ONE DIMENSIONAL APPROACH TO MODELING DAMAGE EVOLUTION OF
GALVANIC CORROSION OF A CONCENTRIC CYLINDRICAL GEOMETRY

A Thesis

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A one-dimensional mathematical model is developed to describe the damage evolution caused by galvanic corrosion of concentric cylinders for Mild Steel / Magnesium and Copper / Aluminum galvanic cells. Laplace’s Equation in a well mixed electrolyte solution above the concentric disks is analyzed using an asymptotic procedure based on disparity in geometric length ratios to develop a one-dimensional model equation for the potential. This equation is solved numerically, to determine the potential, current density, and corrosion caused by the galvanic cell using MATLAB. Experimental polarization curves given in the literature are used as inputs for numerical computation. It is also assumed that there is no mass transport and that the electrolyte thickness is restricted by the Wagner relationship. This model solves for initial time and time dependent solutions. The model accounts for changes in the metal radius length ratio, electrolyte solution height, and overall size of the cell. The 1D model predicts that the corrosion damage in the galvanic cell is linked to the potential drop and current density across the coupled metals.
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I would like to have this paper be in memory of my late father Gregory L. Smith who passed away during April, 2012 at the age of 52.

“The universe is big, its vast and complicated, and ridiculous. And sometimes, very rarely, impossible things just happen and we call them miracles. And that’s the theory. Nine hundred years, never seen one yet, but this would do me.”

- Steven Moffat
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CHAPTER I
INTRODUCTION

The purpose of this thesis is to develop a mathematical model for a dissimilar metal couple in a concentric cylindrical geometry undergoing galvanic corrosion. This model will help understand the corrosion behavior in similar configurations and contribute as a tool in the migration and control of corrosion of metallic structures in future construction projects. Asymptotic methods are used to simplify the mathematical model and a parameter study is conducted to understand the influence of changing system variables on the corrosion.

1.1 Understanding Galvanic Corrosion

The United States spends over a quarter trillion dollars annually on the repair and replacement of materials affected by corrosion alone [1]. There is clearly an immediate need for materials that are more corrosion resistant. Industry is looking for new ways to describe the damage evolution during galvanic corrosion to help protect multi-metallic systems in their equipment and structures [2]. This thesis presents a model that would allow industrial engineers to analyze material interaction. After analyzing the damage evolution model for specific materials, one could make decisions to optimize the reliability of the product.
Corrosion is defined as the deterioration or wearing away of a material or its properties, due to a reaction with the nearby environment [3]. There are a few different types of corrosion including electrochemical and chemical corrosion. Corrosion degradation is mainly caused by electrochemical corrosion. For electrochemical corrosion to occur, there are four parts that are needed: oxidation and reduction reactions, a chemical solution, and a metallic pathway.

Thermodynamics is the study of changes in energy that are caused by a physical or chemical change [4]. If a physical system is unstable, energy levels will change to force the system to be thermodynamically stable, usually referred to as a “steady state”. Depending on the metals under investigation, either the metal is already at steady state, or the metal is unstable with the environment. If the metal is unstable, it will reach the steady state via the electrochemical corrosion process, which could cause a temperature change. Nesic [5] explains that an increase in temperature will increase the rate of any type of corrosion.

Electrochemical corrosion includes galvanic, pitting, and crevice corrosion. Galvanic corrosion begins when two different metals are either in contact with one another, or close enough to induce electrical fields. These electrical fields normally occur at, or near, a surface boundary and in physical contact with a conductive environment. This environment, in most cases, is an electrolytic solution made up of Sodium Chloride (NaCl) and water, more commonly known as salt water. This environment allows for the flow of current, which creates an electronic pathway [6].
Since the electrolyte covers both the anodic and cathodic metals, there is now a galvanic cell that is capable of conducting current. Due to the difference in metallic polarization properties, electrons will flow from the anodic metal to the cathodic metal. The main interest is near the cathode/anode interface, as this is the strongest electron flux point in the system. The electrolyte solution allows for the transport of ions, which depends upon the electrolyte solution conductivity. This conductivity value measures the ability to move ions within the electrolyte. There is a direct correlation between the electrolyte conductivity and the amount of corrosion, i.e. the larger the electrolyte conductivity, the larger the amount of corrosion, and vice versa.

Galvanic corrosion occurs when two different metals are submerged under an electrolyte solution and joined together by a conductive pathway [1, 6]. One way to differentiate between these metals is to look at the resting potential values, or open-circuit potentials (OCP). Once this open circuit potential is measured for a specific metal, this open circuit potential is compared against other metals. This comparison is put into a chart for easy comparison, called a Galvanic Series Chart.

Figure 1.1 shows the Galvanic Series Chart which identifies when two metals are compared, which one would act more cathodic and which one would act more anodic. The more active, corrosion prone metals are in the upper left corner of the chart, while the more noble, corrosion resistant metals are in the lower right corner of the chart. The same electrolyte solution must be used to compare two metals. When the resting potentials are found and compared on the chart, the metal that is more active is the anodic metal, while the metal that is more noble is defined as
the cathodic metal. One must also look at the distance between the metals in Figure 1.1. There is a direct correlation between the open-circuit potential value and the ability to accept the electrons from the anodic metal. The galvanic series shows the ability to accept the current from the other metal, but does not show how the system behaves.

Polarization curves are used to understand how a galvanic system behaves. Polarization curves show the relationship between the normalized potential and current for a specific galvanic system. The upper and lower branch are defined as the anodic and cathodic branches, respectively. The value at which the anodic and ca-
Figure 1.2: Polarization Curves for a two dissimilar metals

The point where the cathodic and anodic branches intersect is defined as the open circuit potential (OCP). When a metal is at open circuit potential, the net current density in the system is equal to zero. Figure 1.2 shows a sample polarization curve for two, unspecified dissimilar metals, which could be used for a galvanic system. Since there are two metals in this polarization curve, each of the metals needs to be defined as either the anodic or cathodic metal. The curve with the higher open circuit potential is defined to be the more noble metal, which leaves the curve with the lower open circuit potential to be defined as the more active metal. The Galvanic Corrosion Potential is defined to be the intersection between the cathodic, noble curve and the anodic, active curve.
1.2 Model Geometry

The concentric cylinder geometry is composed of nested cylinders of two different metals. Above these metals exists the conductive electrolyte solution, assumed (unless specifically stated) to be salt water. A representative diagram of the physical layout is shown in Figures 1.3 and 1.4.

All potentials and current densities are solved for inside of the electrolyte solution domain. These potential and current density values are used to solve for the damage profile in the anodic metal. All referenced boundary conditions relate to the inside of the electrolyte solution domain or to the electrolyte/metal interface.

To simplify this two-dimensional model, assumptions have to be made. First, the electrolyte solution is assumed to be “well-mixed”. This means that there is no ionic species concentration effects and that species transport is neglected. Second, the electrolyte solution thickness is approximated to be a thin film above the galvanic
cell. Third, the Wagner relationship will be assumed [7, 8]. The Wagner relationship requires that the polarization curve slope be steep for the corroding metal, as the product of the polarization curve slope multiplied by the electrolyte solution conductivity must be orders larger than the electrolyte solution height. Other assumptions made are that the oxygen concentration is constant in the electrolyte solution, there are no metal hydrolysis precipitate of either metal, and there is no hydrolysis forming metal hydroxide in the electrolyte.

Using the assumptions stated previously, the governing equations will reduce to Laplace’s Equation. To analyze the damage evolution over time, Faraday’s Law will be used to relate the mass lost due to the electrochemical reactions. The damage evolution equation will be calculated numerically with finite differences.

1.3 Literature Review

Literature suggests numerical techniques have been used to solve for only the initial time current density and potential. The asymptotic method has not been used to solve this problem, and damage evolution has not been considered. Galvanic damage evolution is an area that has not been extensively investigated. The devised model solves for the current density, potential, and physical damage evolution inside the specified boundaries of the electrolyte.

Murer et al. [9] states that the numerical model is defined by the Laplace and Nernst-Planck Equations for the electrolyte solution. Jia et al. [10] studies the relationship between pure Magnesium and Steel. The Laplace Equation was used
to represent the potential in the electrolyte which was solved by using a boundary element method program, BEASY. Their parameter study included varying cathode/anode surface area ratio, varying the electrolyte solution height, and varying the insulation distance.

Jorcin et al. [11] experimented with pure Copper (Cu) and pure Aluminum (Al) concentric disk couples with an outer insulation layer under a bulk sulfate electrolyte solution. The Laplace Equation was again used to represent the potential in the electrolyte solution. This which was solved by using a finite element method program, Femlab, which was then compared against experiential data.

Song [12] states that a two dimensional Laplace equation can be treated as a one dimensional problem if there is a defined small parameter. The same small parameter is used for the asymptotics for eliminating the later order terms. The assumption is first to create a small parameter defined as the ratio of the thickness of the electrolyte on the surface of the metals compared to the length of the entire electrolyte over the galvanic surface. Song investigated the problem using an analytic approach, and found that the closer the location is to a boundary, the steeper the gradient in potentials and current densities.

Deshpande [6] provides polarization data for pure Magnesium and Mild Steel. He goes to say that the corrosion rate of the anodic metal can be related to Faraday’s Law and is also one of the few that has investigated time dependent potential, current density, and damage results.
1.4 Main Results

Deshpande [6] considers a galvanic system made of Mild Steel and Magnesium submerged under an electrolyte solution composed of $0.016 \, M$ Sodium Chloride (NaCl). These results are used to benchmark the damage evolution of Magnesium. This data provides verification for the one-dimensional approximation method used in this thesis. Jorcin [11] has completed corrosion research regarding concentric disks measuring the damage at the cathode/anode interface with SEM microscopes for pure Copper and pure Aluminum. The University of Akron Corrosion Squad [13] has provided polarization data for the 99.9% pure Copper and 99.999% pure Aluminum submerged in a $0.1 \, M$ Sodium Chloride (NaCl). The Copper / Aluminum galvanic system is also analyzed.

