nearer the corrosion potential of the zinc (on the order of

-850 to -900 mV vs. Ag-AgCl), indicating a large degree of polarization from the corrosion potential of the painted steel. The overprotection hypothesis was enforced by these results.

Similar results were obtained computationally from the finite element analysis. Figure 9 indicates lower potentials throughout, suggesting a greater influence of the zinc anodes when compared with the measured potentials shown in figure 11. The results of the reduced-zinc finite element analysis show a significant elevation in potential throughout the tank (except in the immediate region of the remaining two zinc anodes), indicating a lesser cathodic polarization. These results show, however, that the two zinc anodes would still afford adequate protection to the metal components of this cavity. Reduction of the cathodic protection from five to two zinc anodes would reduce the degree of overprotection; therefore, less calcareous deposit formation and a reduced probability of paint blistering would be expected.

The results of the potential measurements and computational analysis confirmed the hypothesis of overprotection. Further finite element analysis led to the conclusion that reduction of zinc anodes from five to two, located at the new positions, would reduce the degree of overprotection while still affording adequate cathodic protection. This recommendation was made to the appropriate ship authority. Subsequent communication with Carson[17] suggested the use of plain carbon steel sacrificial anodes for this system. Investigation of this candidate solution is being pursued along with various zinc anode configurations. Steel's closer free-potential proximity to the constituent metals of this system and its higher degree of anodic polarizability would reduce significantly the degree of polarization of the protected metals, and, thus, the degree of the cathodic reactions which could cause calcareous deposits and paint delamination. It would have to be verified, however, that plain steel "anodes" would be sufficiently more active than the other metals to provide adequate protection.

## CONCLUSIONS AND FUTURE WORK

There are several conclusions that may be drawn from the investigations and developments described in this paper. Previous methods used to determine the corrosion state of a galvanic system or to design a system to mitigate corrosion (e.g., material selection, geometric configuration, or cathodic protection) have not been able to accurately predict electrochemical states of galvanic systems of general systems; a numerical method was required to treat general geometries. None of the earlier methods incorporated the electrodic behaviors of the metal/electrolyte systems, primarily because analytical solutions could not accept this highly nonlinear type of boundary condition (fourth kind) in the Laplace equation problem wherein the surface current densities are dependent on the solution (potential distribution) itself. The electrodic polarization boundary condition was required as the true nonlinear relationship between current density and electrochemical potential ($i=i(\phi)$) as measured in the laboratory potentiostatic polarization curve experiment.

Computational corrosion element analysis described herein is a useful tool for a-priori prediction of current and potential distributions resulting from a system of dissimilar metals immersed in an electrolyte. The boundary value problem for galvanic analysis may be formed exactly and the boundary conditions are legitimately embodied in the electrodic polarization behavior of the metal/electrolyte system, as represented by the polarization curve, and this formulation imposes the necessary and realistic constraint of conservation of charge on the electrolyte. The accuracy limitations of galvanic analysis as developed herein are really only of degree; the closeness of approximation is chosen by the analyst, based on time and funding constraints.

Work has begun in microscopic corrosion analysis[18,19] and in using the potential distribution and the electrodic parameters to perform a secondary calculation of the rate of partial reaction of interest, such as the metal dissolution rate. This is then to be used to redefine the electrode shape and electrolyte chemistry in localized corrosion problems. Work will be directed toward streamlining the reduction of potentiostatic polarization data to derive a set of electrodic parameters. A combination of the finite element and boundary element methods may be warranted, to take advantage of the modeling flexibility of the FEM while adding the infinite domain capability of the BEM. A compromise would be the addition of an "infinite element" type to the finite element method, an improvement that has already begun in the structural FEM.

