

## **Chapter 2**

# **Corrosion basics and computer modeling**

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### **1. A layman's overview of corrosion**

#### **1.1 The cost of corrosion**

Corrosion is the destruction of material resulting from exposure and interaction with the environment. While common usage typically associates corrosion with metals, the destruction of non-metallic materials as a result of exposure to the environment can be considered corrosion; the disintegration of plastics when exposed to sunlight and the rotting of wood are examples of non-metallic corrosion. However, the concern of this chapter is corrosion of metals, especially electrochemical corrosion, and the ability to use computer modeling techniques to predict corrosion.

Corrosion is a natural phenomenon which exists as part of our everyday life. In extreme situations catastrophic failures such as sudden collapse can result when corrosion caused damage undermines the load bearing capability of a structure. Corrosion damage can also result in life threatening situations which are not as dramatic as structural collapse such as contamination by corrosion products from lead piping resulting in possible toxic levels of lead in drinking water supplies.

The cost of corrosion damage is felt by industry, government and individuals regardless of gross earnings, political system or life styles. Repair or replacement costs for bridges and other highway structures are a major cost incurred by regional governments. Repair and replacement costs are incurred by any industry which uses metal structures in processing or storage facilities. Individuals are subject to direct costs related to repair or replacement of personal property, such as automobiles or home hot water heaters, and to indirect costs in the form of higher taxes or higher product prices which result from government and industry costs.

Corrosion is a major problem which must be addressed for safety, environment and economic reasons. Safety concerns are paramount in any situation. Environmen-

tal concerns include consideration of corrosion caused pollution, depletion of resources such as those needed for replacement of the corroded structure and disposal of the corroded structure. Safety and environmental concerns tend to be very hard to define in terms of costs. Economic concerns, however, tend to lend themselves readily to cost estimates. For example, the total cost of metallic corrosion in the United States for 1975 was estimated at \$82 billion or 4.9% of the Gross National Product<sup>1</sup>. This estimate of corrosion considered preventable and non-preventable corrosion. Since corrosion is an inescapable natural phenomenon, it may be more appropriate to estimate only that portion of corrosion damage which cannot be reduced through design or application of preventative technology. Non-preventable corrosion accounted for 60% of the total which corresponds to a cost of \$49 billion for the year. Another method for estimating the cost of corrosion is to consider the impact on a particular community. For example, in the paper industry it was estimated that the cost of corrosion damage increases the cost of paper between \$6 and \$7 per ton<sup>2</sup>. Still another method for estimating the cost of corrosion is to determine the percentage of yearly output which is lost to corrosion. For example, approximately a third of all metal produced by the Soviet Union steel industry in 1965 was lost to corrosion<sup>3</sup>. Again, the issue of what costs should be considered when calculating the cost of corrosion damage must be considered. The amount of metal loss to corrosion, after the recovery of scrap metal is deducted from the total metal loss was 10% of the yearly metal output. As can be seen from these three methods of estimating a cost of corrosion, the economic impact of corrosion is immense but not as well defined as one may originally believe. It is obvious, however, that corrosion is a major problem with large financial implications which must be addressed.

The study of corrosion involves the study of the chemical, physical, metallurgical and mechanical properties of materials. Corrosion is a synergistic phenomenon in which the environment is equally as important as the materials involved. Computer modeling techniques are a powerful tool for the study of complex system response and are therefore an appropriate means for studying corrosion. The theoretical basis needed for the application of computer modeling to selected corrosion problems has existed for several decades<sup>4</sup>. The pace of adaptation of computer modeling techniques to corrosion evaluation has been set by the availability of computer resources and the cost of necessary computer power rather than the development of the mathematical representation of corrosion. The cost and availability of computer resources is constantly changing. Advances in computer technology have tended to result in a continual decrease in computational costs which in turn makes computer modeling a more viable option.

In the recent past computer modeling techniques have been successfully applied to corrosion problems as summarized in review articles by Zamani, Porter and Mufti<sup>5</sup> and Munn<sup>6</sup>. The application of computer modeling techniques to corrosion systems requires an understanding of the physical phenomenon of corrosion and the mathematics which govern the corrosion process. In addition, a knowledge of the numerical procedures which are the basis of computer modeling techniques is necessary for accurate computational analyses. Verification of assumptions by comparison of computer analysis results with experimental or other measured data is a fundamental requirement in the creation of an accurate analysis. The purpose of this chapter is to introduce

the individual who is knowledgeable in computer modeling techniques to the basic concepts of corrosion. Basic corrosion terminology and an introduction to corrosion processes are presented. Detailed examination of the theoretical and applied aspects of corrosion can be found in textbooks, study guides and technical journals. Examples of corrosion evaluation using boundary element techniques are presented in the final section of the chapter.

## 1.2 Chemical and electrochemical corrosion

Corrosion is either chemical or electrochemical in nature. The distinction between chemical and electrochemical corrosion is based on the corrosion causing mechanism. Chemical and electrochemical corrosion are not mutually exclusive and can occur simultaneously.

Chemical corrosion is the direct result of exposure of a material to a chemical and is governed by the kinetics of chemical reactions. Chemical corrosion does not involve the generation of an electrical current. Direct chemical attack, such as the dissolutive of a material by an acid, and selective attack, such as leaching of a specific soluble compound from a material, are two common forms of chemical corrosion. The formation of oxide films on a metal surface is also a form of chemical corrosion.

Electrochemical corrosion is the dissolution of a metal through the oxidation process. Oxidation and reduction chemical reactions occur simultaneously and are interdependent. Corrosion only occurs at the site of the oxidation reactions. Oxidation involves the loss of electrons; reduction involves the gain of electrons. The electron transfer between oxidation and reduction reaction sites establishes the electrical current required for electrochemical corrosion. There is no gain or loss of electrical charge during electrochemical corrosion.

The basic unit in which electrochemical reactions occur is the electrolytic cell. An electrolytic cell consists of three components; an anode, a cathode and the electrolyte. The anode is the site of oxidation and therefore the site of corrosion. The anode and cathode are electrically connected. The medium surrounding the anode and cathode is the electrolyte. The anode and cathode can be the same or different metals. When a structure fabricated of one material is surrounded by an electrolyte and exposed to an electrical current, portions of the structure will act as anodes while the remainder of the structure will act as the cathode. When a structure is fabricated of two metals, the more likely to corrode, or the more active, metal will act as the anode while the less likely to corrode, or nobler, metal will act as the cathode. The metallurgical properties of the anode and cathode directly effect the rate and extent of corrosion. The relative surface area of the anode and cathode will effect the rate of corrosion. Large cathode areas provide a large surface area for reduction to occur. The rate of oxidation of the anode is regulated, in the absence of other limiting factors, by the number of electrons required for reduction of the cathodic surface. A small anodic area will require a greater rate of oxidation to supply the same number of electrons as a larger anodic area. Therefore, the smaller the anodic area with respect to the cathodic area, the greater the rate of corrosion on the anodic area. Conversely, the rate of corrosion can be reduced by increasing the relative size of the anode.

An electrolyte may be a fluid, a gas, a granular solid such as sand or a more com-

plex solid and fluid combination such as a saturated or partially saturated soil. The composition and conducting properties of the electrolyte effect the rate and extent of corrosion. Environmental conditions such as temperature, humidity for gases, water content for soils and pressure effect the rate and extent of corrosion.

When a metal is surrounded by an electrolyte, the metal will establish an electrical potential with the surrounding medium. Electrical potential is directly related to the electrical current in the material. The open circuit or rest potential is the measured electrical potential which occurs when there is no flow of electrical current in the circuit formed by the electrolytic cell. Measured electrical potential is a potential difference. The measured electrical potential is the difference between the electrical potential at the point of interest and the potential of a reference electrode. Reference electrodes are usually chosen based on availability, survivability in the working environment, and traditional use in the working environment. Corrosion is often reported in terms of weight loss per unit time or thickness loss per unit time. The corrosion rate is directly proportional to the measured electrical current. The mass loss is related to the measured electrical current by Faraday's Law:

$$Q = \frac{nFW}{M} \quad (1)$$

where

$F$  = Faraday's number (96 500 Coulombs/equivalent),

$n$  = the number of electrons transferred

$W$  = weight of reacting species

$M$  = molecular weight of reacting species

$Q$  = electrical charge =  $It$

$I$  = electrical current

$t$  = time

If corrosion is assumed to occur uniformly over the metal surface, the corrosion rate can be directly calculated from the mass of metal loss due to corrosion. Rearranging Eq. (1):

$$W = \frac{QM}{nF} \quad (2)$$

Substituting  $Q = It$  into Eq.(2):

$$W = \frac{ItM}{nF} \quad (3)$$

Final re-arrangement yields weight loss per unit of time:

$$\frac{W}{t} = \frac{IM}{nF} \quad (4)$$

### 1.3 Galvanic corrosion

Galvanic corrosion occurs when two or more metals with different electrochemical responses are electrically connected. In the absence of an externally applied electrical current, the difference in open circuit potential creates the electrical current necessary

for electrochemical corrosion. It is impossible to use the differences in open circuit potentials to predict corroding tendencies; galvanic series, such as that shown in Table 1, indicate the relative tendency for metals and metal alloys to corrode. The relative position of the metal in a galvanic series, rather than the value of electrical potential associated with the metal, is indicative of the tendency for corrosion to occur. For example, the more noble or cathodic metals such as platinum, gold and titanium show little tendency to corrode while the more active or anodic metals such as zinc and magnesium alloys will corrode when coupled with any more noble metal. Some metals appear twice in a galvanic series; steel on which a protective oxide film has formed is more noble than the same steel without the protective oxide film. The closer materials are to each other in the galvanic series, the less galvanic corrosion will occur when the two materials are used in combination. When test data for a specific material pairing does not exist, the galvanic series for the environment in which the couple is immersed can be used as an indication of the degree of severity of galvanic corrosion.