After the base case investigation is completed for the one-dimensional approximation, a complete parameter study is performed. This parameter study focuses on changing the radius length of the anodic metal, while keeping a constant cathodic metal radius length, varying the cathodic to anodic metal ratio, varying the electrolyte solution height, as well as scaling up the galvanic system while holding a constant cathodic to anodic metal ratio. The parameter study analysis is completed to show the limitations of the thin film approximation and the Wagner relationship in the galvanic system.
1.5 Paper Outline

This thesis will present important results that investigate time dependent damage evolution as well as time dependent potential and current density values for coaxial concentric disks. The remaining paper is organized as follows. In Chapter II, the formulation of the mathematical model for the electrolyte is developed. The computational approach for the model can be found in Chapter III. The presentation of results can be found in Chapter IV, while a summary and future work follows in Chapter V.
CHAPTER II
FORMULATION OF THE MATHEMATICAL MODEL

This chapter explains how the mathematical model is formulated to estimate the damage evolution in a coaxial cylindrical geometry. First, a transport equation will be stated and assumptions will be considered. Once the transport equation is reduced to the potential equation, this equation will be converted into cylindrical coordinates. Initial conditions and boundary conditions will be presented. After this, the potential equation will be non-dimensionalized in order to use asymptotic methods to set up the equations to solve for the one-dimensional governing equation for the potential.

2.1 General Potential Equation

This section will derive the general two-dimensional potential governing equation and its boundary conditions.

2.1.1 2-D General Potential Equation

Due to the complexity of a galvanic corrosion system, assumptions have to be made to arrive at a simplified mathematical model. For the coaxial cylindrical corrosion problem being investigated, the physics of the problem is driven with the understanding of flux conservation relating to a transport phenomena equation. The Nernst-Planck
equation is given by

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \vec{J}_i,$$

(2.1)

where $C_i$ is the concentration of the $i^{th}$ species and $\vec{J}_i$ is the flux transport of the concentration. The Nernst-Planck equation shows the conservation of mass of a chemical species under the influence of an electrical field [9]. The flux equation is written as

$$\vec{J}_i = -D_i \nabla C_i - Z_i \frac{D_i F_c}{RT} C_i \nabla \phi + \vec{u} C_i,$$

(2.2)

where $D_i$ is the mass diffusion coefficient of the $i^{th}$ species, $Z_i$ is the valence number of the $i^{th}$ species, $F_c$ is Faraday’s constant, $R$ is the universal gas constant, $T$ is the temperature of the electrolyte, $\phi$ is the potential, and $\vec{u}$ is the velocity vector of the electrolyte medium. Note that equation (2.2) has three distinct parts on the right hand side, which represent the diffusion, migration, and convection terms, respectively.

To simplify further, an assumption is made that the electrolyte solution is “well-mixed”. Under this assumption, the concentration of the species in the electrolyte solution is constant throughout the entire solution, therefore the concentration gradients are zero, which results in

$$\nabla C_i = \vec{0}.$$

(2.3)

Hence the diffusion term is zero in equation (2.2).
If the convection of the electrolyte solution is assumed to be zero as well, the Nernst-Planck Equation is reduced to

$$\mathbf{J}_i = -\nabla \left[ -Z_i \frac{D_i F_c}{RT} C_i \nabla \phi \right]. \quad (2.4)$$

Another assumption that should be made is that the governing equation must satisfy electro-neutrality, the sum of all cathodic (positive) charges and the sum of all anodic (negative) charges cancel. This condition leads to

$$\sum_i Z_i C_i = 0. \quad (2.5)$$

These assumptions for the galvanic system along with equations (2.1), (2.3), and (2.5), lead to the conclusion

$$\sum_i Z_i \frac{D_i F_c}{RT} C_i \nabla \phi = 0. \quad (2.6)$$

Knowing that $Z_i, D_i, F_c, R, T$ are all constants, we simplify equation (2.6) to

$$\nabla^2 \phi = 0, \quad (2.7)$$

which is the Laplace Equation, for the two-dimensional potential in the galvanic system.

2.1.2 2-D Electrolyte Boundary Conditions

The boundary conditions at the top, left, and right boundaries of the electrolyte are given by

$$\mathbf{J}_i \cdot \mathbf{n} = 0, \quad (2.8)$$
where $\hat{n}$ is the outward normal derivative to the domain boundary. The flux equation (2.2) reduces equation (2.8) to
\[ \nabla \phi \cdot \hat{n} = 0. \] (2.9)

The bottom boundary condition at the electrolyte/metal interface can be represented by Ohm’s Law, given as
\[ \bar{J}_i \cdot \hat{n} = \frac{i(\phi)}{F_c}, \] (2.10)
where $i(\phi)$ is the current density as a function of the potential and is obtained from the polarization curve. It is known that the current density at the electrolyte/metal interface is given as the difference between the cathodic and anodic current densities, which can be written as
\[ i(\phi) = i_a(\phi) - i_c(\phi). \] (2.11)

Since the anode and cathode are separated physically, one can assume that the cathodic current density can be neglected across the anode and the anodic current density can be neglected across the cathode. Using equations (2.2), (2.3), (2.6), and the assumption that electrolyte is well-mixed, we see the electrolyte conductivity, $\kappa$, can be determined and represented as
\[ \kappa = F_c^2 \sum_i Z_i^2 \frac{D_i}{RT} C_i. \] (2.12)

This allows equation (2.10) to be rewritten as
\[ -\kappa \nabla \phi \cdot \hat{n} = i(\phi), \] (2.13)
which represents the electrolyte’s lower boundary condition, which is in contact with
the cathodic and anodic metals, where $i(\phi) = i_a(\phi)$ along the anode metal and
$i(\phi) = -i_c(\phi)$ along the cathode metal.

2.2 Cylindrical Model

The cylindrical geometry configuration and the electrolyte solution domain with all
of the defined boundary conditions are represented in Figures 2.1 and 2.2.

As stated before, the flux at the left, top, and right boundaries is set to zero, while
the bottom boundary condition is defined by equation (2.13) for the cathodic and
anodic metal domains, respectively. The parameter $w$ is the electrolyte solution
height; $z = w$ corresponds to the electrolyte top surface, $\kappa$ is the electrolyte solution
conductivity, $i(\phi)$ is the current density as a function of potential $\phi$, $r = 0$ is the
radius center of the galvanic system (the origin), $r = F$ represents the cathodic
metal interface radius distance, $r = L$ is the overall galvanic cell radius length,
h$(r,t)$ is the depth of galvanic corrosion based on radius location and time elapsed,
and \( z = -h(r, t) \) is the interface between the electrolyte/metal where corrosion has occurred so that the electrolyte solution extends below \( z = 0 \).

### 2.2.1 2-D Governing Equation in Cylindrical Coordinates

Laplace’s Equation in cylindrical coordinates is

\[
\nabla^2 \phi = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \phi}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \phi}{\partial \theta^2} + \frac{\partial^2 \phi}{\partial z^2} = 0.
\]

(2.14)

Since we know that there is a symmetry around the center axis of the concentric disks, \( \frac{\partial^2 \phi}{\partial \theta^2} = 0 \), then equation (2.14) can be reduced to

\[
\phi_{rr} + \frac{1}{r} \phi_r + \phi_{zz} = 0.
\]

(2.15)

### 2.3 Damage Evolution

Since part of the metal surface will be degrading away over time due to galvanic corrosion, a function can be given as

\[
F(r, z, t) = z + h(r, t) = 0,
\]

(2.16)

where \( h \) is defined as the depth of corrosion in the \( z \)-direction. Knowing that equation (2.16) is set equal to zero and that the function is assumed to be continuous and differentiable over the entire domain, then the derivative of \( F \) with respect to time is

\[
\frac{dF}{dt} = F_r r_t + F_z z_t + F_t t_t = 0.
\]

(2.17)

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Converting the potential gradient into component vector form and determining the unit outward normal vector, $\hat{n}$, we find:

$$\nabla \phi = < \phi_r, \phi_z >, \quad \hat{n} = \frac{-\nabla F}{\| F \|} = \frac{< F_r, F_z >}{\| F \|} = \frac{< -h_r, -1 >}{\sqrt{1 + h_r^2}}. \quad (2.18)$$

Substituting the normal vector in terms of $h$ of equation (2.19) into equation (2.17) and dividing by the denominator of equation (2.19) we obtain

$$\frac{dF}{dt} \frac{1}{\| F \|} = \frac{h_r u + v}{\sqrt{1 + h_r^2}} = 0. \quad (2.20)$$

To solve for the normal velocity of the electrolyte, equation (2.20) should be rewritten in the form

$$\frac{h_r u + v}{\sqrt{1 + h_r^2}} = \frac{< u, v > < h_r, 1 >}{\sqrt{1 + h_r^2}} = \frac{h_t}{\sqrt{1 + h_r^2}} \quad (2.21)$$

Substituting equations (2.18) and (2.19) into the bottom boundary condition for the electrolyte solution will result in

$$\frac{< \phi_r, \phi_z > \cdot < -h_r, -1 >}{\sqrt{1 + h_r^2}} = \frac{-\phi_r h_r - \phi_z}{\sqrt{1 + h_r^2}} = \frac{-i(\phi)}{\kappa}, \quad (2.22)$$

the boundary condition for the electrolyte/metal interface. The square root in equation (2.22) is approximated by Taylor Expansion as

$$\frac{1}{\sqrt{1 + h_r^2}} = (1 + h_r^2)^{-\frac{1}{2}} = \left( 1 - \frac{1}{2} h_r^2 + \frac{3}{8} h_r^4 + \cdots \right) \quad (2.23)$$

where in this thesis, only the first three terms of the expansion will be used. Substituting the Taylor Expansion into equation (2.22) gives

$$\left( 1 - \frac{1}{2} h_r^2 + \frac{3}{8} h_r^4 \right) (-\phi_r h_r - \phi_z) = \frac{-i(\phi)}{\kappa}. \quad (2.24)$$
For future use, a distributed form of equation (2.24) is given by

\[-\phi_z - \phi_r h_r + \frac{1}{2} h_r^2 \phi_z + \frac{1}{2} h_r^3 \phi_r - \frac{3}{8} h_r^4 \phi_z - \frac{3}{8} h_r^5 \phi_r = \frac{-i(\phi)}{\kappa}.\] (2.25)

The damage evolution equation is driven by Faraday’s Law is

\[\vec{v} \cdot \hat{n} = \frac{i_a(\phi) M_w}{Z F_c \rho},\] (2.26)

where \(\vec{v} \cdot \hat{n}\) is the normal velocity of the electrolyte/metal interface, \(i_a(\phi)\) is the anodic current density, \(M_w\) is the molecular weight of the anodic metal, \(Z\) is the number of valance electrons of the anodic metal, \(\rho\) is the density of the anodic metal, and \(F_c\) is Faraday’s constant. The normal velocity (2.21) and equation (2.26) gives the rate of corrosion

\[\frac{h_t}{\sqrt{1 + h_t^2}} = \frac{i_a(\phi) M_w}{Z F_c \rho}.\] (2.27)