It has been shown that the proven methods of numerical analysis may be successfully applied to the galvanic corrosion prediction problem. This capability depends on an understanding of the principles of electrochemistry and the numerical analysis method employed, translation of electrodic polarization behavior into boundary conditions, and the art and experience involved in the geometric and pseudo-transient modeling of these problems.
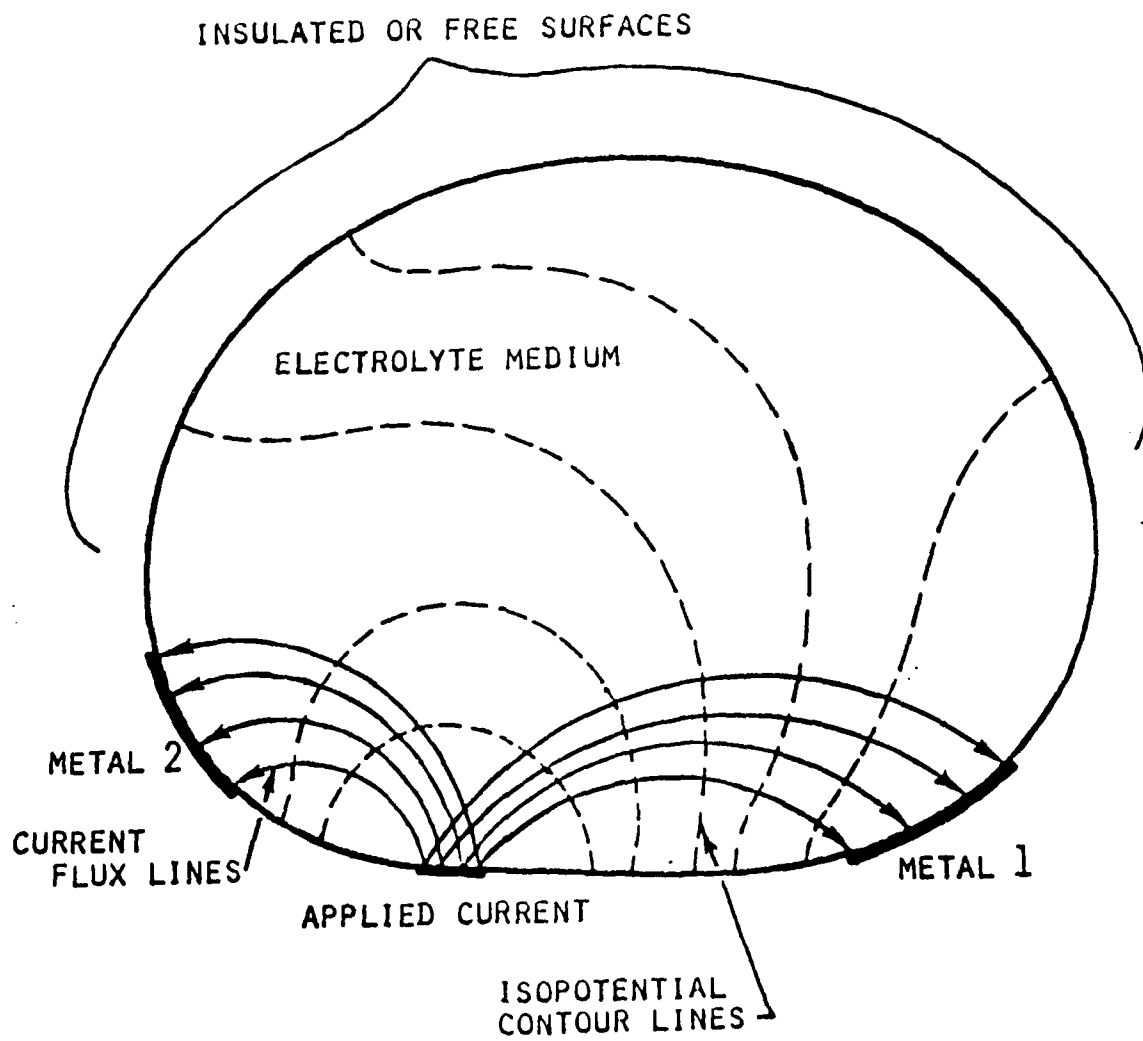
INSULATED OR FREE SURFACES