#### 1.4 Physical varieties of corrosion

Corrosion damage can be divided into many categories based on the physical characteristics of the damaged metal. Simple definitions of a few frequently encountered types of corrosion damage are given in this section. This abbreviated list of physical corrosion damage categories is meant to give the reader a glimpse at the variety of corrosion related damage possible.

General corrosion gives the appearance of an uniform wasting away of the metal. General corrosion is often the result of multiple adjacent anodic and cathodic regions on the metal surface. The corrosion appears to be uniform over the metal surface due to the relatively small spacing between anodic sites. Detailed examination of the apparently uniformly corroding surface on a microscopic scale will find a mixed pattern of anodic and cathodic regions.

Cavitation damage occurs at solid-liquid interfaces, such as the surface of a submerged structure. Repeated collapse of vapor bubbles may cause physical damage to the solid surface which may result in pits. Pits can also be formed by preferential corrosion at sites where the collapse of vapor bubbles has resulted in localized damage of oxide films. The relatively small areas of film damage result in small localized anodic regions which experience accelerated corrosion due to a large cathode to anode surface area ratio. Pits are formed by corrosion which extends below the original metal surface.

Fretting corrosion is localized damage between contacting surfaces. The corrosion process is accelerated by relative motion of the two surfaces. Fretting corrosion requires initial contact between the two metal surfaces as well as relative motion sufficient to expose the surfaces to the corroding environment. Abrasion between the surfaces, either due to grinding between the surfaces or scratches caused by grit or other contamination between the surfaces, can result in damage to the metal surfaces and to any covering oxide film. The damaged areas will then act as anodic sites for accelerated corrosion due to large cathode to anode surface area ratios.

In microbiological induced corrosion the destruction of metal is caused directly or indirectly by bacteria, fungi or other microbiological organisms. Anaerobic organ-

isms, aerobic organisms and their digestive by-products all act as corroding agents. Microbiological induced corrosion is often a time dependent system which involves the layering of anaerobic and aerobic organisms. Some environmental characteristics, such as temperature and flow conditions, can promote growth of the biological organisms involved and therefore enhance corrosion. Microbiological induced corrosion can be controlled by the use of growth inhibitors such as chemical treatments and stringent water quality controls.

Selective attack, or leaching, is the removal of a soluble compound from an alloy. Dealloying of brass, or dezincification, is a common form of leaching. Dezincification occurs when brass is electrically connected to zinc. The material left after dezincification is a very porous copper with poor mechanical properties. The visible sign of dezincification is a change from the typical yellowish color of brass to the reddish color of copper. The copper material which remains is subject to sudden failures because of the low material strength. Dezincification is only one example of leaching corrosion.

Stray current corrosion results from the flow of electrical current through a path other than intended. The sources of stray current are often extraneous to the structure damaged and unknown to the analyst until corrosion is observed. Even after a corrosion problem has been identified, the source of stray electrical current may remain a mystery. The stray current creates an anodic site at the point where it enters the structure. The effect of the stray current may be to change a surface which is initially a cathode into an anode. The resulting electrical circuit may have no resemblance to the original circuit. Stray current corrosion often occurs due to faulty design of a system other than the one in which corrosion is observed.

## **2 Material polarization response**

In the evaluation of material or system performance an appropriate material characterization is necessary. In the case of electrochemical corrosion the material behavior of interest is the electrical current-electrical potential relationship.

The sensitivity of the electrical current-electrical potential relationship to environmental and electrolyte characteristics must be considered when defining an appropriate characterization. The accuracy of any performance or corrosion damage prediction, whether based on analytical, experimental or computational analysis will depend on how well the system defined in the analysis matches both the real structure and the environment surrounding the structure. Factors which are essential in defining the electrolytic cell where corrosion occurs are the geometry of the structure under evaluation, the location of electrical sources or sinks, the strength of the electrical sources or sinks and the characteristics of the electrolyte surrounding the structure. Time dependent variation in electrical current-electrical potential response are important for many situations such as the evaluation of structures which experience extreme seasonal variations in temperature or water salinity. The accuracy of any evaluation will depend on the accuracy of the system model and the electrical current-electrical potential response. The number and magnitude of differences between experimental and service conditions will determine whether analysis results will be approximate to the real world situation or completely erroneous.

## 2.1 Polarization definitions

Polarization is the relationship between electrical current and electrical potential. It is an observed behavior resulting from the combined effects of multiple oxidation and reduction reactions which are dependent on many variables. The relationship between electrical current and electrical potential may or may not be linear. It may or may not be possible to develop a mathematical function which represents the relationship. Polarization is generally referred to as a characteristic of the metal but is dependent on metal and electrolyte composition.

Anodic polarization response is the behavior of the corroding metal. Cathodic polarization response is the behavior of the non-corroding metal. Much of the application of computer modeling techniques to corroding systems is in the evaluation of corrosion prevention systems. Corrosion prevention systems attempt to maintain the metal of interest in the cathodic state so an understanding of the behavior of non-corroding metal is essential.

Polarization response is either activation or concentration controlled. Activation polarization occurs when the electrical current-electrical potential relationship is controlled by the rate of a specific chemical reaction in the corrosion process. The only limitation imposed on the critical reaction is its associated rate of reaction. Idealized cathodic activation polarization, Fig. 1, is:

$$\eta_{act} = \beta \log \frac{i}{i_o} \quad (5)$$

where

$\eta_{act}$  = measured potential  
 $\beta$  = constant (Tafel slope)  
 $i_o$  = initial electrical current  
 $i$  = electrical current

Anodic response will follow the same mathematical form. Because activation polarization is limited by the kinetics of a specific reaction, the polarization response is dependent on temperature and all other parameters which effect the chemical reaction rate.

Concentration polarization occurs when corrosion is limited by whether a specific chemical reaction can occur. In other words, polarization is controlled by the concentration of a chemical component required by a specific reaction in the corrosion process. One particular type of concentration polarization is diffusion controlled polarization. In this case, the ion diffusion rate to the metal surface limits the rate of the reduction reaction since the diffusion rate limits the available of the required ion. Idealized diffusion rate limited cathodic concentration polarization response (Fig. 1) is:

$$\eta_{conc} = 2.3 \frac{RT_{a.w.}}{nF} \log \left( 1 - \frac{i}{i_L} \right) \quad (6)$$

where

- $\eta_{conc}$  = measured potential  
 $R$  = gas constant  
 $n$  = number of electrons transferred  
 $T_a$  = absolute temperature  
 $F$  = Faraday's number  
 $i_L$  = limiting diffusion electrical current  
 $i$  = electrical current

Eq. (6) is based on the Nernst equation.

In summary, a limiting rate of a chemical reaction governs activation polarization while the availability of a necessary chemical components governs concentration polarization.

The total, or measured, polarization is a combination of activation and concentration polarization. Activation polarization usually controls for corrosion related reactions which have low chemical reaction rates while concentration polarization will become dominate when the governing reactions have higher reaction rates. Measured polarization response can be idealized by the linear combination of concentration and activation polarization responses for cathodic polarization:

$$\eta_c = \eta_{act} + \eta_{conc} \quad (7)$$

An idealized measured cathodic polarization curve is shown in Fig. 2.

Linear polarization is, as the name implies, that portion of the total polarization response which is linear in nature with respect the logarithm of the electrical current density. The slope of the linear portion of the polarization curve is often referred to as the Tafel slope.

The effects of the formation of oxide films are not addressed by the polarization curves presented in Figs. 1 and 2. The formation of oxide films greatly reduces the electrical current associated with a defined value of electrical potential and the polarization relationship becomes multi-valued with respect to electrical current. The value of electrical potential associated with an electrical current value will depend on whether the reading is taken prior to oxide film formation, after film formation or after film destruction. The effects of film formation is demonstrated for polarization which is initially anodic in Fig. 3. The initial behavior of the metal can be described using activation polarization definition as given in Eq. (5). Prior to oxide formation the metal represented in Fig. 3 is exhibiting anodic behavior. The formation of an oxide film transforms the active material to a more noble material with a reduced tendency to corrode and the electrical current density is reduced to a relatively small limiting value. The limiting value of electrical current density may be as much as  $10^6$  times lower than the maximum active region electrical current density<sup>7</sup>. At higher levels of electrical potential, oxide films tend to break down and the material is returned to an active state showing increased anodic polarization; this is the transpassive region. The formation of oxide films may cause a metal to shift from anodic to cathodic and finally return to anodic behavior depending on the other metallic components of the electrolytic cell.

## 2.2 Mixed potential response

When two metals are electrically connected and surrounded by an electrolyte, the measured electrical potential of both metals will change from the open circuit potentials. The cathodic metal will become more anodic and the anodic metal will become more cathodic. The two metals will reach electrical potentials which are somewhere between the open circuit potentials of the two metals.