2.4 Asymptotic Problem

Since the governing equation and boundary conditions have been paired together to solve for the potential in the electrolyte domain, the use of asymptotics will begin. To complete this method, a small parameter, \(\epsilon\), will be defined. For this domain, an assumption can be made such that the thickness of the electrolyte, \(w\), is much smaller than the entire galvanic cell radius length, \(L\), so that

\[\epsilon = \frac{w}{L} << 1.\] (2.28)

To non-dimensionalize the governing system (2.25), we choose characteristic values to make variables non-dimensional. \(\phi\) is scaled with a characteristic value \(E_c\), \(i\) is
Table 2.1: Variables for Non-Dimensionalization

<table>
<thead>
<tr>
<th>Variable</th>
<th>Non-Dim. Variable</th>
<th>Characteristic Value</th>
<th>Non-Dim. Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi )</td>
<td>( \tilde{\phi} )</td>
<td>( E_c )</td>
<td>( \tilde{\phi} = E_c \phi )</td>
</tr>
<tr>
<td>( i )</td>
<td>( \tilde{i} )</td>
<td>( I_c )</td>
<td>( \tilde{i} = I_c i )</td>
</tr>
<tr>
<td>( r )</td>
<td>( \tilde{r} )</td>
<td>( L )</td>
<td>( \tilde{r} = Lr )</td>
</tr>
<tr>
<td>( z )</td>
<td>( \tilde{z} )</td>
<td>( w )</td>
<td>( \tilde{z} = wz )</td>
</tr>
<tr>
<td>( h )</td>
<td>( \tilde{h} )</td>
<td>( w )</td>
<td>( \tilde{h} = wh )</td>
</tr>
</tbody>
</table>

scaled with \( I_c \), \( r \) is scaled with \( L \), \( z \) is scaled with \( w \), and \( h \) is scaled with \( w \), as shown in Table 2.1.

This leads to the partial derivatives in non-dimensional form,

\[
\frac{\partial \phi}{\partial r} = \frac{\partial E_c \tilde{\phi}}{\partial L \tilde{r}} = \frac{E_c}{L} \tilde{\phi}, \quad (2.29)
\]

\[
\frac{\partial h}{\partial r} = \frac{\partial w \tilde{h}}{\partial L \tilde{r}} = \frac{w \tilde{r}}{L} \tilde{h}, \quad (2.30)
\]

\[
\frac{\partial \phi}{\partial z} = \frac{\partial E_c \tilde{\phi}}{\partial w \tilde{z}} = \frac{E_c}{w} \tilde{\phi}, \quad (2.31)
\]

\[
\phi = \tilde{i}(\tilde{\phi}) I_c. \quad (2.32)
\]

To non-dimensionalize equation (2.25), substitute equations (2.29 - 2.32) to get

\[
- \frac{E_c \tilde{\phi}}{w} \tilde{z} - \frac{E_c w \tilde{z}}{L^2} \tilde{h} \tilde{\phi} \tilde{r} - \frac{1}{2} \left( - \frac{w^2 E_c \tilde{h} \tilde{z} \tilde{\phi}}{L^3 w} - \frac{w^3 E_c \tilde{z} \tilde{\phi}}{L^4} \right) + \frac{3}{8} \left( - \frac{w^4 E_c \tilde{h} \tilde{z} \tilde{\phi}}{L^4 w} - \frac{w^5 E_c \tilde{z} \tilde{\phi}}{L^6} \right) = \frac{-i(\tilde{\phi}) I_c}{\kappa}. \quad (2.33)
\]
Multiplying equation (2.33) by \( \frac{w}{E_c} \), substituting \( \epsilon \) from equation (2.28), and collecting similar \( \epsilon \)-powered terms we obtain

\[
-\tilde{\phi}_z - \epsilon^2 \left( \tilde{h}_\tau \tilde{\phi}_\tau - \frac{1}{2} \tilde{h}_\tau^2 \tilde{\phi}_z \right) + \epsilon^4 \left( \frac{1}{2} \tilde{h}_\tau^3 \tilde{\phi}_\tau - \frac{3}{8} \tilde{h}_\tau^4 \tilde{\phi}_z \right) - \epsilon^6 \left( \frac{3}{8} \tilde{h}_\tau^5 \tilde{\phi}_\tau \right) = -\frac{i(\tilde{\phi}) I_c w}{E_c \kappa}. \tag{2.34}
\]

On the right hand side of equation (2.34), the group \( \frac{I_c w}{E_c \kappa} \) exists. Performing a unit analysis on this group will show that it is non-dimensional. We define this group as

\[
\tilde{W} = \frac{I_c w}{E_c \kappa}. \tag{2.35}
\]

Since the Wagner relationship \( (w \ll \frac{\Delta \phi}{\Delta i \kappa}) \) is being assumed, the non-dimensional group should be small, which implies size \( O(\epsilon^2) \). The Wagner relationship implies that the current density does not affect the potential to leading order. Understanding that the non-dimensional group is in the \( O(\epsilon^2) \) problem, we write equation (2.34) as

\[
-\tilde{\phi}_z - \epsilon^2 \left( \tilde{h}_\tau \tilde{\phi}_\tau - \frac{1}{2} \tilde{h}_\tau^2 \tilde{\phi}_z \right) + \epsilon^4 \left( \frac{1}{2} \tilde{h}_\tau^3 \tilde{\phi}_\tau - \frac{3}{8} \tilde{h}_\tau^4 \tilde{\phi}_z \right) - \epsilon^6 \left( \frac{3}{8} \tilde{h}_\tau^5 \tilde{\phi}_\tau \right) = \epsilon^2 \left( -i(\tilde{\phi}) \tilde{W} \right) \tag{2.36}
\]

2.4.1 The \( O(1) \) Asymptotic Problem

Before any reduction of equation (2.34) happens for the \( O(1) \) and \( O(\epsilon^2) \) problems, an asymptotic expansion needs to be applied to \( \tilde{\phi} \), giving

\[
\tilde{\phi} = \tilde{\phi}_0 + \epsilon^2(\tilde{\phi}_1) + \epsilon^4(\tilde{\phi}_2) + \cdots. \tag{2.37}
\]

The same process is completed on the partial derivatives

\[
\begin{align*}
\tilde{\phi}_\tau &= \tilde{\phi}_0 + \epsilon^2(\tilde{\phi}_{1\tau}) + \epsilon^4(\tilde{\phi}_{2\tau}) + \cdots \tag{2.38} \\
\tilde{\phi}_{\tau\tau} &= \tilde{\phi}_{0\tau\tau} + \epsilon^2(\tilde{\phi}_{1\tau\tau}) + \epsilon^4(\tilde{\phi}_{2\tau\tau}) + \cdots \tag{2.39} \\
\tilde{\phi}_{zz} &= \tilde{\phi}_{0zz} + \epsilon^2(\tilde{\phi}_{1zz}) + \epsilon^4(\tilde{\phi}_{2zz}) + \cdots \tag{2.40}
\end{align*}
\]

\[20\]
Next, when substituting the asymptotic expansions into (2.15) and taking only the $O(1)$ terms, we see equation (2.15) is reduced to

$$\tilde{\phi}_{0zz} = 0,$$  

(2.41)

which is true, if and only if

$$\tilde{\phi}_{0zz} = 0 \quad s.t. \quad \tilde{\phi}_{0z} = 0 \quad at \quad \tilde{z} = 0 \quad and \quad \tilde{z} = 1,$$  

(2.42)

assuming that $w$, is small. Integrating $\tilde{\phi}_{0zz}$ with respect to $\tilde{z}$ and applying the boundary condition that $\tilde{\phi}_{0z} = 0$ gives

$$\int \tilde{\phi}_{0zz} \, d\tilde{z} = \tilde{\phi}_{0z} = A(r) = 0.$$  

(2.43)

Next, equation (2.43) is integrated with respect to $z$ once more to give

$$\int \tilde{\phi}_{0z} \, dz = \tilde{\phi}_0 = B(r),$$  

(2.44)

the solution to the $O(1)$ potential equation, except $B(r)$ is an arbitrary function which needs to be defined. To solve for $B(r)$ the next order of magnitude in the asymptotic sequence, $O(\epsilon^2)$, is needed.

2.4.2 The $O(\epsilon^2)$ Asymptotic Problem

To solve the $O(\epsilon^2)$ asymptotic part of the potential equation, we substitute the asymptotic expansions into equation (2.15) and take only the $O(\epsilon^2)$ terms to get

$$\frac{1}{r} \tilde{\phi}_{0\tilde{r}} + \tilde{\phi}_{0\tilde{r}\tilde{r}} + \tilde{\phi}_{1\tilde{z}\tilde{z}} = 0.$$  

(2.45)

Solving for $\tilde{\phi}_{1\tilde{z}\tilde{z}}$, we find

$$\tilde{\phi}_{1\tilde{z}\tilde{z}} = -\frac{1}{r} \tilde{\phi}_{0\tilde{r}} - \tilde{\phi}_{0\tilde{r}\tilde{r}}.$$  

(2.46)
As before, integrate equation (2.46) with respect to $z$ to give

$$
\int \tilde{\phi}_{1z\tilde{z}} \, d\tilde{z} = \int \left( -\frac{1}{r} \tilde{\phi}_{0\tilde{r}} - \tilde{\phi}_{0\tilde{r}\tilde{r}} \right) \, d\tilde{z},
$$

(2.47)

which results in

$$
\tilde{\phi}_{1z} = -\frac{1}{r} \tilde{\phi}_{0\tilde{r}} \tilde{z} - \tilde{\phi}_{0\tilde{r}\tilde{r}} \tilde{z} + A.
$$

(2.48)

Since the top boundary of the electrolyte solution is defined as $\tilde{\phi}_{z}(\tilde{r}, \tilde{z}; t) = 0$, then equation (2.48) at $\tilde{z} = 1$ reduces to

$$
A = \frac{1}{r} \tilde{\phi}_{0\tilde{r}} + \tilde{\phi}_{0\tilde{r}\tilde{r}},
$$

(2.49)

which is substituted back into equation (2.48), to give $\tilde{\phi}_{1z}$ as

$$
\tilde{\phi}_{1z} = -\frac{1}{r} \tilde{\phi}_{0\tilde{r}} \tilde{z} - \tilde{\phi}_{0\tilde{r}\tilde{r}} \tilde{z} + \frac{1}{r} \tilde{\phi}_{0\tilde{r}} + \tilde{\phi}_{0\tilde{r}\tilde{r}}.
$$

(2.50)