ELECTROLYTE MEDIUM

METAL 2

CURRENT
FLUX LINES

APPLIED CURRENT

METAL 1

ISOPOTENTIAL
CONTOUR LINES

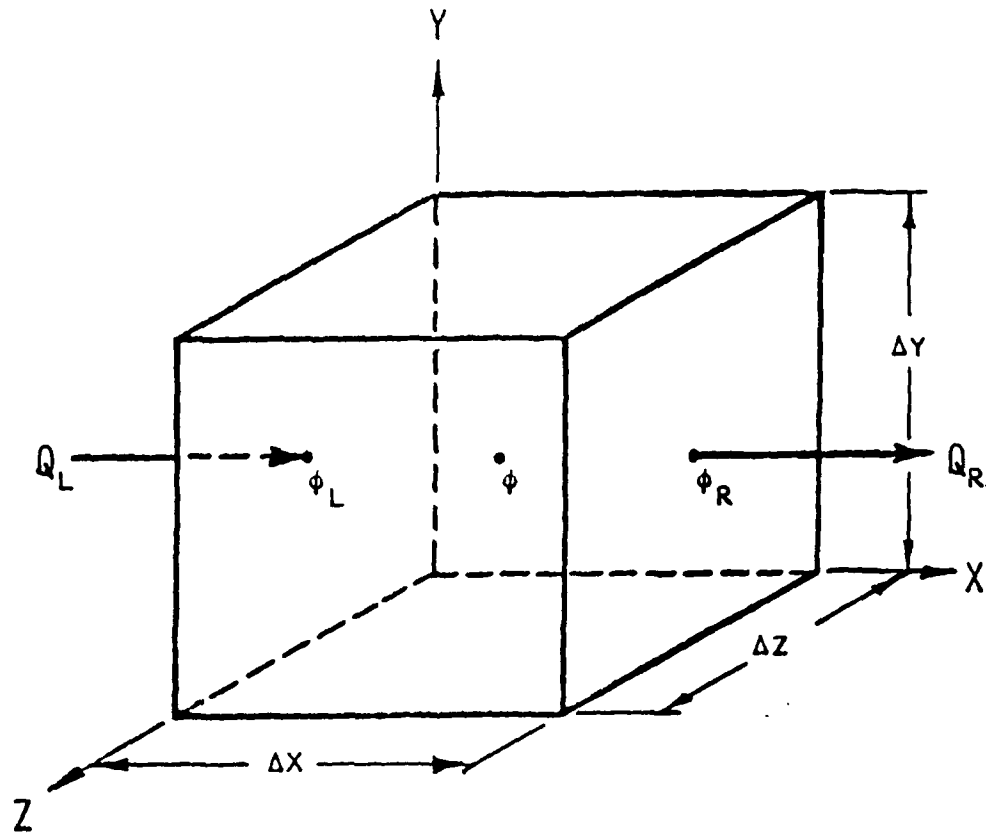FIGURE 1 - THE GALVANIC CORROSION PROBLEM