The mixed potential theory defines this electrochemical corrosion behavior. The hypotheses of the mixed potential theory are:

- Any electrochemical reaction can be divided into multiple partial oxidation and reduction reactions.
- There is no accumulation or loss of electrical charge during the electrochemical corrosion process.

The first hypothesis recognizes the chemical kinetics of electrochemical corrosion. The second hypothesis requires that the oxidation and reduction reactions are in a state of equilibrium. It is this balancing of reactions which causes the anodic and cathodic metals to achieve some intermediate electrical potential when connected. The mixed potential theory is one of the basic tools for the evaluation of electrochemical corrosion. It is important to note that the concept of mixed potential is a theory which is based on experimental observations and correlation between theoretical and experimental response should not be taken as proof of the theory<sup>8</sup>. This does not diminish the importance of the theory.

## 2.3 Electrolyte characteristics

The amount of corrosion which occurs in any system is dependent on both the metal and the electrolyte. The corrosion response of a metal, represented by the measured polarization response, will vary depending on the constituents of the electrolyte and their concentrations. In establishing experimental criteria to determine polarization response it is best to match experimental and service condition electrolytes as near as possible. In order to introduce the complexities encountered due to electrolyte constituents two characteristics of fluids, the hydrogen ion concentration and the dissolved salt concentration, are briefly discussed.

Reviewing basic chemistry, the hydrogen ion concentration is measured by the  $pH$  of a solution. Metals which are stable in both acidic ( $pH < 7.0$ ) and basic ( $pH > 7.0$ ) solutions exhibit corrosion damage which is independent of hydrogen ion concentration. Some metals, such as zinc and aluminum, exhibit a parabolic corrosion-hydrogen ion concentration behavior; corrosion rates are high for high and low  $pH$  values while corrosion rates are near zero for neutral and low  $pH$  values in both the acid and basic range. More typical of metals is a direct relationship between rates of corrosion and level of acidity; the more acid the solution, the higher the rate of corrosion.

Dissolved salt concentration effects on the electrolyte-material system are dependent on the concentration and type of dissolved salts. In general, there are aggressive salt ions and inhibitive salt ions. Aggressive ions accelerate corrosion activity when compared to a salt free solution. In general inhibitive ions decrease the corrosion rate

through the formation of protective films. Ions can be either aggressive and inhibitive depending on their concentration and the concentration of oxidizing agents in the electrolyte solution. Aggressive salts ions, such as Cl<sup>-</sup> associated with seawater, will become corrosion inhibitors if there is insufficient oxygen available. This effect of oxygen content can be seen in the observed corrosion rates for metals exposed to seawater environments; maximum corrosion occurs in the splash zone where oxygen is readily available and minimum corrosion occurs at depths where only a limited amount of oxygen is available.

Electrolytes may be homogeneous or non-homogenous. In order to determine if an electrolyte can be considered as a homogeneous medium, the electrical behavior of the volume in the immediate vicinity of the anode and cathode must be evaluated. Variations of electrolyte constituent near the anode and cathode surfaces will have a greater effect than variations at a distance. At distances sufficiently far from the anode and cathode surfaces, variations in the electrolyte constituency will have negligible effects on the measured polarization response. The volume of electrolyte which has an influence on measured polarization response will vary depending on the materials involved and the electrolyte. An electrolyte may be considered to be homogeneous if there are no local variations which result in variations in material polarization response. For example, high levels of turbulence near a metal surface may result in localized variations in polarization response. However, in the absence of high flow rates or turbulence a complex mixture of dissolved salts, biological agents and other constituents such as seawater can be considered to behave as a homogeneous electrolyte.

#### 2.4. Experimental polarization curves

Measured polarization response, determined through appropriate experimental procedures, incorporates all effects of activation polarization, concentration polarization, formation or destruction of oxide films, formation of any biological layers, effects of electrolyte characteristics and oxidizing agent availability. Briefly stated, the measured response is a synergistic total response which explicitly includes all factors. As in any experimental procedure, there are minimum requirements for the successful measuring of polarization response. A primary consideration in designing experiments to measure the polarization response is to design the experiments so the primary corrosion mechanism is electrochemical corrosion. Monitoring and cent rolling methods must be established which do not disturb the system in ways which result in meaningless measurements; this issue is common to any experimental procedure.

In an ideal situation, special test procedures to determine the polarization response would be defined which correspond to expected service conditions. Special test specimens which are representative of the structure to be evaluated would be used in the experiments. Unfortunately time and financial considerations may eliminate all possibilities of special testing procedures. Therefore, a basic understanding of the standardized test methods which may be used to obtain polarization response is necessary.

Polarization response testing can be divided into two broad subgroups; constant electrical current and constant electrical potential tests. In constant electrical current

experiments the polarization curve is developed from measured potential values for defined values of electrical current. Discrete steps are taken between different electrical current levels. The assumption of constant electrical current testing is that the polarization response is a single valued function with respect to electrical current. With the formation of oxide films, polarization response does not maintain this single value characteristic. Therefore, constant electrical current, or galvanostatic, tests methods are not capable of defining changes in polarization response which result from the formation of oxide films. Galvanostatic tests are therefore of limited use for oxide film forming metals which will be in service for any significant period of time. Potentiostatic and potentiodynamic testing are based on maintaining a constant value of electrical potential. These testing techniques can be used to obtain valid polarization response curves for metals which form oxide films.

Potentiostatic testing involves the adjusting of electrical current to maintain a constant electrical potential value. The polarization response is developed by creating a series of electrical current-electrical potential data points. The changes in electrical potential are defined as part of the experimental procedure. The input electrical current is increased until the desired electrical potential is reached. Since potentiostatic conditions allow the establishment of steady state conditions at each electrical potential level, the test method allows for the formation and growth of protective films. In potentiodynamic testing procedures the electrical potential is continuously increased. Electrical current and electrical potential are recorded for specific intervals in time. These two test methods should produce interchangeable results<sup>10</sup> but there is evidence that this is not a valid assumption for some materials<sup>11</sup>.

The choice of experimental technique to determine polarization response should be based on the expected service conditions. Ideally, the exact service conditions are duplicated in the experimental determination of polarization response. However, when this is not possible, test procedures which most closely resemble the service conditions should be selected.

### 3 Mathematical basics

In electrochemical corrosion there is no loss or gain of electrical current during the corrosion process:

$$\frac{\partial i_x}{\partial x} + \frac{\partial i_y}{\partial y} + \frac{\partial i_z}{\partial z} = 0 \quad (8)$$

where  $i_x$ ,  $i_y$  and  $i_z$  are the components of the electrical current vector.

The electrical current is directly related to the first derivative of the electrical potential,  $\Phi$ :

$$i = -\sigma \left( \frac{\partial \Phi}{\partial x} + \frac{\partial \Phi}{\partial y} + \frac{\partial \Phi}{\partial z} \right) \quad (9)$$

where  $\sigma$  is the conductivity of the electrolyte.

Combination of Eqs.(8) and (9):

$$-\sigma \left( -\frac{\partial}{\partial x} \left( \frac{\partial \Phi}{\partial x} \right) - \frac{\partial}{\partial y} \left( \frac{\partial \Phi}{\partial y} \right) - \frac{\partial}{\partial z} \left( \frac{\partial \Phi}{\partial z} \right) \right) \quad (10)$$

The conductivity may be a functional relationship or a constant value.

Assuming a constant value for conductivity allows for the reduction of Eq.(10) to the Laplace equation:

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} = 0 \quad (11)$$

When the Laplace equation is used as the governing equation for electrochemical corrosion the effects of electrical sources and sinks are incorporated into the mathematical model through boundary condition definitions.

Regions of the boundary which have fixed values of potential are defined by:

$$\Phi = C_1 \quad (12)$$

where  $C_1$  is a constant. Voltage sources are boundary conditions of the first or Dirichlet type. In this type of boundary conditions the dependent variable, the electrical potential, has a defined value. Defined values of voltage can be used to model impressed anodes or other electrical sources where the voltage is held constant for steady state conditions.

Electrical current sources or sinks are defined by:

$$i = \frac{\partial \Phi}{\partial n} = C_2 \quad (13)$$

where  $n$  is the normal to the boundary and  $C_2$  is a constant. Electrical sources and sinks are boundary conditions of the second or Neumann types. The normal derivative of the dependent variable, the electrical current or current density, is assigned a defined value. Painted surfaces are often represented as:

$$i = \frac{\partial \Phi}{\partial n} = 0 \quad (14)$$

Neumann boundary conditions can also be used to model impressed current anodes or other electrical current sources when the electrical current can be represented as a constant value. Any electrical source which does not vary in time can be represented in this fashion.

The electrical current, or current density, of an exposed metal surface is determined from the material polarization response and the measured electrical potential on the metal surface:

$$i = f(\Phi) \quad (15)$$

where  $f$  represents a functional relationship. In the Tafel response region, the polarization relationship between electrical current and electrical potential is linear, however, in general the relationship is nonlinear. The anodic and cathodic polarization responses typically are not represented by one analytical solution. Polarization response is a boundary conditions of the third or Cauchy type in which the boundary conditions has a functional dependency on the dependent variable, the electrical potential in this case. Cauchy boundary condition are also known as mixed boundary conditions.