Now that the partial differential equation is defined for $\tilde{\phi}_{1z}$, the remaining boundary condition will be solved. When equation (2.25) is non-dimensionalized with the asymptotic expansion terms, then the equation which represents the non-dimensionalized bottom electrolyte boundary condition is given as

$$
-\tilde{\phi}_{0\tilde{z}} - \epsilon^2 \left( \tilde{\phi}_{1z} + \tilde{h}_{0\tilde{r}} \tilde{\phi}_{0\tilde{r}} - \frac{1}{2} \tilde{h}_{0\tilde{r}}^2 \tilde{\phi}_{0\tilde{z}} \right) = \epsilon^2 \left( -i(\tilde{\phi})\tilde{W} \right).
$$

(2.51)

Since equation (2.43) defines $\tilde{\phi}_{0z} = 0$ then this term will cancel out of equation (2.51) to give

$$
\tilde{\phi}_{1z} = i(\tilde{\phi})\tilde{W} - \tilde{h}_{0\tilde{r}} \tilde{\phi}_{0\tilde{r}},
$$

(2.52)

which is the simplified non-dimensionalized bottom electrolyte boundary condition which will be used for the matching assumption at the boundary. Since both the
\( O(\epsilon^2) \) partial differential equation and the boundary conditions are solved for, setting them equal to each other will give the governing equation for the potential and this process will give

\[
-\frac{1}{r^2}\phi_{0r} \ddot{z} - \phi_{0rr} \dddot{z} + \frac{1}{r} \phi_{0r} \dot{\phi} + \phi_{0rr} = i(\ddot{\phi})\dddot{W} - \dddot{h}_{0r} \dddot{\phi}_{0r}. \tag{2.53}
\]

Substituting equation (2.44) into equation (2.53) we find

\[
-\frac{1}{r} B_{r} \ddot{z} - B_{rr} \dddot{z} + \frac{1}{r} B_{r} \dot{\phi} + B_{rr} \phi_{0r} = i(\ddot{\phi})\dddot{W}. \tag{2.54}
\]

Defining the damage height as \(-\dddot{z} = \dddot{h}(r, t)\) and substituting equation (2.54) will result in

\[
\frac{\dddot{h}}{r} B_{r} + \dddot{h} B_{rr} \dddot{z} + \frac{1}{r} B_{r} \dot{\phi} + B_{rr} \dddot{h}_{0r} = i(\ddot{\phi})\dddot{W}, \tag{2.55}
\]

which can be written as,

\[
\frac{1}{r} \left(1 + \dddot{h}(r, t)\right) \left(\dddot{\phi}_{0r}\right) = i(\ddot{\phi})\dddot{W}. \tag{2.56}
\]

the potential equation for both the leading order and the perturbation solution.

Since the non-dimensionalization of \( h_r^2 \) shows that the derivative of the damage with respect to space is \( O(\epsilon^2) \), equation (2.27) is reduced to

\[
h_t = i a(\phi) M_w \frac{ZF_c \rho}{Z}. \tag{2.57}
\]

Equation (2.57) has a corresponding initial condition given as \( h(r, 0) = 0 \), since there is no initial damage.

The main advantage of using an asymptotic approach is that a two-dimensional problem can be reduced down to a one-dimensional problem. This results from the
thin film approximation ($w << L$) and non-dimensional group that was included in the $\mathcal{O}(\epsilon^2)$ solution.

2.5 Matching Flux and Potentials

The Divergence Theorem explains the reasoning behind the matching potentials and matching flux at the cathode/anode interface, $r = F$.

When the Divergence Theorem is applied to solve for the potential it gives

$$\int \int_R \nabla^2 \phi \, dA = \int_C \frac{\partial \phi}{\partial n} \, ds = 0, \quad (2.58)$$

where the double integral over the closed two-dimensional ($r, z$) electrolyte solution area is rewritten as the net sum of the surface integrals over the piece-wise smooth boundaries of the electrolyte domain, $C$ [14].

Since the boundary conditions for the electrolyte solution $\phi_z = 0$ at the top electrolyte boundary and $\phi_r = 0$ at the left and right electrolyte boundaries respectively, then the only contributing boundary that effects the line integral is the bottom, the electrolyte/metal interface.

Stenta [7] shows that the final result from the Divergence Theorem is that the change in potential on both sides of the cathode/anode interface must be equal. Also, the potentials must match at the cathode/anode interface for continuity.
2.6 Ohm’s Law

Ohm’s Law states that the electric voltage in an electric system is equal to the product of current $I$ and the resistance $R$,

$$V = IR. \quad (2.59)$$

For the galvanic system at initial time, the re-dimensionalized potential equation for the anode is shown as

$$\frac{1}{r}[wr\phi_r]_r = i_a \quad (2.60)$$

where $\kappa$ is the electrolyte solution conductivity, $\phi$ is the potential, and $i_a$ is the anodic current density. Ohm’s Law can describe the relationship for the voltage drop through the electrolyte solution. Since the partial derivative is in relation to length, we approximate the derivative equation (2.60) to give

$$\Delta \phi = i_a \frac{L^2}{w\kappa}. \quad (2.61)$$

When taking into account the third dimension, depth, equation (2.61) is multiplied by $\frac{D}{D}$ to give

$$\Delta \phi = [i_aLD] \left[ \frac{L}{wD\kappa} \right], \quad (2.62)$$

which can be seen as equivalent to equation (2.59) where $[i_aLD]$ describes the current and $\left[ \frac{L}{wD\kappa} \right]$ describes the resistance.

There is a direct relationship between the current and voltage drop as well as the resistance and voltage drop. If there is a large voltage drop, then there is a large current and/or a large resistance. An electrical system with a larger voltage
drop allows for a larger change in potential across the entire cathode/anode domain, 
$[0, F] \cup [F, L]$. If there is a smaller current or resistance, then the potential drop is smaller, which leads to a restricted potential drop through the cathode/anode domain. This electrical resistance effect is an important driving force when analyzing the corrosive behavior of a galvanic cell.

A corrosive system will vary in degree of corrosion severity based on the voltage drop across the domain. For more aggressive systems, the large domain along with the thin film environment, will define the upper bound for the voltage drop. The opposite holds for a less aggressive system as a small domain along with bulk electrolyte environments, will define the lower bound for the voltage. Now, the one-dimensional potential equation (2.60) along with the rate of corrosion damage equation (2.57), can be solved using a numerical iterative scheme.

2.7 Formal Problem Statement

For the galvanic system under investigation, the completed potential equations to be solved in cylindrical coordinates are

\[
\kappa \frac{1}{r} [w r \phi_r]_r = -i_c(\phi) \quad 0 < r < F, \quad (2.63)
\]

\[
\kappa \frac{1}{r} [(w + h)(r \phi_r)]_r = i_a(\phi) \quad F < r < L. \quad (2.64)
\]

At initial time, $t = 0$, the lower boundary position of the electrolyte/metal interface is located at $z = 0$ and no damage, $h$, has occurred. The damage in the cathodic metal region is zero, while the damage occurs in the anodic metal region. The cur-
rent density of the electrolyte is \( i_a(\phi) \) and \(-i_c(\phi)\), across the anodic and cathodic metals, respectively. The negative current density implies that the potential across the cathode will be concave downward whereas the positive current density implies that the potential across the anode will be concave upward.

The damage equation is given by

\[
h_t = \frac{i_a(\phi) M_w}{ZF_c \rho}, \quad F < r < L
\]

and at initial time, \( h(r, 0) = 0 \).

The boundary conditions for equations (2.63 - 2.64) are:

\[
\phi_r (r = 0) = 0 \quad (2.66)
\]

\[
\phi (r = F^-) = \phi (r = F^+) \quad (2.67)
\]

\[
\phi_r (r = F^-) = \phi_r (r = F^+) \quad (2.68)
\]

\[
\phi_r (r = L) = 0 \quad (2.69)
\]
CHAPTER III

COMPUTATIONAL APPROACH

The complete problem, equations (2.63 - 2.69), will be solved in MATLAB [15], using
the \texttt{bvp4c} routine [16], which is a boundary value problem solver. The boundary value
problem algorithm for this problem is adaptive, but we interpolate to a uniform grid
for damage evolution. At each time step, the potential is computed and the damage
profile is updated.

3.1 Numerical Domain

A finite difference method is a scheme in which derivatives in a differential equation
is substituted with an appropriate approximation [17, 18]. The galvanic corrosion
model needs to be discretized into the temporal and spatial grids. The process of
transforming the derivative equation into this approximation is called “discretizing
the equation”. Once an equation has been discretized, this equation is now known
as the “discrete equation”. In the scheme of this problem, the discretization will
be solved over the the discretized grid \((x_j, t_n)\). Each discretization in space will
be represented by the index \(j\), where \(j\) represents the current grid position in the
\(x\) direction. This means that \(j - 1, j, \) and \(j + 1\) represent the grid point to the
left, grid point at current position, and grid point to the right, respectfully. Each

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discretization in time will be represented by the variable $n$, where $n$ represent the current grid position in time. This means that $n - 1$, $n$, and $n + 1$ represents the previous time step, current time step, and next time step. One should note quantities at the next time step $n + 1$ are unknown.

A computational molecule, as shown in Figure 3.1, shows the points that are included in a finite difference method for the forward, central, and backwards difference methods.

![Figure 3.1: Computational Molecules for Forward, Central, and Backwards Differences (from Left to Right)](image)

The time and space grid size, the total simulation run time, and the tolerance for the boundary value problem solver are numerical inputs to the program. The
integer \( n_{\text{max}} \) represents the total index length of the time grid, which is defined by

\[
n_{\text{max}} = \frac{\text{hrs} \times 60\text{ sec/min} \times 60\text{ min/hr}}{dt} + 1, \tag{3.1}
\]

where \( dt \) represents the time increment. The integer \( j_{\text{max}} \) defines the index length of the spatial grid, where \( dr \) defines the spatial increment. In this investigation, both the time and spatial grids are constant. The uniform spatial grid is only used to solve for damage evolution.

In regards to the \textit{bvp4c} solver, a tolerance value is required to define the adaptive grid. This user-defined tolerance value is used to define the relative error allowed for the solution to the potential differential equation. The smaller the tolerance, the finer the grid across the potential solution domain, which minimizes error. Due to severe slopes in the domain caused by the metal interface, there are more adaptive grid points located in these areas of the potential domain. Similarly, there are fewer adaptive grid points located in areas of very small slope or flatter areas.