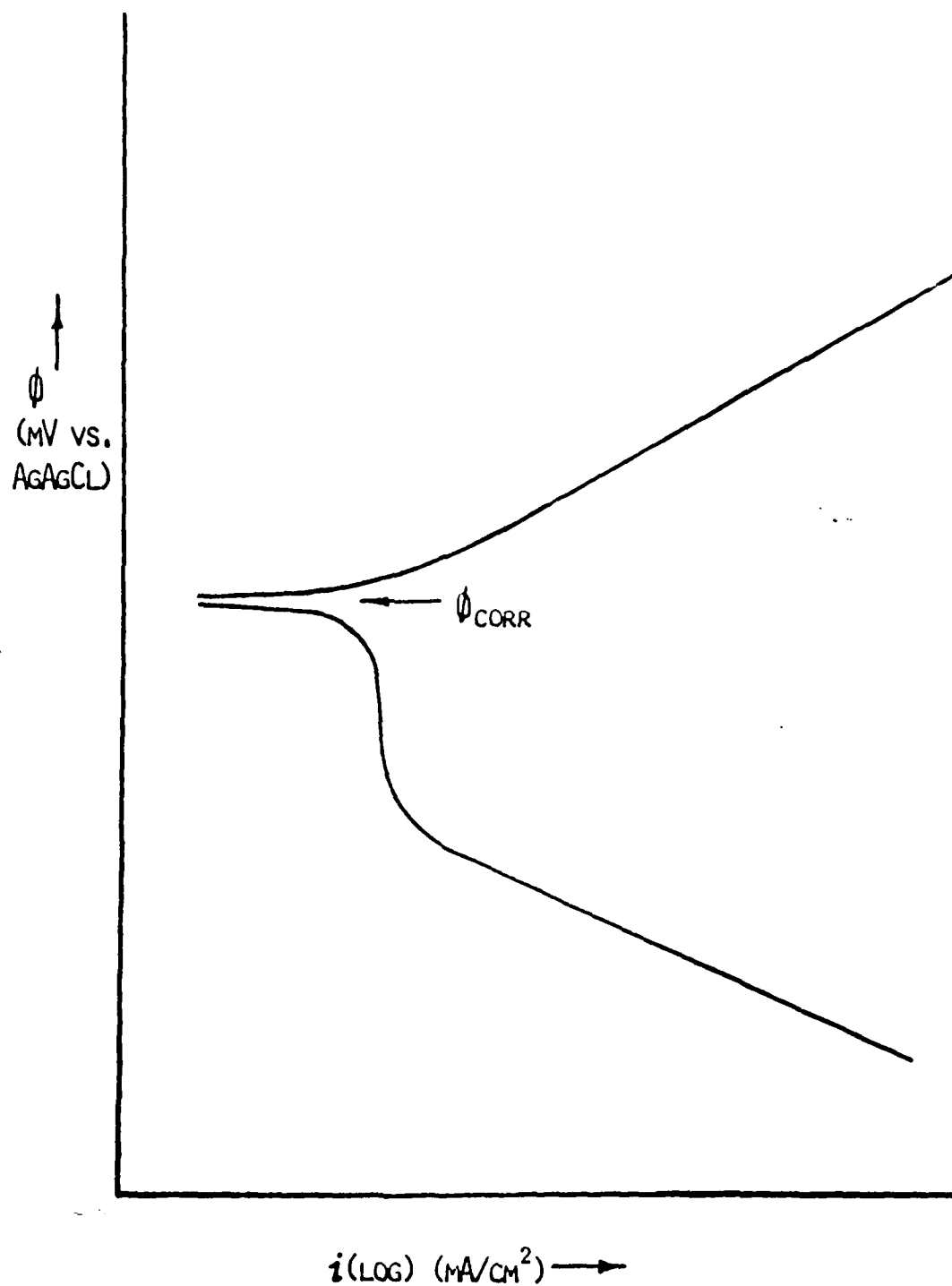FIGURE 2  -  INFINITESIMAL ELEMENT OF ELECTROLYTE CONTINUUM

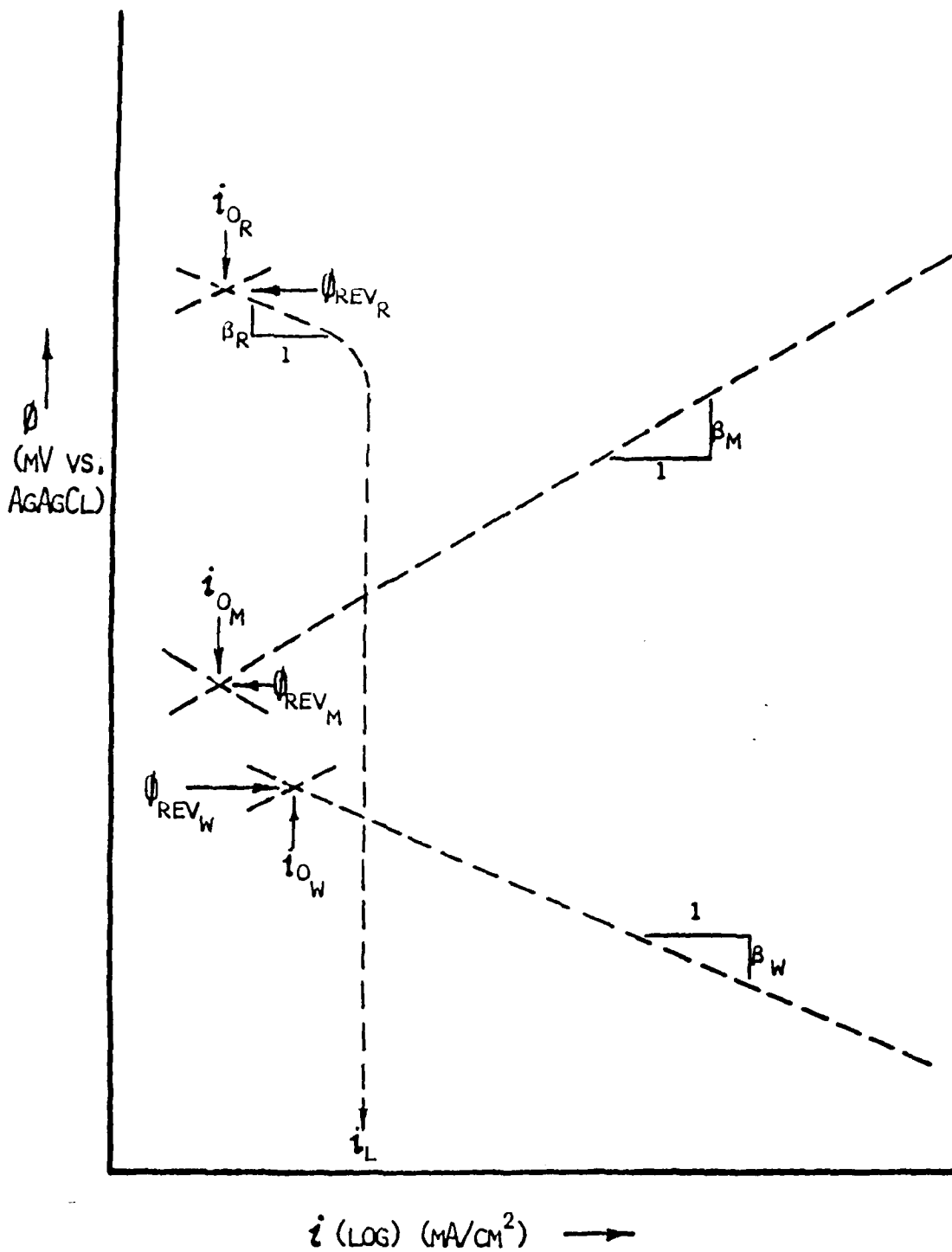FIGURE 3 — APPLIED CURRENT (TOTAL) POLARIZATION CURVE
FOR A METAL IN AN ELECTROLYTE