## 4 Corrosion prevention

Corrosion is a natural phenomenon which cannot, using strict definitions, be eliminated. However, if the rate of corrosion can be reduced so that the amount of corrosion which occurs over the lifetime of a structure is negligible, corrosion has been, for all practical purposes, eliminated. Good design practices and a knowledge of fundamental corrosion behavior can be combined to greatly reduce corrosion damage. Often the primary goal of computer modeling is to evaluate the performance of a corrosion prevention system.

Three common corrosion prevention techniques are summarized in this section; material selection based on electrical compatibility, cathodic protection and painting or coating. The techniques described are not the only methods available to reduce corrosion. Each of the techniques can be readily modeling with existing boundary element techniques.

### 4.1 Material selection based on electrical compatibility

Galvanic corrosion occurs when materials having different open circuit potentials and polarization responses are electrically connected. The amount of galvanic corrosion which occurs can be reduced by judicious selection of materials based on their location in the galvanic series or by more detailed evaluation of the electrical current generated when the two materials are connected. The magnitude of the electrical current will depend on the electrolyte conductivity, the ratio of cathodic to anodic material surface area, and the cathodic and anodic material polarization behavior. All of these factors will determine the driving force for the resulting electrical current. The greater the electrical current generated, the greater the corrosion rate on the anodic material.

In the design of joints or connections in which two or more different materials are used, galvanic corrosion response must be taken into consideration. Material compatibility with respect to rest potential and possible corrosion damage is as important as basic structural characteristics such as yield strength and ultimate strength.

Computer modeling techniques can be readily used to determine the galvanic corrosion electrical current associated with different material combinations. Parametric studies can be performed to determine which, of all possible material combinations, results in the lowest galvanic electrical current and therefore the lowest corrosion rate. Computer models will explicitly address geometric and relative area concerns as well as determining the effects of differences in polarization responses.

### 4.2 Cathodic protection

Cathodic protection uses electrochemical properties of metals to insure that the metal of interest becomes the cathode of an electrolytic cell. Corrosion is allowed to occur but the electrochemical properties are taken advantage of in such a way that the anode is defined and corrosion damage is contained to a specific area.

In galvanic corrosion, the more active metal preferentially experiences corrosion. Cathodic protection using sacrificial anodes takes advantage of the galvanic properties of two metals. The sacrificial anode is a volume of metal added to the structure for

the purpose of being destroyed by corrosion. The sacrificial anode metal is chosen so that it is more active than the metal to be protected. Classical examples of sacrificial anode systems are zinc, aluminium and magnesium anodes used to protect steel structures in aquatic or moist environments, such as seawater spray, partially saturated soils and saturated soils. Zinc, aluminium or magnesium are more active than steel so these materials will become the anode and will preferentially corrode before corrosion occurs on the cathode, i.e. the steel structure. Since the system is designed so that the anode is known, the length of time required for complete destruction of the anode by corrosion can be determined. Prior to complete destruction of the sacrificial anode, additional sacrificial anodes can be placed on the structure providing a continual supply of material which can corrode without effecting structural integrity.

Sacrificial anode cathodic protection systems are not perfect. Sacrificial anodes may corrode non-uniformly and are not able to adjust dynamically to increased electrical current demands which result from changes in the service conditions, environment or increased area to be protected due to surface damage. The structure itself is required to have an increased load bearing capacity because of the added weight of the sacrificial anodes. Uneven corrosion of the anodes will also effect the system corrosion prevention performance. The region of cathodic material which can be protected by a single anode is dependent on the metal's polarization characteristics and the conductivity of the electrolyte. Despite the limitations, sacrificial anode systems are widely used.

Existing boundary element methods, which incorporate first, second and third type boundary conditions capabilities, can be used for modeling sacrificial anodes. Sacrificial anodes can be defined as sources with physical dimensions and location or can be defined as point sources. Prescribed voltage values along with defined polarization response completely define the anode material behavior.

Impressed current cathodic systems and sacrificial anode systems prevent corrosion in the same manner; by cathodically polarizing the material to be protected. Impressed current systems use an external power supply as the source of electrons required for polarization of the metal to be protected. An external power supply may have more than one location, or impressed current anode, where current is supplied to the system.

Some problems associated with sacrificial anodes are eliminated by the use of impressed current systems. Impressed current systems can be adjusted to meet dynamic changes in the system. Whether an impressed current system can adjust to provide adequate protection will depend on the system design. The added weight of sacrificial anodes is replaced by the added weight of the required power supplies. For a large structure, the difference in added weight can be significant. The area which can be protected by an impressed current anode is typically greater than the area which can be protected by a sacrificial anode. The extent of metal which may be protected by a single impressed current anode is dependent on the electrolyte conductivity and the available power supply. The cathodic material polarization response, of course, also plays a role in the extent of cathodic material which can be protected by a single anode.

Impressed current systems may be modeled using existing boundary element techniques. The impressed current anodes can be defined with specific areas and locating.

They can be assigned values of electrical voltage or electrical current density. The boundary conditions defining impressed current anodes are held constant through out the analysis thus modeling a constant power supply.

### 4.3 Paints and coatings

Paints and coatings are used to protect from corrosion in the same manner; the paint or coating is used to isolate the metal to be protected from the environment. A coating can be a layer of a non-corroding metal plated to the metal to be protected, a paint and primer system or a naturally forming surface film. The term 'paint' may or may not imply cosmetic or ascetic purposes in addition to corrosion protection. Paints are a combination of pigment and medium containing the pigment. In this brief description of paint and coating systems, the terms paint and coating will be used interchangeably.

There are a wide variety of paints available and marketed for use as corrosion inhibitors. Different paints have been developed for different materials and environments. The selection of a suitable paint is only the first step in the creation of an effective corrosion prevention system. Surface preparation, application methods, number of layers, combinations of different layers of different types of paints or primers and thickness of layers are features which define a paint system.

Unfortunately, painted surfaces are not free from defects regardless of the care taken during application. Mechanical damage, such as scratches or chipping, and flaws from incorrect application procedures result in areas of exposed metal. These exposed areas can be either small or large. If only relatively small areas of metal are exposed through paint damage, corrosion can become severe. The remaining painted surface acts as the cathode while the small exposed region of metal acts as the anode. The large cathode to anode surface area ratio results in severe corrosion attack because of galvanic corrosion behavior. In order to avoid severe corrosion damage at small isolated areas of paint damage, secondary protective systems, such as cathodic protection, are often used with painted surfaces.

Paint systems can be incorporated in boundary element models by defining an electrical current density of zero for a well painted surface. Specific experimentally obtained painted surface polarization data can also be used if a more exact solution is required. Areas of paint damage can be modeled by assigning metal polarization response to specified elements. Mesh size can become an issue when modeling a structure which has small areas of paint damage. Extremely small damage on a relatively large structure may require combining local and global models for accurate representation. Location of paint damage can be as crucial as the extent of paint damage. Identification of paint damaged areas should be based on observations from full scale structures whenever possible. In the case of damage due to erosion, impingement or other effects which may occur randomly along the structure, statistical approaches may be required to determine representative damage locations.

The descriptions of protection systems given are brief summaries. The design of a corrosion protection system is a complex task. Detailed information on the three systems described as well as other preventative measures can be found in the literature.

## 5 Example computer modeling of corrosion systems

The ability to use computational modeling techniques to evaluate electrochemical corrosion has been established. Finite element and boundary element methods have been used to model geometrically complex structures ranging from tube-to-tube-sheet connections in steam generators<sup>12</sup> to offshore piping platforms<sup>13</sup>. Reviews by Nazami, Porter and Mufti<sup>5</sup>, Munn<sup>6</sup> and DiGiorgi and Kaznoff<sup>14</sup> show the versatility of computer modeling as applied to corroding systems.

Computer modeling techniques can be used to determine the electrical current density-electrical potential values for the entire surface area of a structure. Boundary conditions of the first, second and third type are combined to represent a particular structure, the surrounding medium, and all associated electrical sources or sinks. Polarization response is used by the computer solution algorithm to correlate electrical current levels and electrical potential values for the exposed areas of metal. The polarization response is the material constitutive response required for the numerical solution and can be thought of as equivalent to the stress-strain response required for structural evaluations. As with any constitutive response, inaccuracies or inappropriate values will result in variation between computational and observed results.

Any computer method which can be used to solve the governing equations can be used to predict electrochemical behavior. Solution accuracy may be identical for different analysis methods, i.e. finite element and boundary element, however the ease of computer model formulation may be very different<sup>5</sup>. It may be simpler to model the physical characteristics of a specific structure experiencing electrochemical corrosion using a particular modeling technique. In the case of a structure submerged or buried in an relatively large volume of electrolyte, boundary elements techniques are a more natural choice. The volume of interest which must be modeled to determine electrochemical behavior is that of the electrolyte surrounding the structure. The metal surface of interest is that at the solid-electrolyte interface. Modeling using finite difference techniques is restrictive with respect to the degree of geometric complexity which can be achieved. Often the structure to be evaluated is not geometrically simple and either boundary element or finite element techniques are required to accurately model the structure. Modeling using finite element techniques becomes tedious and complicated because geometric complex three-dimensional models must be generated. Boundary element techniques require only modeling of the structure-electrolyte interface instead of the entire electrolyte volume. Therefore significant reductions in model complexities are possible when boundary element techniques are used rather than finite element techniques. In addition, the model created is a two-dimensional shell of the structure rather than a full three-dimensional representation of the volume surrounding the structure. The outer limits of the electrolyte are modeled as the outer edges of a box or other simple structure completing the boundary element model. In the case of a structure in an infinite or semi-infinite volume of electrolyte the resulting two-dimensional shell type boundary element model is typically a simpler model than would be required by for finite element evaluation of the structure. Modeling concessions necessary for the creation of any computer model, which may result in loss of accuracy, will not be as severe for the simpler boundary element model.