Since the adaptive grid system, the \textit{bvp4c} numerical solver, is only required for the potential solution domain, \( dr \) and \( j_{\text{max}} \) are used to give uniform grid spacing for the damage spacing. The defined grid system and tolerance are chosen small enough so that there is minimal error when solving calculations, but yet large enough to have an efficient computational speed. This is a well known optimization issue where computational speed is balanced against numerical accuracy.
3.2 Discretization of the Damage Equation

The equation for the updating of the galvanic corrosion damage equation is approximated by Euler’s Method and can be written as

\[ h_{j}^{n+1} = h_{j}^{n} + \frac{i_{a}(\phi(x_{j}, t_{n}))M_{w}}{ZF_{c}\rho} dt. \tag{3.2} \]

The discrete equation is solved over an equally spaced grid, where the metal below could either be cathodic or anodic. The boundary value problem solver procedure needs the damage derivative, \( h_{r} \), to solve for the anodic potential equation. This is obtained by second order finite differences:

\[
\begin{align*}
(h_{r})_{1}^{n+1} &= \frac{1}{2dr}(-3h_{1}^{n} + 4h_{2}^{n} - h_{3}^{n}) \quad \text{for } j = 1 \tag{3.3} \\
(h_{r})_{j}^{n+1} &= \frac{1}{2dr}(h_{j+1}^{n} - h_{j-1}^{n}) \quad \text{for } j = 2 : n - 1 \tag{3.4} \\
(h_{r})_{j_{\text{max}}}^{n+1} &= \frac{1}{2dr}(h_{j_{\text{max}}-2}^{n} - 4h_{j_{\text{max}}-1}^{n} + 3h_{j_{\text{max}}}^{n}) \quad \text{for } j = j_{\text{max}}. \tag{3.5}
\end{align*}
\]

3.3 Cylindrical Potential Equation

To numerically set up the cylindrical coaxial galvanic system corrosion model, the governing potential equation needs to be discretized. The first order system of differential equations for the cylindrical coaxial model potential are

\[
\begin{align*}
z_{2}' &= z_{2}, \tag{3.6} \\
z_{2}' &= -i(z_{1}) - \kappa \frac{1}{r} (w + h)(z_{2}r)_{r}. \tag{3.7}
\end{align*}
\]

For the inner cathodic region, the potential equation (3.7) is written as

\[
\phi_{rr} = \frac{-i_{c}(z_{1}) - \kappa \frac{1}{r} \frac{1}{10} z_{2} (w + h + rh_{r})}{\kappa (w + h)}, \tag{3.8}
\]

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Table 3.1: Cylindrical Coaxial Analytics and Numerical Boundary Conditions

<table>
<thead>
<tr>
<th>Description</th>
<th>Location</th>
<th>Analytic BC</th>
<th>Numerical BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Flux</td>
<td>$r = 0$</td>
<td>$\phi_r = 0$</td>
<td>$Er(2, 1) - 0$</td>
</tr>
<tr>
<td>Matching Potentials</td>
<td>$r = F$</td>
<td>$\phi(r^+) = \phi(r^-)$</td>
<td>$Er(1, 1) - El(1, 2)$</td>
</tr>
<tr>
<td>Matching Flux</td>
<td>$r = F$</td>
<td>$\phi_r(r^+) = \phi_r(r^-)$</td>
<td>$Er(2, 1) - El(2, 2)$</td>
</tr>
<tr>
<td>No Flux</td>
<td>$r = L$</td>
<td>$\phi_r = 0$</td>
<td>$Er(2, end) - 0$</td>
</tr>
</tbody>
</table>

while for the outer anodic region, equation (3.7) is written as

$$\phi_{rr} = \frac{i_a(z_1) - \kappa}{r + \frac{10^{-12}}{\kappa}} \frac{z_2 (w + h + rh_r)}{\kappa (w + h)}.$$  \hspace{1cm} (3.9)

Equations (3.8) and (3.9) include a small correction term, $10^{-12}$, which is added to the denominator of the $\frac{1}{r}$ term to prevent a possible division by zero, the disk center. This small correction term does not have any effect on the numerical results. The analytic boundary conditions for the cylindrical coaxial system are shown with their corresponding numerical coding representation in Table 3.1.

The locations of $r = 0$ and $r = L$ correspond to the coaxial center location of the disks and far-field boundary of the outer anodic metal, respectively. Matching the potentials and flux at the interface forces the concavity of the potential to change at this location. After these equations are discretized, and a model defined, then the defined geometries are defined for the base cases and the parameter study.
3.4 Numerical Model Parameters

For the purpose of this thesis, we will use two different galvanic cell systems, Mild Steel & Magnesium and Copper & Aluminum. From the Galvanic Series, Magnesium and Aluminum act as the more active and anodic metals. Material properties are needed for input into the numerical model to solve for the damage equation.

Table 3.2: Input Material Properties and Constants

<table>
<thead>
<tr>
<th>Variable</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (0.1 M NaCl)</td>
<td>$\kappa_a$</td>
<td>0.0105</td>
<td>( \text{S/cm} )</td>
</tr>
<tr>
<td>Conductivity (1.6 wt% NaCl)</td>
<td>$\kappa_m$</td>
<td>0.0271</td>
<td>( \text{S/cm} )</td>
</tr>
<tr>
<td>Magnesium Molecular Weight</td>
<td>$M_w$</td>
<td>24.31</td>
<td>( \text{g/mol} )</td>
</tr>
<tr>
<td>Magnesium Density</td>
<td>$\rho_m$</td>
<td>1.74</td>
<td>( \frac{\text{g}}{\text{cm}^3} )</td>
</tr>
<tr>
<td>Magnesium Valence Number</td>
<td>$Z_m$</td>
<td>2</td>
<td>( e^- )</td>
</tr>
<tr>
<td>Aluminum Molecular Weight</td>
<td>$M_w$</td>
<td>26.982</td>
<td>( \text{g/mol} )</td>
</tr>
<tr>
<td>Aluminum Density</td>
<td>$\rho_a$</td>
<td>2.7</td>
<td>( \frac{\text{g}}{\text{cm}^3} )</td>
</tr>
<tr>
<td>Aluminum Valence Number</td>
<td>$Z_a$</td>
<td>3</td>
<td>( e^- )</td>
</tr>
<tr>
<td>Faraday’s Constant</td>
<td>$F$</td>
<td>96485.33</td>
<td>( \text{Coulombs/mol} )</td>
</tr>
</tbody>
</table>

The molecular weight, $M_w$, the density, $\rho$, the valence electrons $Z$, and the electrolyte solution conductivity, $\kappa$, used for each material must be specified, and are given in Table 3.2 [19, 20, 21, 22]. Besides the material specific data, physical
geometric information must be defined including the electrolyte solution height, \( w \), the radius length between the center to the cathode/anode interface, \( F \), and the length of the overall radius length between the center to the far-field of the anodic metal, \( L \). In regards to the electrochemical reactions, Faraday’s constant is defined as well as the valance electrons with respect to the material under investigation. The electrolyte solution is also assumed to cover the top of the cathode/anode domain uniformly.

The last input required from the material properties for a given galvanic couple are the polarization curves for the metal couple under investigation. For the Mild Steel / Magnesium system, Deshpande [6] has included the experimental polarization curve results in the literature that is represented in Figure 3.2. For the Copper / Aluminum system, Lillard et al. [23] has also produced polarization curves that are shown in Figure 3.3.

User inputs such as temporal and spatial step sizes, an initial guess for the potential at the interface, and certain model parameters are needed to run the \textit{bvp4c} solver. The tolerance of the solver is set at \( 10^{-12} \) to allow the solver to come to have a high degree of accuracy. If the tolerance is not met in 5000 iterations, the solution found after these iterations will be used to continue the computations. The solver also requires an initial guess (at initial time) for the potential at the interface, given in computer code as \( z_{\text{init}} \). An initial guess is picked to allow the model to converge at initial time. From this, the potential value at the cathode/anode interface is used as the solvers initial guess.
Figure 3.2: Mild Steel / Magnesium Polarization Curve

Figure 3.3: Copper / Aluminum Polarization Curve
For all base cases and parameter studies, the model is ran for 72 hrs, with a temporal step size of 15 min., or $dt = 900 \text{ sec.}$ The spatial step size is given as $dr = 0.001 \text{ cm.}$ The temporal and spatial step lengths are chosen with the concept of stability versus runtime in mind.

Computation time will vary from 15 to 25 minutes, depending on varying metal properties, cathode and anode radius lengths, and electrolyte solution heights for the 72 hour simulation. If the temporal step is decreased to improve accuracy, then the run time will be increased. Due to the slow process of the galvanic corrosion, larger time steps are allowed. The length of the inner metal is of importance as the initial potential curves change as the length changes. This is due to the polarization curves seen in Figures 3.2 and 3.3.
CHAPTER IV
PRESENTATION OF RESULTS

This chapter will show the results of all different parameter studies investigated. Once base cases are explained for both metal combinations, a parameter study will be presented.

4.1 Baseline Parameter Values

For this investigation, only two different material combinations will be considered. Regarding the geometric sizing, different ratios of cathodic metal to anodic metals will be investigated, as well as varying the electrolyte solution height.

In regards to the metal combinations, the two that will be looked at are Mild Steel (MS) / Magnesium (Mg) and Copper (Cu) / Aluminum (Al). The MS/Mg system has been investigated through experiments and modeling in a electrolyte solution of 1.6 wt% Sodium Chloride (NaCl) [6]. The Cu/Al system has been chosen to be investigated by the University of Akron Corrosion Engineering Group due to the multitude of uses in industry. The experiments conducted by Dr. Scott Lillard and his research students had 99.99% pure Copper and 99.999% pure Aluminum submerged under a 0.1 M NaCl electrolyte solution. The variables that describe the coaxial geometry configuration are listed in Table 4.1.
Table 4.1: Baseline Parameter Values

<table>
<thead>
<tr>
<th>Description</th>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte Solution Height</td>
<td>w</td>
<td>0.100</td>
<td>cm</td>
</tr>
<tr>
<td>Simulation Time</td>
<td>hrs</td>
<td>72.00</td>
<td>hrs</td>
</tr>
<tr>
<td>Temporal Step Size</td>
<td>dt</td>
<td>900</td>
<td>sec</td>
</tr>
<tr>
<td>Spatial Step Size</td>
<td>dr</td>
<td>0.001</td>
<td>cm</td>
</tr>
<tr>
<td>Inner Metal Radius</td>
<td>F</td>
<td>2.000</td>
<td>cm</td>
</tr>
<tr>
<td>Overall Metal Radius</td>
<td>L</td>
<td>2.828</td>
<td>cm</td>
</tr>
</tbody>
</table>

4.2 Polarization Curves

As mentioned in Chapter I, polarization curves are used in the model. These curves first have to come from experimentation done in a scientific laboratory. Literature sources [6, 23] give polarization curves that describe the anodic and cathodic parts of the metals under investigation. The experimental data needs to be smoothed for numerical work. For this thesis, a linear approximation was used, although other options were available such as exponential, logarithmic, or power function approximations. Figures 4.1 and 4.2 show the linear approximations of the experimentally found polarization curves shown in Chapter III. Again, the line with positive slope is the anodic branch and the line with negative slope is the cathodic branch.
Figure 4.1: Linear Approximation Curves for the Mild Steel & Magnesium

Figure 4.2: Linear Approximation Curves for the Copper & Aluminum
4.3 MS/Mg System: Base Case Investigation

A comparison of Deshpande’s data [6] with the MS/Mg system will be shown for initial time first. Time dependent solutions will also be investigated for the potential, current density, and corrosion damage. The geometry used for comparison is a nested cylindrical system with a Mild Steel on the inside and Magnesium on the outside. The cathode has a radius length of 2 cm and the overall metal system has a radius length of 2.828 cm, to keep a surface area ratio equal to 1. An electrolyte solution thickness of 0.100 cm is used. Since the thin film approximation, \( w \ll L \), needs to hold true, a \( \frac{w}{L} \) ratio of 0.2 is acceptable.