FIGURE 4

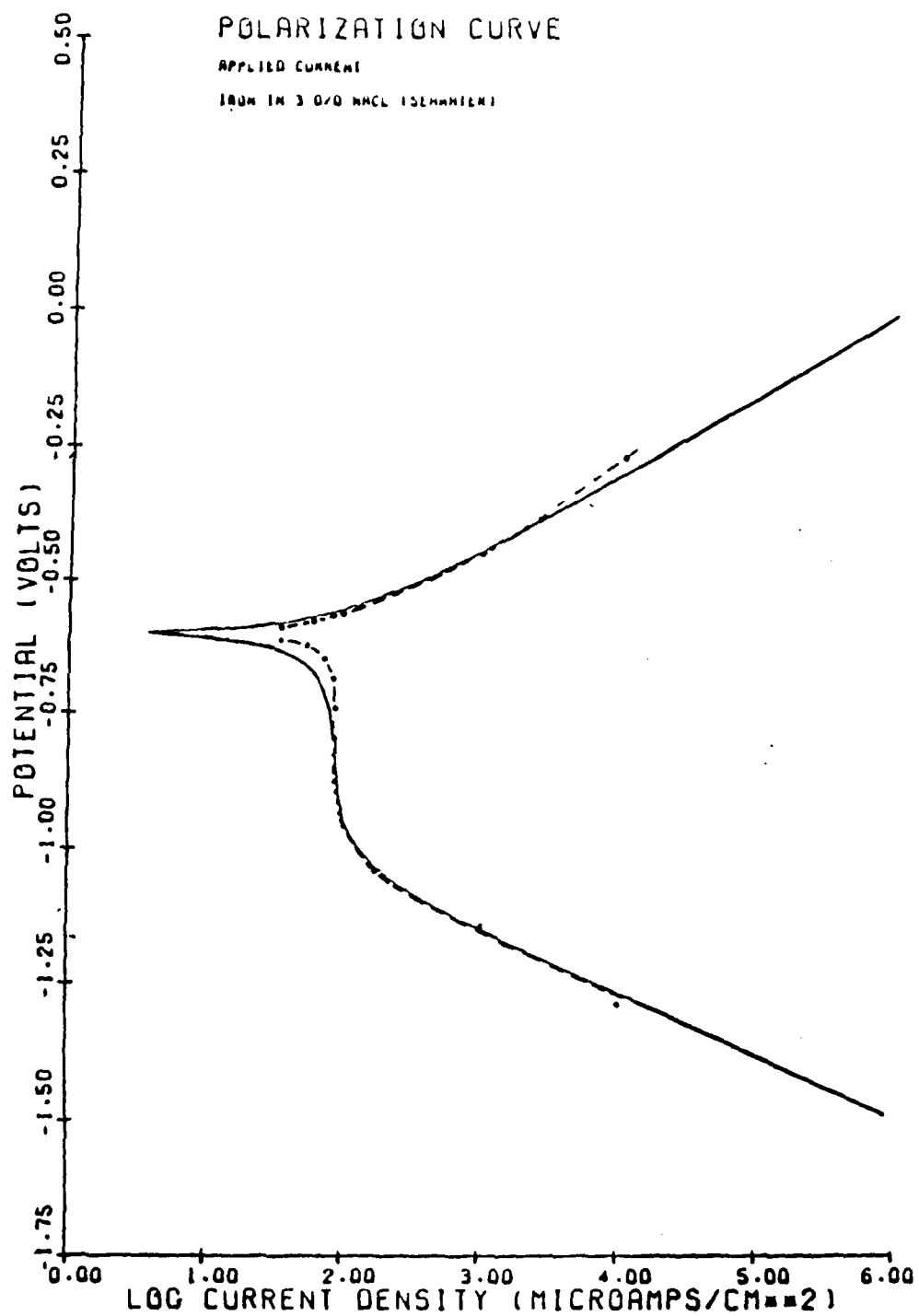INDIVIDUAL PARTIAL REACTIONS ON A METAL IN AN ELECTROLYTE

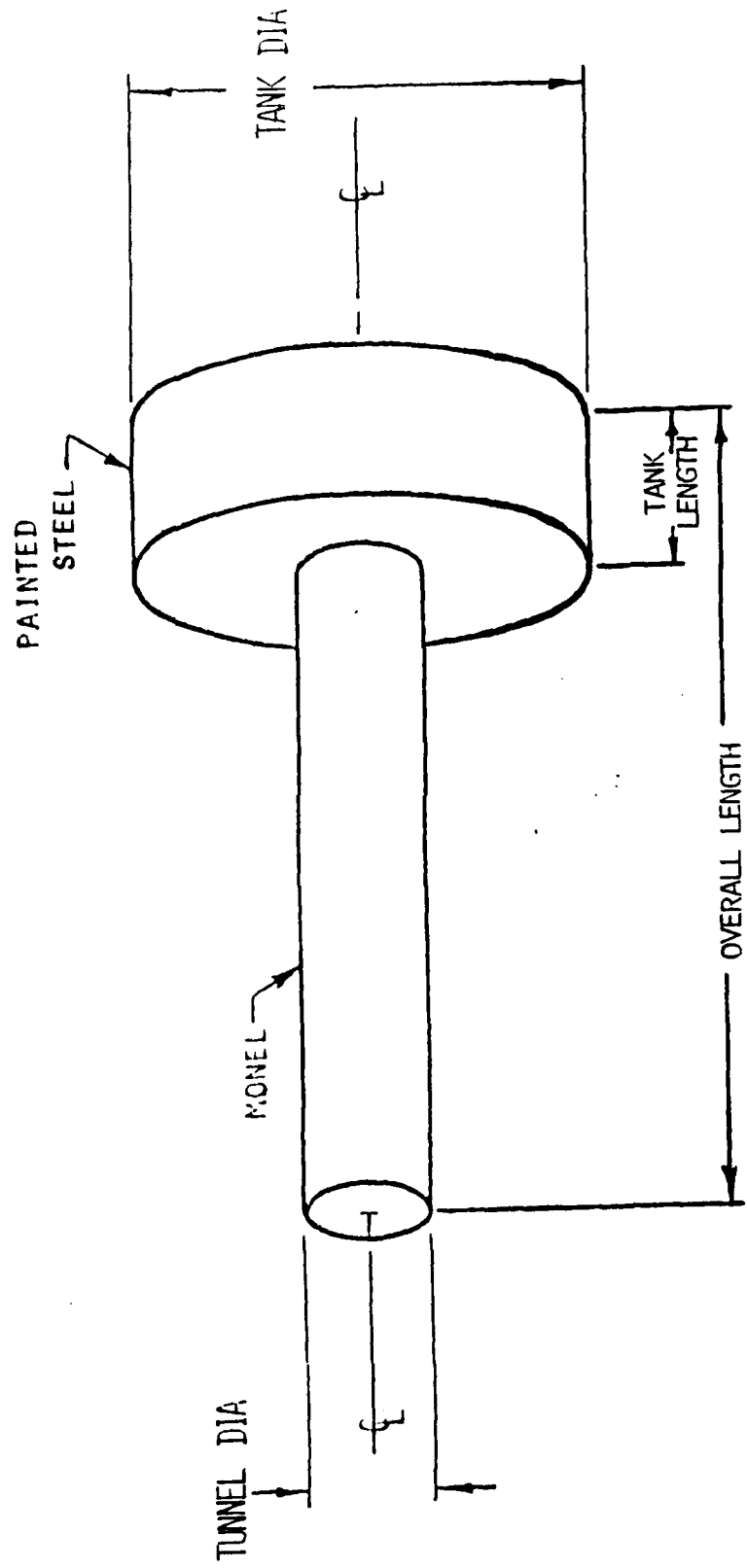FIGURE 5 - MEASURED AND SYNTHESIZED POLARIZATION
CURVES FOR IRON IN 3% SODIUM CHLORIDE SOLUTION