In this section, two example are presented which demonstrate the application of

boundary element techniques to the evaluation of structures in infinite electrolyte domains. The infinite electrolyte domain is representative of structures set afloat in deep water or buried in thick soil strata. In both of these cases, the extent of the electrolyte surrounding the structure is large in comparison to the size of the structure. In the first example, a pipe of two different materials is submerged in a tank of seawater. The galvanically generated electrical current is determined for a series of different connection geometries. The parametric study performed demonstrates the ability to use computer modeling as a design tool to determine the configuration with the lowest electrical current and therefore the lowest rate of corrosion. In the second analysis, the impressed current cathodic protection system of a ship is modeled and the electrical current required to maintain protection against corrosion is determined. The second analysis addresses such issues as multiple material properties, complex geometries and comparison with experimental results.

### 5.1 Piping system evaluation

One of the advantages of computer modeling is the capability of comparing system performance. This capability allows the designer to consider the effects of changes in system design on overall system performance without the cost associated with performing an experimental evaluation of each configuration. The boundary element technique example involves the determination of the most beneficial connection of two galvanically incompatible materials in a piping system which is submerged in seawater. A parametric approach is used to determine the most desirable configuration.

The ideal piping system would be fabricated from one material and if two materials were joined they would be electrically compatible minimizing the resulting galvanic corrosion. Piping systems, however, often consist of several materials which are electrically incompatible resulting in galvanic corrosion damage to the piping system. Piping systems commonly include a variety of connections such as piping of the same diameter but different materials as well as pieces of piping of different diameters which may or may not be of the same material.

The boundary element technique example problems is the evaluation of possible connections between two pieces of piping of different materials. The two metals chosen for study are Inconel and Copper-Nickel (CuNi) alloy. These particular metals were chosen for the demonstration problem because the difference in open circuit potentials and polarization response will result in galvanic corrosion. It is the intent of the computer modeling and analysis to determine how galvanic corrosion can be minimized for these two materials and not whether significant galvanic corrosion occurs. A commercial boundary element code was used in all evaluations. There were no external applied electrical current or voltages. The only driving force used in the analysis was the difference in material polarization responses for the Inconel and CuNi alloy. The analysis used standard program features and no special computer coding to analyze the piping.

A straight pipe consisting of equal lengths of the 10.2 cm diameter Inconel and CuNi alloy was evaluated. The total length of the pipe is 934.7 cm. The pipe is submerged in the center of a 914.4 cm diameter tank filled with seawater. A boundary element model of 260 elements and 463 nodes was created of the exterior surface of

pipe and the surrounding seawater. Quadratic elements were used to model the piping sections, linear elements were used to model the tank boundary. Small elements were used in the region near the connection between the two materials in order to accurately capture the electrical current density and electrical potential gradients near the material interface. Axisymmetric modeling was used so that the model, shown in Fig. 4, represents the outline of a 1° slice of the circular piping and surrounding seawater. The volume of seawater surrounding the pipe is large but finite. Nonlinear polarization response curves<sup>11</sup> were used to characterize the material behavior. The seawater was modeled as a homogeneous electrolyte with a constant conductivity of  $0.05 \text{ Ohms}^{-1}\text{-cm}^{-1}$ .

The electrical current density does not vary significantly along the anodic section of piping with the maximum electrical current density of  $4.8 \times 10^{-6}$  to Amperes/cm<sup>2</sup> occurring at the material interface. The approximately constant electric current density will result in corrosion which will be uniform along the length of the CuNi section of piping. The amount of corrosion at any location can be approximated by that caused by the maximum electrical current density. The corrosion rate can be determined using Faraday's law and the appropriate material properties, as shown in Eq. (7). Based on the maximum electrical current density, the corrosion rate for the submerged pipe is 0.11 mm/yr.

The second pipe to be evaluated is fabricated from equal length sections of 30.4 cm diameter Inconel pipe and 10.2 cm diameter CuNi pipe. The total length is 934.7 cm. Four different piping connections were considered; a step connection, and a 121.9 cm long taper of Inconel. The piping was submerged in a 914.4 cm diameter tank filled with seawater. The pipe and the tank were modeled using an axisymmetric boundary element model of 445 linear elements and 450 nodes was created of the step connection geometry. Element size was larger than that of the previous two material straight pipe model and the increase in element size was based on the results of the previous analysis.

In all cases, step and taper connections, the maximum electrical current density occurs in the CuNi alloy, the anode, at the material interface. The maximum electrical current densities for the different connection geometries are:

- step connection  $-9.7 \times 10^{-6}$  Amperes/cm<sup>2</sup>
- Inconel taper  $-12.0 \times 10^{-6}$  Amperes/cm<sup>2</sup>
- CuNi taper  $-8.5 \times 10^{-6}$  Amperes/cm<sup>2</sup>

It is apparent from the maximum electrical current density that the piping connection which would result in the least amount of galvanic corrosion is the taper connection with the taper fabricated from CuNi alloy. The oxidation rate of the CuNi alloy must balance the reduction rate of the constant surface area of Inconel. Therefore, the lowest corrosion rate will occur for the connection which has the smallest cathode to anode area ratio.

As demonstrated in this example, it is possible to evaluate the performance of different piping system configurations once materials have been selected. While not demonstrated in the study presented, it is possible to generate corrosion rate information for different material combinations for similar piping system geometries. It is

also a relatively simple matter to apply the parametric study approach presented to more complex structures. While it may not be possible to prevent all corrosion related failures due to the complex interaction of structure and environment, it is possible to predict failure in many cases when corrosion evaluation is included in the design process. The simple studies performed show the versatility of boundary elements and computer modeling as a design tool.

## 5.2 Impressed current cathodic protection system analysis

Evaluations of an existing impressed current cathodic protection (ICCP) systems on U.S. Navy CG class surface ship were performed using commercial boundary element code. Electric current requirements for a six anode single zone and a six anode two zone system are evaluated for static (ship at rest) and dynamic (ship underway) conditions<sup>16</sup> The example presented in this section is the evaluation of the six anode single zone system for static conditions. A zone is an independently controlled power supply used to provide the electrical current to the impressed current anodes. Anodes within a control zone have identical voltages and electrical current values. Therefore, the six anodes of the system studied have identical voltage values assigned. The magnitude of electrical current for each anode is used for a system solution check. The magnitude of electrical current is calculated by the boundary element program and should be equal for all anodes.

The computer modeling results are compared with experimental data obtained through physical scale model testing. Physical scale model testing involves the scaling of geometric dimensions of the structure and scaling of the electrolyte conductivity<sup>17</sup>. Physical scale modeling experimental results have been successfully compared with data obtained from tests performed on full size ships<sup>17</sup>. The ability to use scale model test results, which can be related to full size ship data, increases confidences in the reliability of computational results. The physical scale model experiments were performed using a scaling factor of 1/96 for the models and seawater conductivity.

The ship geometry and ICCP system examined is shown in schematic form in Fig.6. The boundary element model consists of half of the hull geometry taking advantage of port and starboard symmetry to reduce the mesh size. Only the portion of the ship hull below the water line is required to be modeled. The boundary element model of the CG class surface ship consists of 573 quadrilateral constant value elements and 700 nodes (Fig. 6).

The boundary element model of the CG class ship geometry developed has the following features:

- detailed modeling of the complex curvature of the hull surface
- inclusion of rudder as geometrically distinct but electrically connected component
- inclusion of propeller assembly as geometrically distinct but electrically connected component
- use of nonlinear polarization response curves to represent material behavior

- use of three separate materials (steel, nickel-aluminum-bronze (n-a-b) and paint) to model separate regions of the ship.

The impressed current anodes have finite areas and fixed locations and are explicitly included in the boundary element model through use of constant voltage boundary conditions. The total electrical current into the system through the impressed current anodes and the total electrical current leaving the system through the exposed metal sections are compared as a check on the accuracy of the calculated solution.

Three different materials are used to model the hull, propellor and rudder in the model. The hull is assumed to be undamaged paint and therefore no electrical current is allowed to be transmitted to the hull surface. The propellor and rudder are modeled as bare nickel-aluminum-bronze (n-a-b) and steel, respectively. Nonlinear representations of polarization response were used for steel and n-a-b. Seawater is defined as a homogeneous electrolyte with a constant conductivity of  $0.05 \text{ Ohms}^{-1} \text{ cm-l}$ .