4.3.1 Initial Time Solutions

The following figures are at initial time, therefore, no damage has occurred. There are damage profiles for the time dependent solutions. Figure 4.3 shows the potential across the MS/Mg system. At the interface, the corrosion potential is \(-1.311 \text{ V}\). The voltage drop across the 2 cm Mild Steel allows the potential to reach \(-1.105 \text{ V}\) in the Mild Steel at \( r = 0 \). The potential value at the outer boundary of Magnesium reaches \(-1.421 \text{ V}\), which shows a total change in potential of 0.316 V.

Figure 4.4 shows the current density across the MS/Mg system. At the interface, the current density has a vertical asymptote. The current density in the Mild Steel at \( r = 0 \) is \(-2.906 \times 10^{-4} \frac{A}{cm^2}\). The current density value at the outer boundary of Magnesium reaches \(5.212 \times 10^{-4} \frac{A}{cm^2}\).
Figure 4.3: Mild Steel / Magnesium Potential Curve: 1D model initial time simulation. The cathode radius length is $[0,2]$ cm, the anode radius length is $[2,2.828]$ cm, a surface area ratio of 1, with an electrolyte solution height of 0.100 cm.

Figure 4.4: Mild Steel / Magnesium Current Density Curve: 1D model initial time simulation. The cathode radius length is $[0,2]$ cm, the anode radius length is $[2,2.828]$ cm, a surface area ratio of 1, with an electrolyte solution height of 0.100 cm.
4.3.2 Time Dependent Solutions

The following graphs will help to further benchmark Deshpande’s work analyzing the potential, current density, and physical damage over time. The following figures have values taken after each 24 hours of simulation (0, 24, 48, and 72 hours).

Figure 4.5: Mild Steel / Magnesium Potential Curve: 1D model over a 72 hour simulation. The cathode radius length is [0,2] cm, the anode radius length is [2,2.828] cm, a surface area ratio of 1, with an electrolyte solution height of 0.100 cm.

Figure 4.5 shows the potential across the MS/Mg system over a 72 hour simulation. At the MS/Mg interface (2 cm), the potential increases in the positive direction over the 72 hours. This potential increase over time is caused by increasing cathode/anode surface area ratios due to corrosion at the anode surface. In regards to the time steps notated on Figure 4.5, the potential at the MS/Mg interface (2 cm) gives $-1.311, -1.296, -1.284$, and $-1.274 \text{ V}$, respectively. The voltage
drop across the 2 cm Mild Steel allows the potential to reach $-1.105, -1.104, -1.102,$ and $-1.100 \, V$, at the same time steps, in the Mild Steel at $r = 0$. The potential value at the outer boundary of Magnesium reaches $-1.421, -1.414, -1.408$ and $-1.402 \, V$, respectively, which shows that there is a large potential drop.

Figure 4.6: Mild Steel / Magnesium Current Density Curve: 1D model over a 72 hour simulation. The cathode radius length is $[0,2] \, cm$, the anode radius length is $[2,2.828] \, cm$, a surface area ratio of 1, with an electrolyte solution height of $0.100 \, cm$.

The large potential drop leads to current density localized near the interface. Figure 4.6 shows the current density across the MS/Mg system over a 72 hour simulation. At the MS/Mg interface (2 cm), the current density shows a vertical asymptote that increases in magnitude over the 72 hours. One should note that for both material boundaries away from the interface, the current density approaches zero.
Figure 4.6 also shows that the cathodic and anodic currents do not balance through time. In Figure 4.6 one can see that the areas enclosed by the current densities (the anodic and cathodic currents) balance at time $t = 0$ because no damage has yet occurred to the anodic metal. However, the balance no longer occurs as time progresses and damage occurs. The explanation is that a portion of the cathodic metal is exposed upon corrosion of the anodic metal. The area enclosed by the cathodic current density figures in Figure 4.6 does not take into account the contribution to the current from this portion of the cathodic metal. Adding the current contribution from the exposed cathodic surface to the area enclosed by the cathodic current density gives the total cathodic current. This value does balance the area under the anodic current density so that the total anodic current does balance the total cathodic current [7]. The current density can be given by integrating the potential equation over the cathodic and anodic domains respectively, given as

\[ \kappa \frac{1}{r} [ wr \phi_r ]_r = \int_0^{F_-} -i_c(\phi) \, dr, \quad (4.1) \]

\[ \kappa \frac{1}{r} [(w + h)(r \phi_r)]_r = \int_{F_+}^{L} i_a(\phi) \, dr. \quad (4.2) \]

Equations (4.1) and (4.2) show that the damage term is not accounted for in the cathodic region, which explains the current not balancing. If the damage term is added to the cathodic current density curve, then the total net currents would balance.
Figure 4.7: Mild Steel / Magnesium Damage Curve: 1D model over a 72 hour simulation. The cathode radius length is \([0,2]\) cm, the anode radius length is \([2,2.828]\) cm, a surface area ratio of 1, with an electrolyte solution height of 0.100 cm.

Figure 4.7 shows the damage evolution from the 1D model for the MS/Mg system over time. At the MS/Mg interface (2 cm), the damage causes a maximum value depth of 0.000, 0.049, 0.117, and 0.205 cm for 0, 24, 48, and 72 hours, respectively. The damage in the cathodic (Mild Steel) region will stay zero throughout. The damage in the anodic (Magnesium) region decreases as the distance of radius length increases away from the MS/Mg interface. Figure 4.7 also shows that there is a large amount of localized corrosion near the interface.
4.4 Cu/Al System: Base Case Investigation

For the investigation of the Cu/Al galvanic system with a 0.1 M NaCl electrolyte solution, with a electrolyte height, \( w \), of 0.100 cm, the potential, current density, and the corrosion evolution will be investigated. For this analysis the length of the cathode, the length of the anode, and the height of the electrolyte solution will be held constant.

4.4.1 Initial Time Solutions

The following graphs will help describe the Cu/Al setup. Figures 4.8 and 4.9 show the potential and the current density at initial time. Due to initial time, there is no damage present in the Cu/Al galvanic system.

Figure 4.8 shows that there is a small potential drop across the Cu/Al system at initial time. At the interface (2 cm), the corrosion potential is \(-0.572\) V. The voltage drop across the 2 cm Copper allows the potential value to reach \(-0.549\) V in the Copper at \( r = 0 \). The potential value at the outer boundary of Aluminum reaches \(-0.581\) V, which shows a total change in potential across the entire surface of 0.032 V.

Figure 4.9 shows no localized current density across the Cu/Al system at initial time. At the interface (2 cm), the current density has a vertical asymptote. The current density in the Copper at \( r = 0 \) is \(-2.140 \times 10^{-5} \ A/cm^2\). The current density value at the outer boundary of Aluminum reaches 2.493 \times 10^{-5} \ A/cm^2\).
Figure 4.8: Copper / Aluminum Potential Curve: 1D model initial time simulation. The cathode radius length is [0,2] cm, the anode radius length is [2,2.828] cm, a surface area ratio of 1, with an electrolyte solution height of 0.100 cm.

Figure 4.9: Copper / Aluminum Current Density Curve: 1D model initial time simulation. The cathode radius length is [0,2] cm, the anode radius length is [2,2.828] cm, a surface area ratio of 1, with an electrolyte solution height of 0.100 cm.
4.4.2 Time Dependent Solutions

The following graphs will help further explain the Cu/Al galvanic system by analyzing the potential, current density, and physical damage over time. For ease, the following figures have values taken after each 24 hours of simulation (0, 24, 48, and 72 hours). Due to the nature of the polarization curves, there is very small change in the potential and the current density.

Figure 4.10 shows a small potential across the Cu/Al system over a 72 hour simulation. At the Cu/Al interface (2 cm), the potential increases in the positive direction over the 72 hours. This potential increase over time is caused by increasing cathode/anode surface area ratios. In the regards to the time steps notated on Figure 4.10, at time 0, 24, 48, and 72 hours the potential at the Cu/Al interface (2 cm) gives $-0.57177$, $-0.57175$, $-0.57173$, and $-0.57170$ V, respectively. The voltage drop across the 2 cm Copper allows the potential value to reach $-0.54916$, $-0.54914$, $-0.54913$, and $-0.54911$ V, in regards to the same time steps, in the Copper at $r = 0$. The potential value at outer boundary of Aluminum reaches $-0.58122$, $-0.58119$, $-0.58117$ and $-0.58117$ V, respectively. Figure 4.11 is a magnification of Figure 4.10 which shows time dependent solutions for the potential of the Cu/Al system.

Figure 4.12 shows that there is no localization of current density across the Cu/Al system over a 72 hour simulation. At the Cu/Al interface (2 cm), the current density shows a vertical asymptote that increases in magnitude over the 72 hours. Note that for both material boundaries away from the interface, the current density approaches zero.
Figure 4.10: Copper / Aluminum Potential Curve: 1D model over a 72 hour simulation. The cathode radius length is \([0,2] \text{ cm}\), the anode radius length is \([2,2.828] \text{ cm}\), a surface area ratio of 1, with an electrolyte solution height of \(0.100 \text{ cm}\).

Figure 4.11: Magnification of the Copper / Aluminum Potential Curve: 1D model over a 72 hour simulation. The cathode radius length is \([0,2] \text{ cm}\), the anode radius length is \([2,2.828] \text{ cm}\), a surface area ratio of 1, with an electrolyte solution height of \(0.100 \text{ cm}\).
Figure 4.12: Copper / Aluminum Current Density Curve: 1D model over a 72 hour simulation. The cathode radius length is [0,2] cm, the anode radius length is [2,2.828] cm, a surface area ratio of 1, with an electrolyte solution height of 0.100 cm.