FIGURE 6 — SHIPBOARD SEAWATER TANK — EXTERNAL VIEW
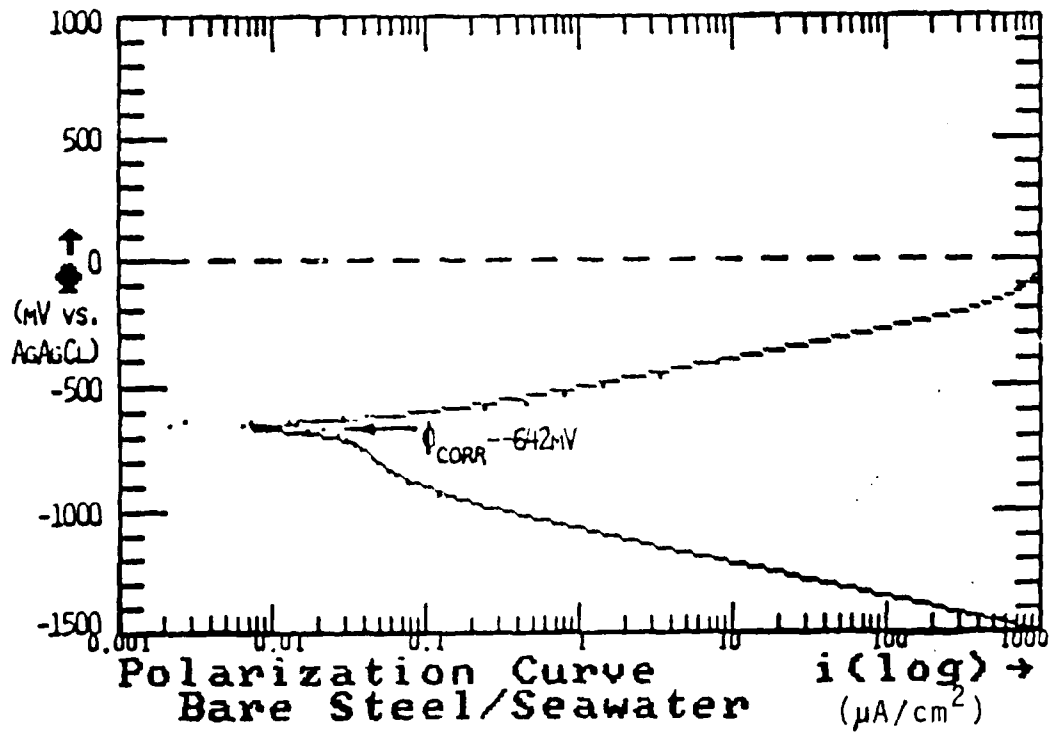
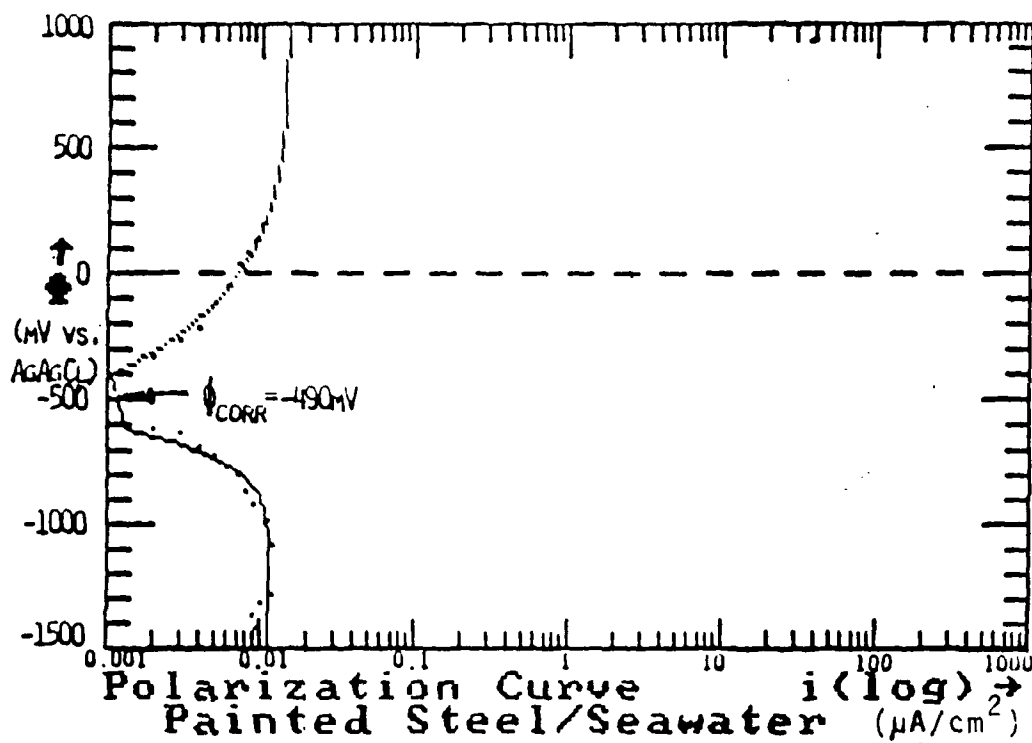FIGURE 7 - ELECTRODIC POLARIZATION CURVE
BARE STEEL IN SEAWATER