The material configuration of the physical scale model test specimens and the surface ship as represented by the computer models are different. There are four differences between physical scale model test ship and computer model material definitions. These differences must be taken into consideration when comparing global and local results. The first two differences are a result of mesh refinement limits resulting from time and financial limitations. The scale model test ship contains the bilge keel. The boundary element does not. The bilge keel can be idealized as a narrow ridge which is perpendicular to the hull as shown in Fig. 5. The bilge keel acts as a deflector and shields a portion of the hull from electrical current flow and the associated electrical potential of the seawater at the hull surface. The boundary element does not contain the bilge keel because it was felt at the time of original modeling that the bilge keel does not act as a significant geometric feature. Subsequent work indicates that this may not have been a valid assumption. The physical scale model test ship also contains docking blocks which represent 1% of the total surface area. The docking blocks are bare steel and are located along the port-starboard centerline. The docking blocks were not included in the computer model because of the mesh size limits resulting from time and financial limitations. Docking blocks are relatively small geometric features and it was felt that they were smaller than the level of detail required. The third and four differences in the two models deal directly with the representation of the rudder and propellor. The rudder in the physical scale model test ship is painted. The rudder in the boundary element model was bare steel. It was the intent of the original computer model to represent extreme damage to the rudder. Finally in the boundary element model the propellor is modeled as a solid disk as opposed to the detailed propellor of the physical scale model test ship. These variations in material assignments for different components will effect the total required electrical current because of differences in exposed metal areas.

It is often unfortunately the case that experimental and computer models are not identical. The reasons for differences in the two models can vary from miscommunication to inability to create as refined a computer model as necessary. The analyst must recognize the areas of difference and be able to identify results which can be compared. The ideal situation occurs when there is an one-to-one correspondence between experimental specimens and computer models. In this case, the value which

can be meaningfully compared is the total electrical current absorbed by the propeller.

ICCP systems are controlled by defining a target electrical potential associated with a specified reference cell. Corrosion will not occur when steel is cathodically polarized to an electrical potential of -0.85 volts measured with a Silver-Silver Chloride (Ag/AgCl) electrode. Physical scale model experimental results used for comparison are for reference cell readings of -0.85 Ag/AgCl. In the boundary element analysis, a reference cell potential range of -0.83 to -0.87 volts Ag/AgCl is used to define the target condition. In order to bound all possible solutions, upper and lower bound solutions are defined based on electrical current requirements. The upper bound solution is defined as that which requires more electrical current and is therefore associated with a reference cell reading of -0.87 volts Ag/AgCl. One design problem associated with ICCP systems is the ability to locate a reference cell which is truly representative of the hull surface condition. It is also possible to determine, by examination of all hull surface potentials, how well the reference cell reading represents the potential of the entire hull surface.

Since the boundary element program uses an iterative solution technique it is possible that the electrical current values associated with impressed current anodes may not be exactly equal for anodes within a zone. The solution tolerance will effect the variation in currents determined as part of the boundary element solution. Because of the iterative nature of the solution procedure a tolerance on electrical current equivalency is required to determine solution acceptance with regards to the criteria imposed on each power supply zone. The impressed current anodes belonging to the same zone must have a total electrical current input within 0.5 Amperes of the other anodes attached to the same power supply for the solution to be considered valid.

The current and voltages required for a lower bound solution (reference cell at -0.83 volts Ag/AgCl) for the single zone system at static conditions are:

$$V_A = V_B = V_C = -1.3 \text{ volts}, \quad I_A = I_B = I_C = 3.2 \text{ to } 3.4 \text{ Amperes} \quad (16)$$

where the locations of anodes  $A, B$  and  $C$  are as defined in Fig.5. The range in electrical current for anodes is due to the iterative nature of the boundary element technique. A more refined mesh and tighter convergence tolerances will eliminate this variation. The negative voltage value indicates voltage supplied to the system for the particular boundary element formulation used in the analysis.

The upper bound solution (reference cell at -0.87 volts Ag/AgCl) requirements are:

$$V_A = V_B = V_C = -1.45 \text{ volts}, \quad I_A = I_B = I_C = 3.7 \text{ to } 4.0 \text{ Amperes} \quad (17)$$

Electrical potential profiles for the port-starboard centerline and for the side of the hull at a depth of 3.0m. are shown in Fig.7. Computer and physical scale model test data show similar trends.

Physical scale model and computer results indicate that electrical potential values on the rudder and propeller are less than required for corrosion prevention despite the electrical potential at the reference cell. The range in electrical potential on the rudder side tip of the propeller is -0.76 to -0.82 volts Ag/AgCl. The physical scale model measured electrical potential for the same location is -0.72 volts Ag/AgCl.

Despite the good agreement in electrical potential values, both along the two profiles chosen and for a specific point, there is a large discrepancy in the total electrical current calculated from physical scale model tests and the computer modeling solutions. Boundary element solutions result in a range of total current required from 20.2 to 23.8 Amperes. Of this total, 10.0 to 10.6 Amperes is delivered to the propellor. Physical scale test data indicates a total current requirement of 63.9 Amperes with 43.1 Amperes delivered to the propellor. Possible explanations of the difference in the amount of electrical current delivered to the propellor are the uncertainty in the material polarization response curves used in the computational model and the presence of the bilge keel in the physical scale model. The n-a-b polarization curve was determined using filtered seawater and small laboratory test specimens<sup>11</sup>. The laboratory data used may not be the most appropriate for the conditions and material surface features of the n-a-b used in the physical scale experiments. It is possible that more appropriate polarization curves may result in increased accuracy of computer results. The bilge keel has been observed to act to deflect the flow of electrical current and may be partially shielding the reference cell in the experiments.

Based on the analysis performed the boundary element method has been demonstrated to accurately predict global behavior. Differences between experimental and computational results can be attributed to variation inherent in the material polarization response and to geometric characteristics not included in the boundary element model. Additional mesh refinement, which will allow for inclusion of the docking block and bilge keel features should also result in an improvement in total electrical current requirements. It is interesting to note the relative sensitivity of the electrical potential profile and total electrical current. Electrical potential profiles, which are a global structure response, are less sensitive to mesh refinement and material characterization issues than total electrical current, which is the integration of the local current density response.

Once the desired accuracy of computer modeling is obtained and verified by comparison with experimental data, the versatility of computer modeling can be exploited by the analysis. Power supply zones connecting various anodes can be created by changing the defined voltage or electrical current or current density boundary conditions for anode elements. By simply changing the value of boundary condition definitions the analyst can explore all possible power zone combinations and power source limitations. The reference cell location, which may or may not yield electrical potential values which are indicative of potential levels in regions of interest such as the propellor, can be changed to any existing node location and need not be predefined. Electrical potential profiles and contours which show the global response of the ship can be used to determine system performance. Anode placement can be altered by redefining prescribed boundary conditions to different elements. Different operating conditions, defined by temperature, salinity or ship speed, can be evaluated by changing the resistivity of seawater and the material polarization response. The list of possible combinations is, for all practical purposes, endless.

### 5.3 Summary

The two examples presented in this section demonstrate the versatility of the boundary element method. The ability to modify existing systems, whether by changes in materials or geometry, is a powerful aspect of computer analysis. The examination of beneficial or adverse effects of design variations, intentional or as a result of fabrication difficulties, are another positive feature of computer analysis. While understanding of the mathematics of the computer programming and of the physical phenomena is necessary for the successful completion of a computer analysis, this should not deter one from the use of this powerful tool. Commercial boundary element computer codes are readily available or it is possible to create special purpose codes within a reasonable amount of time based on the existing technology. In summary, the corrosion characteristics of a system may be determined using existing computer modeling techniques.

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## **Galvanic Series**

### **Metals Exposed to seawater**

#### **Noble (Cathodic)**

Platinum

Gold

Titanium

Silver

Type 316,317 Stainless Steels (Passive, with Oxide Film)

Nickel

Nickel-Aluminum-Bronze

7030 Copper Nickel

Lead

Tin Bronzes

Silicone Bronzes

Manganese Bronze

Copper

Tin

Naval Brass, Red Brass, Yellow Brass

Type 316,317 Stainless Steel (Active, without Oxide Film)