Figure 4.13: Copper / Aluminum Damage Curve: 1D model over a 72 hour simulation. The cathode radius length is [0,2] cm, the anode radius length is [2,2.828] cm, a surface area ratio of 1, with an electrolyte solution height of 0.100 cm.
Figure 4.13 shows that the 1D model gives minimal, non-localized damage evolution for the Cu/Al system over time. At the Cu/Al interface (2 cm), the damage causes a maximum value depth of 0.000, 9.086×10^{-5}, 1.818×10^{-4}, and 2.727×10^{-4} cm for 0, 24, 48, and 72 hours, respectively. The damage in the cathodic region will stay zero throughout. The damage in the anodic region will decrease as the distance of radius length increases away from the Cu/Al interface. The Cu/Al base case investigation was run to analyze the effects of the polarization curve data found by Lillard et al. [13, 23].

4.5 Parameter Study: Varying Electrolyte Solution Height

The following subsection will describe the effects of varying the electrolyte solution height in the two systems while considering a constant geometry (i.e. using the geometry from the base case). The electrolyte solution height parameter study will use electrolyte solution heights of 0.025, 0.100, and 0.400 cm.

4.5.1 MS/Mg System: Varying Electrolyte Solution Height

Figure 4.14 shows how the potential changes over changes in initial electrolyte height for the base case cathode/anode surface area ratio of 1. Figure 4.14 also shows that as the electrolyte height increases, the potential difference decreases. This increase in electrolyte thickness leads to a decrease in the resistance through the electrolyte solution, which, through Ohm’s Law, gives a smaller voltage drop. At the MS/Mg interface for each electrolyte solution, the potential decreases and has the values of
Figure 4.14: Mild Steel / Magnesium Potential Curve: 1D model for a 72 hour simulation. The cathode radius length is [0,2] cm, the anode radius length is [2,2.828] cm, a surface area ratio of 1, while varying the height of the electrolyte solution.

$-1.1994, -1.2725, \text{ and } -1.3047 \, V$, respectively. The voltage drop across the cathodic Mild Steel allows the potential value to reach $-1.0071, -1.0998, \text{ and } -1.1825 \, V$, respectively, in regards to increasing electrolyte height, in the Mild Steel at $r = 0$. The potential value at the outer boundary of Magnesium reaches $-1.4295, -1.4014, \text{ and } -1.3705 \, V$, respectively. These smaller potential drops lead to lower current density values across the electrolyte.

Figure 4.15 shows the current density of the MS/Mg galvanic system over the radius length for various electrolyte solution heights after a 72 hour simulation. At the MS/Mg interface for each different electrolyte heights there is an asymptote, going from negative to positive for all cases, due to metal alignment. When looking at the current densities from the most negative value on the cathodic metal’s outside
boundary, the current density decrease from $-1.123 \times 10^{-3}$, $-3.218 \times 10^{-3}$, and $-5.118 \times 10^{-3} \ \frac{A}{cm^2}$ for each of the electrolyte solution heights, respectively. The current density increases and converges to zero as the radius length reaches $r = 0$, which agrees with the stated “no flux” conditions. When looking at the current densities from the most positive value on the anodic metal’s inner boundary, the current density decreases from $8.539 \times 10^{-2}$, $1.588 \times 10^{-2}$, and $7.584 \times 10^{-3} \ \frac{A}{cm^2}$, for each of the electrolyte solution heights, respectively. The current density also decreases and converges to zero as the radius length reaches the far-field boundary, which again, agrees with the stated “no flux” conditions. The magnitude of current density on the asymptote for each of the heights are $8.651 \times 10^{-2}$, $1.910 \times 10^{-2}$, and $1.270 \times 10^{-2} \ \frac{A}{cm^2}$, with respect to the increasing initial electrolyte height.
Figure 4.16 shows that when the initial electrolyte solution height increases, the damage at or near the metal interface decreases. For the increasing electrolyte solution height, the maximum damage depth at the interface for the anodic Mild Steel is 0.7521, 0.2036, and 0.1286 cm, respectively. Corrosion depth decreases as the distance away from interface increases. For the MS/Mg galvanic system, there is steep/localized corrosion damage near the cathode/anode interface. This is caused from the more aggressive MS/Mg system, shown in the polarization curve, Figure 4.1.
4.5.2 Cu/Al System: Varying Electrolyte Solution Height

Figure 4.17 shows how the potential changes over changes in initial electrolyte height for the base case cathode/anode surface area ratio setup.

Figure 4.17: Copper / Aluminum Potential Curve: 1D model for a 72 hour simulation. The cathode radius length is \([0,2]\) cm, the anode radius length is \([2,2.828]\) cm, a surface area ratio of 1, while varying the height of the electrolyte solution.

Figure 4.17 also shows that as the electrolyte height increases, the difference in potential over the entire radius length decreases. This increase in electrolyte thickness leads to a decrease in the resistance through the electrolyte solution, which, through Ohm’s Law, gives a smaller voltage drop. At the Cu/Al interface for each electrolyte solution, the potential decreases and has the values of from \(-0.5733\), \(-0.5717\), and \(-0.5706\) V, respectively. The voltage drop across the cathodic Copper metal allows the potential value to reach \(-0.5164\), \(-0.5491\), and \(-0.5637\) V, respectively, in regards
Figure 4.18: Copper / Aluminum Current Density Curve: 1D model for a 72 hour simulation. The cathode radius length is [0,2] cm, the anode radius length is [2,2.828] cm, a surface area ratio of 1, while varying the height of the electrolyte solution.

to increasing electrolyte height, in the Copper at \( r = 0 \). The potential value at the outer boundary of Aluminum reaches \(-0.5999, -0.5811, \) and \(-0.5733 \) V, respectively. As before, these smaller potential drops lead to lower current density values across the electrolyte.

Figure 4.18 shows the current density of the Cu/Al galvanic system over the radius length for various electrolyte solution heights after a 72 hour simulation. The small potential drops shown in Figure 4.17 will give non-localized current densities. At the Cu/Al interface for each different electrolyte heights there is an asymptote, going from negative to positive for all cases, due to metal alignment. When looking at the current densities from the most negative value on the cathodic metal’s outside boundary, the current density decreases from \(-3.362 \times 10^{-5}, -3.265 \times 10^{-5}, \) and
The cathode radius length is [0,2] cm, the anode radius length is [2,2.828] cm, a surface area ratio of 1, while varying the height of the electrolyte solution.

\[ -3.196 \times 10^{-5} \, \frac{A}{cm^2}, \] for each of the initial electrolyte solution heights, respectively.

The current density increases and converges to zero as the radius length reaches the radius center, which agrees with the stated “no flux” conditions. When looking at the current densities from the most positive value on the anodic metal’s inner boundary, the current density increases from \(2.946 \times 10^{-5}\), \(3.048 \times 10^{-5}\), and \(3.124 \times 10^{-5}\) \(\frac{A}{cm^2}\), for each of the electrolyte solution heights, respectively. The current density also decreases and converges to zero as the radius length reaches the far-field boundary, which again, agrees with the stated “no flux” conditions. The difference between the current density values on the asymptote with respect to the increasing initial electrolyte solution heights are \(6.308 \times 10^{-5}\), \(6.313 \times 10^{-5}\), and \(6.320 \times 10^{-5}\) \(\frac{A}{cm^2}\).
Figure 4.19 shows that when the initial electrolyte solution height increases, the damage at or near the metal interface decreases. For the increasing electrolyte solution height, the maximum damage depth at the interface for the anodic mild steel is $2.628 \times 10^{-4}$, $2.726 \times 10^{-4}$, and $2.795 \times 10^{-4}$ cm, respectively. Corrosion depth decreases as the distance away from interface increases. For the Cu/Al galvanic system, there is shallow/spread corrosion damage across the entire anodic metal domain. This is caused from the less aggressive Cu/Al system, found in the polarization curve, Figure 4.2.

As the electrolyte height is increased, the voltage drop over the system decreases because of the decrease in resistance in the electrolyte. Since the assumption of a thin film and the Wagner relationship needs to hold throughout this parameter study, the electrolyte height will have a maximum height. Also, there has to be an electrolyte solution height to allow galvanic corrosion by definition.

4.6 Parameter Study: Varying the Surface Area Radius Ratio

For the parameter study, the surface area ratio of the cathodic metal compared to the anodic metal will be investigated, first by holding the radius length of the cathodic metal constant and changing the radius length of the anodic metal and secondly by holding the overall radius length constant and changing the radius length of the cathodic metal. Surface area ratios of 1, 2, and 4 will be shown.
Figure 4.20: Mild Steel / Magnesium Potential Curve: 1D model for a 72 hour simulation. The cathode radius length is [0, 2] cm with a surface area ratio of 1, 2, and 4, with an electrolyte solution height of 0.100 cm.

4.6.1 MS/Mg System: Constant Cathode, Increasing Anode

The following subsection will describe the effects of varying the surface area ratio of the two metals and considering a constant cathodic radius length after 72 hours of computer simulation.

Figure 4.20 shows the potential across the MS/Mg throughout the galvanic system for a varying anodic length with a constant cathodic length. Figure 4.20 shows that there is a trend when decreasing the cathode/anode surface area ratio. As the anodic metal length increases, the potential at far-field decreases, converging to the open circuit potential (OCP). As the potential drop over the system increases, this leads to more localized current densities at the interface.
Figure 4.21: Mild Steel / Magnesium Current Density Curve: 1D model for a 72 hour simulation. The cathode radius length is $[0,2]$ cm with a surface area ratio of 1, 2, and 4, with an electrolyte solution height of 0.100 cm.

Figure 4.21 shows the current density across the MS/Mg throughout the galvanic system for increasing surface area ratios with a constant cathodic radius length. Figure 4.21 shows that the current density does not change at the interface when varying the anodic radius length.

Figure 4.22 shows the damage across the MS/Mg throughout the galvanic system for a varying surface area ratio with a constant cathodic radius length. Figure 4.22 shows that the maximum damage values at the interface change while varying the surface area ratio. Maximum corrosion damage at the cathode/anode interface decreases as the cathode/anode surface area ratio decreases, which controls the voltage drop. Figure 4.23 is a magnification of Figure 4.22 which shows the damage effects of the varying surface area ratio for the MS/Mg system.
Figure 4.22: Mild Steel / Magnesium Damage Curve: 1D model for a 72 hour simulation. The cathode radius length is [0,2] cm with a surface area ratio of 1, 2, and 4, with an electrolyte solution height of 0.100 cm.