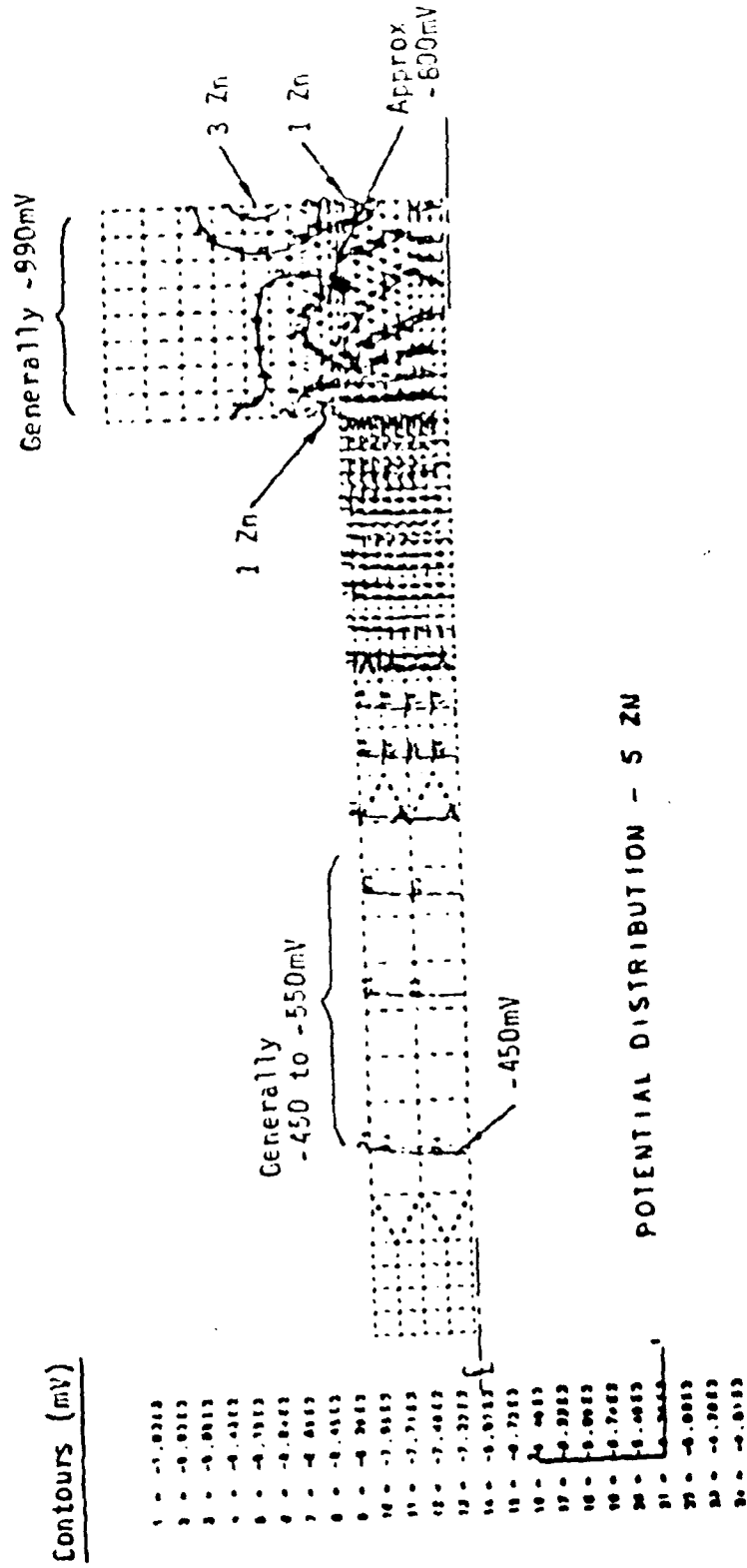FIGURE 8 — ELECTRODIC POLARIZATION CURVE
PAINTED STEEL IN SEAWATER

FIGURE 9 — SHIPBOARD SEAWATER TANK
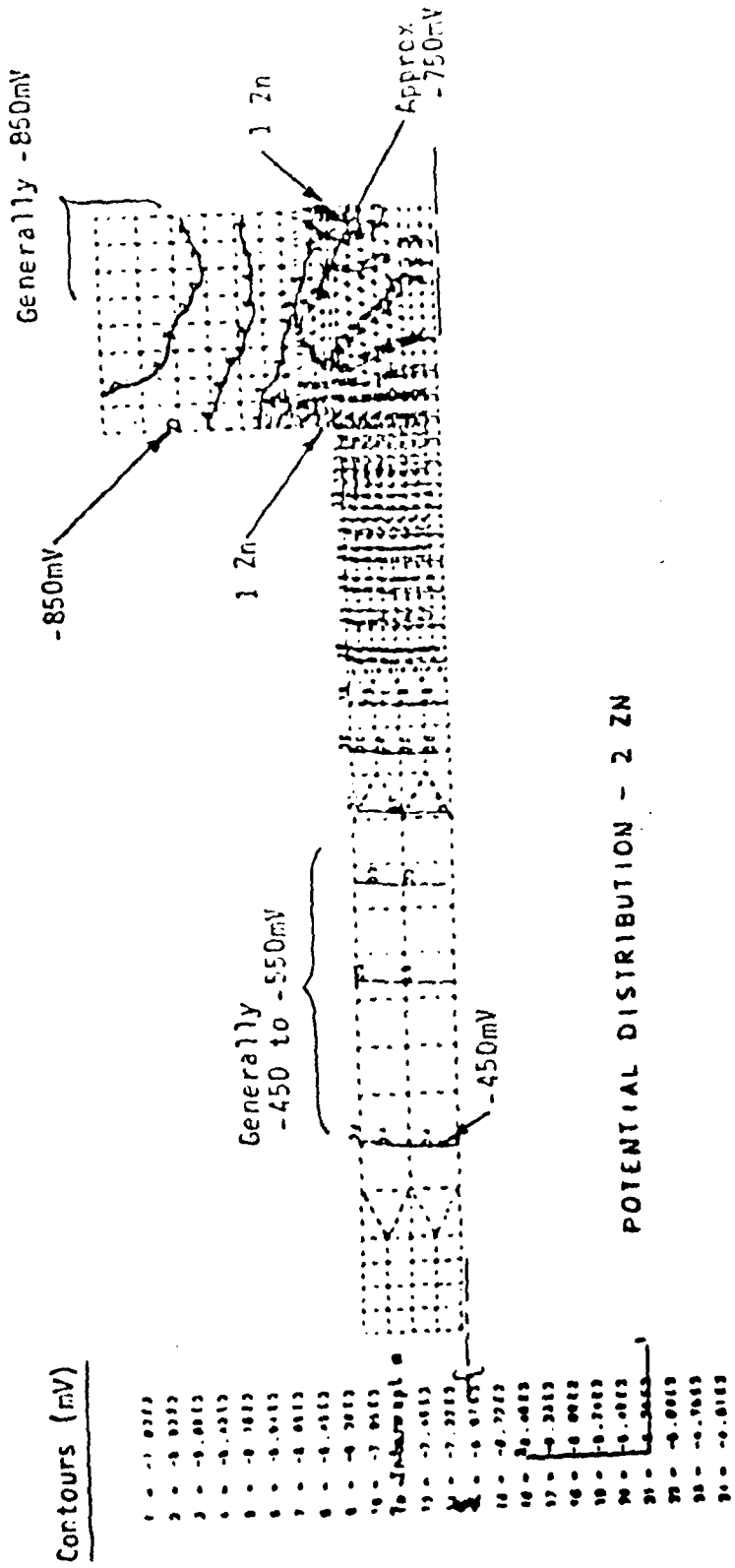STEADY-STATE POTENTIAL DISTRIBUTION – DESIGNED (FIVE-ZINC ANODE) CASE

FIGURE 10 - SHIPBOARD SEAWATER TANK