Low Alloy Steel

Mild Steel, Cast Iron

Aluminium Alloys

Zinc

Magnesium

#### **Active (Anodic - Corroding Surface)**

Table 1

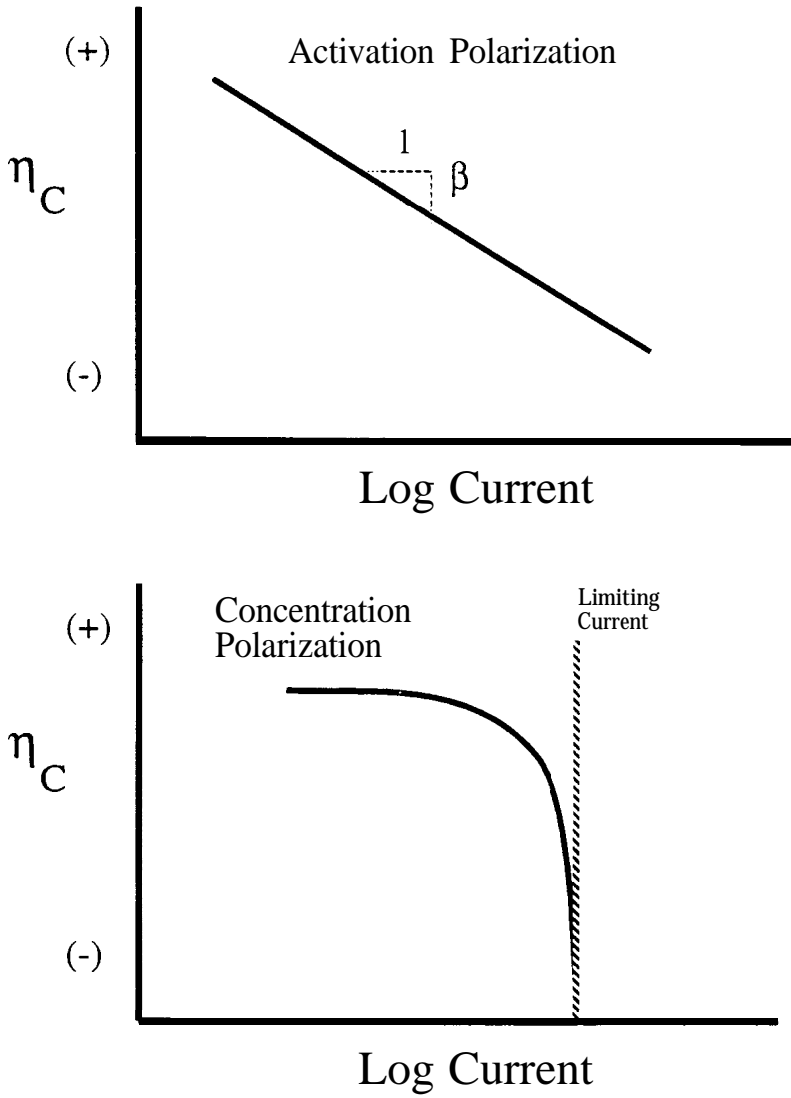


Figure 1

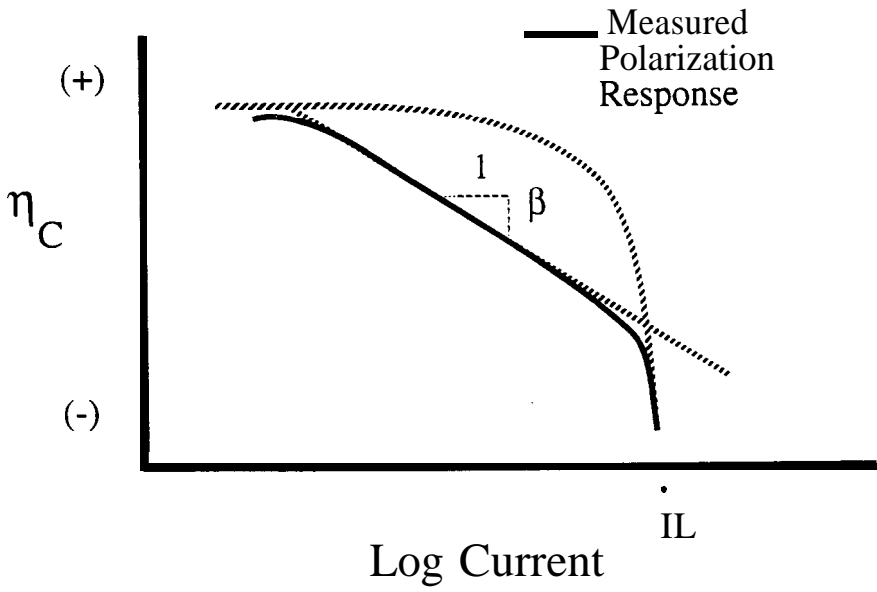


Figure 2