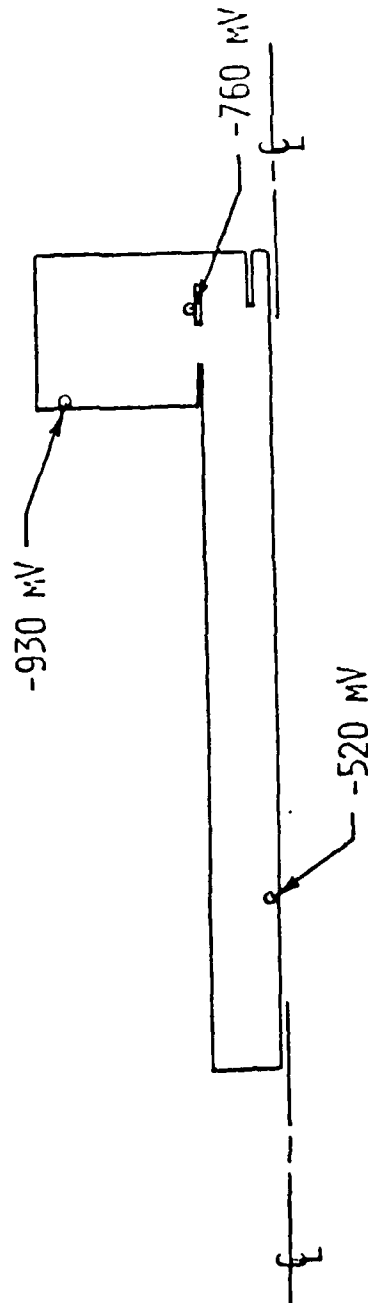STEADY-STATE POTENTIAL DISTRIBUTION - MODIFIED (TWO-ZINC ANODE) CASE

FIGURE 11 - SHIPBOARD SEAWATER TANK
AXISYMMETRIC CROSS-SECTION VIEW WITH MEASURED POTENTIALS VS. AgAgCL REF.

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