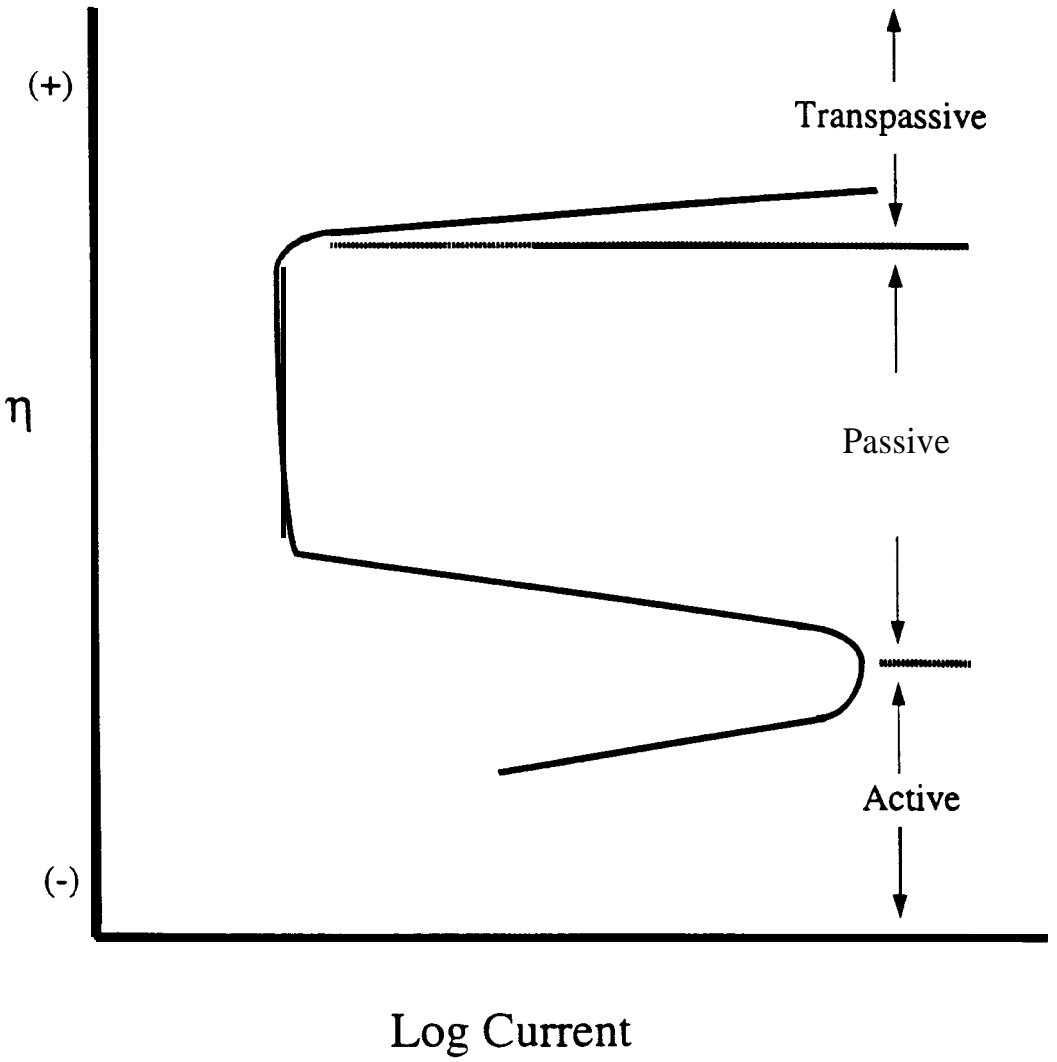


Figure 3

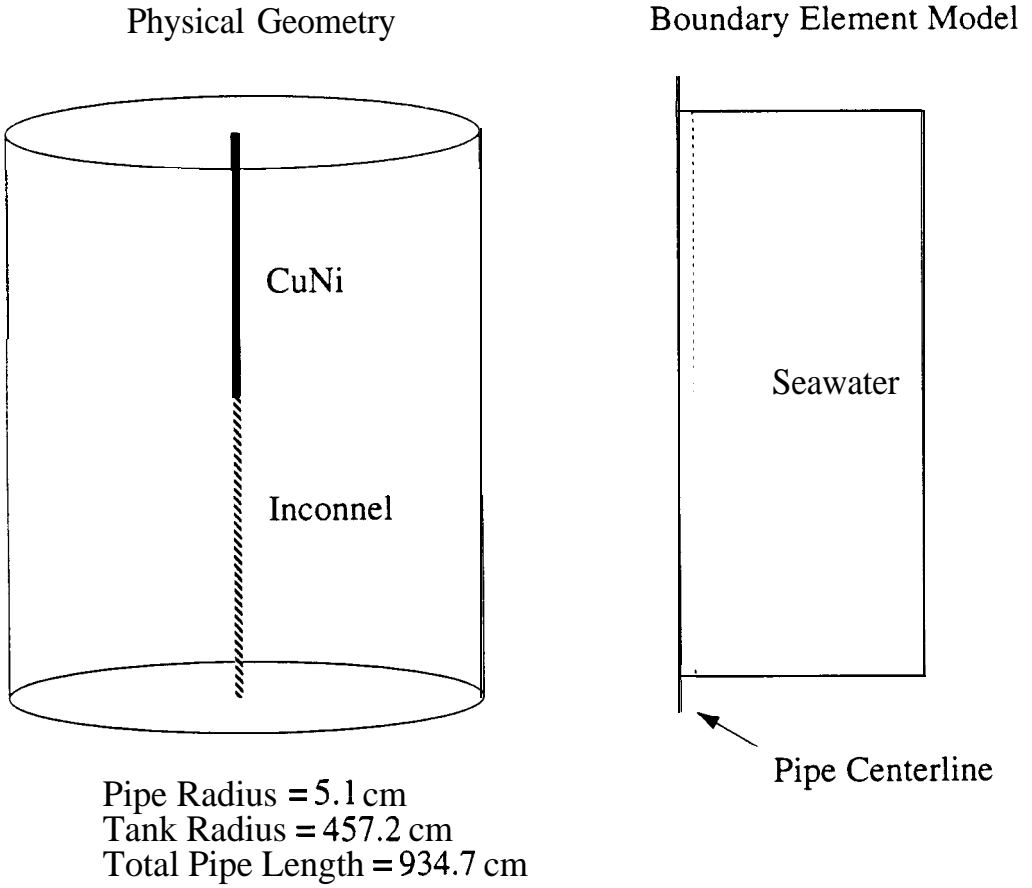


Figure 4

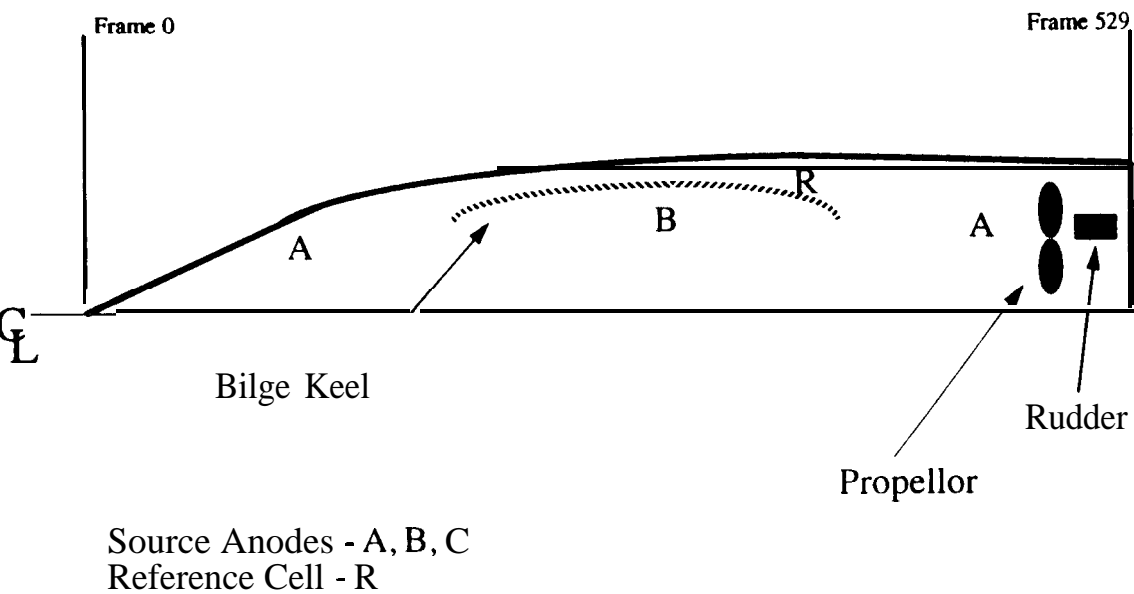


Figure 5

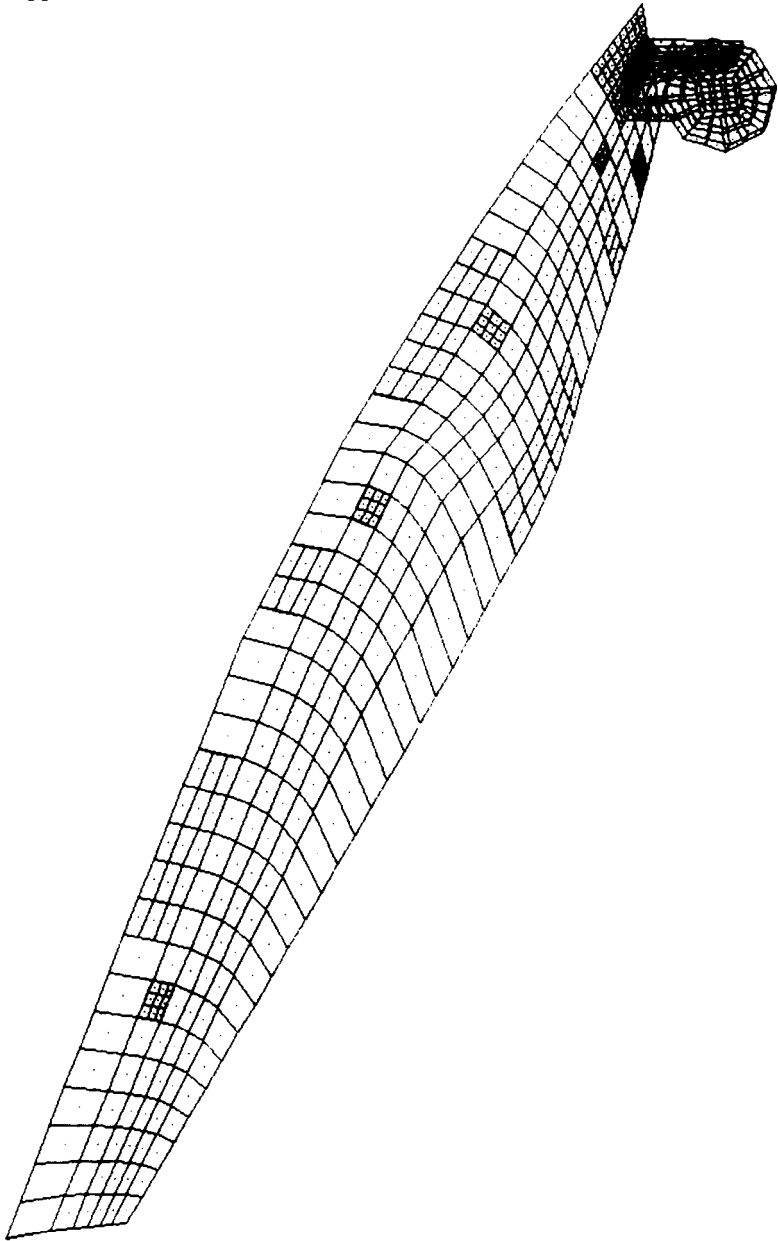


Figure 6

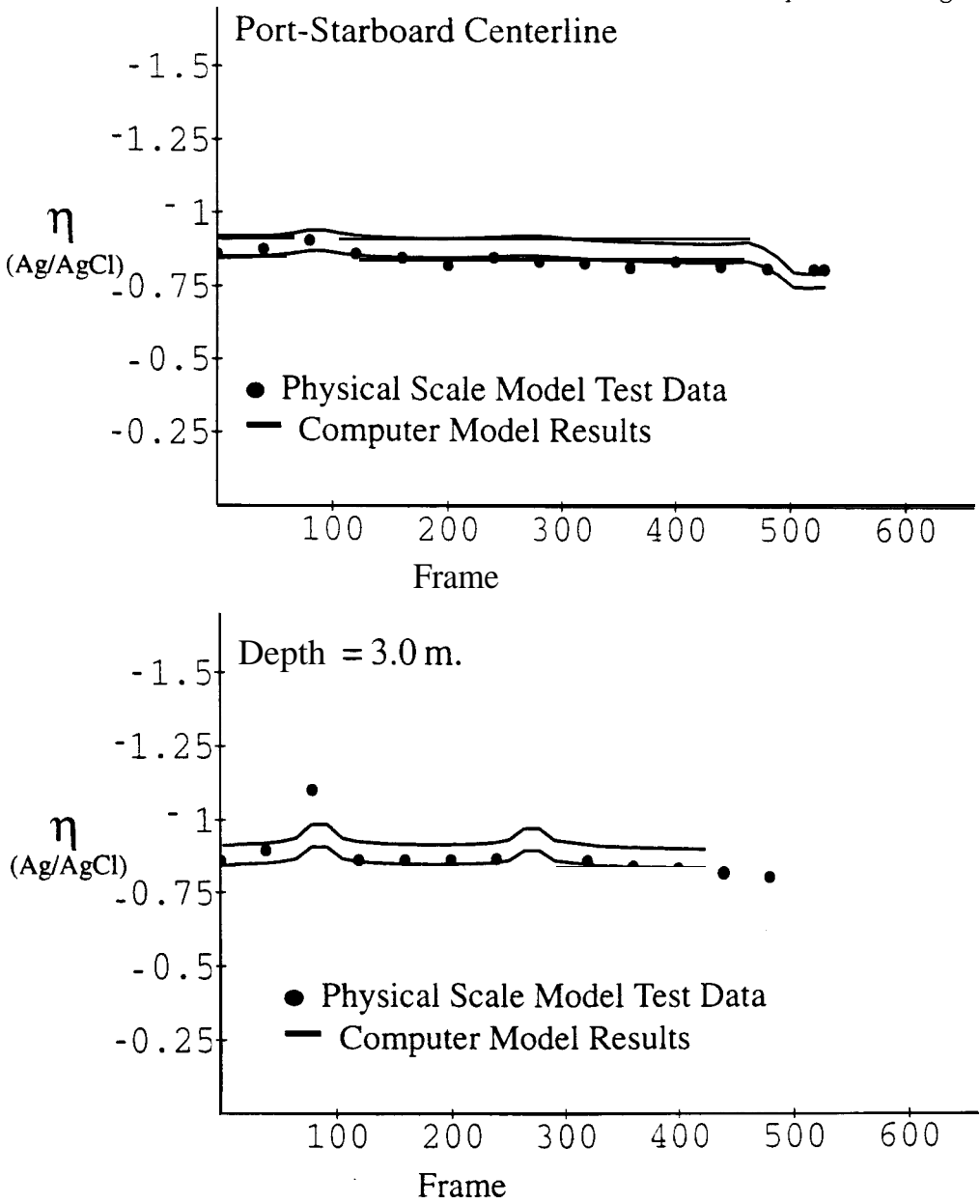


Figure 7