Figure 4.23: Magnification of the MS/Mg Damage Curve: 1D model for a 72 hour simulation. The cathode radius length is [0,2] cm with a surface area ratio of 1, 2, and 4, with an electrolyte solution height of 0.100 cm.
4.6.2 Cu/Al System: Constant Cathode, Increasing Anode

Figure 4.24 shows the potential across the Cu/Al throughout the galvanic system for a varying cathode/anode surface area ratio with a constant cathodic radius length. Figure 4.24 shows that there is a trend when decreasing the cathodic/anodic metal surface area ratio. As the cathodic/anodic metal surface area ratio decreases, the potential at far-field decreases, converging to the open circuit potential (OCP).

Figure 4.24: Copper / Aluminum Potential Curve: 1D model for a 72 hour simulation. The cathode radius length is [0,2] cm with a surface area ratio of 1, 2, and 4, with an electrolyte solution height of 0.100 cm.

Figure 4.25 shows the current density across the Cu/Al throughout the galvanic system for a varying cathodic/anodic metal surface area ratio. Figure 4.25 shows that the current density changes at the interface while varying cathode/anode surface area ratio.
Figure 4.25: Copper / Aluminum Current Density Curve: 1D model for a 72 hour simulation. The cathode radius length is [0,2] cm with a surface area ratio of 1, 2, and 4, with an electrolyte solution height of 0.100 cm.

Figure 4.26 shows the damage across the Cu/Al throughout the galvanic system for a varying cathodic/anodic metal surface area ratio with a constant cathodic radius length. Figure 4.26 shows the damage while varying the anodic radius length. The maximum corrosion damage at the cathode/anode interface decreases due to the cathodic/anodic surface area decreases, which controls the voltage drop across the electrolyte.

4.6.3 MS/Mg System: Increasing Cathode, Constant Anode and Overall Radius

The following will describe the effects of varying the cathodic/anodic metal surface area ratio while holding the entire overall radius length constant. Since the overall radius length of the entire system is held constant, as the surface area ratio increases, the radius length of the anodic metal decreases. The following will explain the surface
Figure 4.26: Copper / Aluminum Damage Curve: 1D model for a 72 hour simulation. The cathode radius length is [0.2] cm with a surface area ratio of 1, 2, and 4, with an electrolyte solution height of 0.100 cm.

Figure 4.27 shows the potential of the MS/Mg galvanic system over the radius length for various cathode/anode surface areas ratios after a 72 hour simulation. At the MS/Mg interface for each, the potential increases positively from $-1.277$, $-1.272$, and $-1.268$ V. The voltage drop across the cathodic Mild Steel allows the potential value to reach $-1.113$, $-1.108$, and $-1.058$ V, in regards to increasing cathodic/anodic ratios, in the Mild Steel at $r = 0$. The potential value at the outer boundary of Magnesium reaches $-1.491$, $-1.465$, and $-1.431$ V, respectively.
Figure 4.27: Mild Steel / Magnesium Potential Curve: 1D model for a 72 hour simulation. The cathode radius length is varied $[0, F]$ cm and the remaining radius length of the anode is $[F, 4]$ cm with an electrolyte solution height of 0.100 cm.

Figure 4.28: Mild Steel / Magnesium Current Density Curve: 1D model for a 72 hour simulation. The overall radius length is 4 cm, while varying the cathode radius length, $[0, F]$ cm, will give surface area ratios of 0.25, 0.50, and 1.00, with an electrolyte solution height of 0.100 cm.
Figure 4.28 shows the current density of the MS/Mg galvanic system over various cathodic/anodic metal surface area ratios after a 72 hour simulation. An asymptote located at the MS/Mg interface for each of the ratios, going from negative to positive for all cases, due to metal alignment. When looking at the current densities from the most negative value on the cathodic metal’s outside boundary, the current density increases positively from $-3.403 \times 10^{-3}$, $-3.163 \times 10^{-3}$, and $-2.999 \times 10^{-3}$ $\frac{A}{cm^2}$ for the cathode/anode ratios respectively, and increase back to zero as the radius length reaches the radius center, which agree with the stated conditions. When looking at the current densities from the most positive value on the anodic metal’s inner boundary, the current density increases positively from $1.452 \times 10^{-2}$, $1.632 \times 10^{-2}$, and $1.777 \times 10^{-2}$ $\frac{A}{cm^2}$ for the cathodic/anodic metal surface area ratios respectively, and decrease back to zero as the radius length reaches the far-field boundary, which agree with the stated conditions. The difference between the current density values on the vertical asymptote are $1.792 \times 10^{-2}$, $1.949 \times 10^{-2}$, and $2.077 \times 10^{-2}$ $\frac{A}{cm^2}$, for the each of the cathode/anode ratios, respectively.

When looking at the damage for the varying cathode/anode ratio, Figure 4.29 shows that the MS/Mg suffers focused local corrosion near the interface. For the increasing cathode/anode ratio, the maximum damage depth at the interface is $-0.1866$, $-0.20616$, and $-0.22207$ cm, respectively.
4.6.4 Cu/Al System: Increasing Cathode, Constant Anode and Overall Radius

The following will describe the effects of varying the cathode/anode metal surface area ratio while holding the overall radius length constant. Since the radius length of the entire system is held constant, as the radius of the cathodic metal increases, the radius of the anodic metal decreases. The following will explain the surface area ratio effects in regards to the Cu/Al system.

Figure 4.30 shows the potential of the Cu/Al galvanic system over the radius length for varying cathodic/anodic metal surface area ratios (0.25, 0.50, and 1.00) after a 72 hour simulation. At the Cu/Al interfaces for each ratio, the potential increases positively from $-0.5994$, $-0.5861$, and $-0.5726 \text{ V}$, respectively. The voltage drop across the cathodic Copper allows the potential value to reach $-0.5713$, $-0.5524$, $-0.5445$, $-0.5366$, and $-0.5287 \text{ V}$, respectively.
Figure 4.30: Copper / Aluminum Potential Curve: 1D model for a 72 hour simulation. The overall radius length is 4 cm, while varying the cathode radius length, [0,F] cm, will give surface area ratios of 0.25, 0.50, and 1.00, with an electrolyte solution height of 0.100 cm.

and −0.5354 V, in regards to increasing cathodic/anodic ratio, in the Copper at r = 0. The potential value at the outer boundary of Aluminum reaches −0.6295, −0.6100, and −0.5890 V.

Figure 4.31 shows the current density of the Cu/Al galvanic system over the radius length for varying cathodic/anodic surface area ratios after a 72 hour simulation. An asymptote located at the Cu/Al interface for each of the ratios, going from negative to positive for all cases, due to metal alignment. Analyzing the current densities from the most negative value on the cathodic metal’s outside boundary, the current density increases positively from $-5.483 \times 10^{-5}$, $-4.274 \times 10^{-5}$, and $-3.320 \times 10^{-5}$ $\frac{A}{cm^2}$ for the cathode/anode surface area ratios respectively, and increases to zero as the radius length reaches the radius center, which agrees with the stated “no
Figure 4.31: Copper / Aluminum Current Density Curve: 1D model for a 72 hour simulation. The overall radius length is 4 cm, while varying the cathode radius length, [0,F] cm, will give surface area ratios of 0.25, 0.50, and 1.00, with an electrolyte solution height of 0.100 cm.

flux” conditions. When looking at the current densities from the most positive value on the anodic metal’s inner boundary, the current density increases positively from $1.695 \times 10^{-5}$, $2.247 \times 10^{-5}$, and $2.991 \times 10^{-5} \, \frac{A}{cm^2}$ for the cathode/anode surface area ratios respectively, and decrease back to zero as the radius length reaches the far-field boundary, which agree with the stated “no flux” conditions. The difference between the current density values on the asymptote for each of the ratios are $7.178 \times 10^{-5}$, $6.521 \times 10^{-5}$, and $6.311 \times 10^{-5} \, \frac{A}{cm^2}$, respectively.

When looking at the damage for the varying cathode/anode surface area ratio for the Cu/Al galvanic system, Figure 4.32 shows that this system is causing the balanced corrosion both near the interface and throughout the anodic surface. For the increasing cathode/anode surface area ratios, the maximum damage depth at
Figure 4.32: Copper / Aluminum Damage Curve: 1D model for a 72 hour simulation. The overall radius length is 4 cm, while varying the cathode radius length, [0,F] cm, will give surface area ratios of 0.25, 0.50, and 1.00, with an electrolyte solution height of 0.100 cm.

the interface is $-1.516 \times 10^{-4}$, $-2.010 \times 10^{-4}$, and $-2.674 \times 10^{-4}$ cm, respectively. As the cathode/anode surface area ratio varies, while the electrolyte height is constant, all results are shifted with minimal change in magnitude of the potential and current density. The larger cathode surface area leads to a larger current. The smaller anode area forces the current density to increase to balance currents. Therefore, when the cathode/area surface area ratio is increased, the damage is more severe.

4.7 Parameter Study: Scale Up Effects

The following section will describe the effects of varying the overall radius length while keeping a cathode/anode metal surface area ratio of 1, with a constant electrolyte solution height of 0.100 cm, determined after a 72 hour simulation. To study the
effects of scaling up the galvanic cell we will use cathodic radius lengths of 2, 3, and 4 cm split the surface area equally between cathodic and anodic domains.

4.7.1 MS/Mg: Scale Up Effects

Figures 4.33 - 4.35 show the effects of scaling up the overall radius length on the potential, current density, and damage over time for the MS/Mg galvanic system, while keeping a cathode/anode metal surface area ratio of 1.

Figure 4.33 shows how the potential changes while scaling up the overall radius length while keeping a constant cathode/anode ratio of 1 and holding a constant height of the electrolyte solution of 0.100 cm. At the MS/Mg interface for each overall radius length, the potential increases and has the values of $-1.2725$, $-1.2673$, and $-1.1264 \text{V}$, respectively. The voltage drop across the cathodic Mild Steel metal allows the potential value to reach $-1.0997$, $-1.0506$, and $-1.0141 \text{V}$, respectively, in regards to increasing overall radius length, in the Mild Steel at $r=0$. The potential value at the outer boundary of Magnesium reaches $-1.4014$, $-1.4256$, and $-1.4605 \text{V}$, respectively. Figure 4.33 also shows that as overall radius length increases, the potential difference over the entire radius length increases and has the voltage differences of $-0.3016$, $-0.3849$, and $-0.4460 \text{V}$, respectively.

Figure 4.34 shows how the current density changes while scaling up the overall radius length while keeping a constant cathode/anode surface area ratio of 1.00 and holding a constant height of the electrolyte solution of 0.100 cm. At the MS/Mg interface for each different overall radius length there is an asymptote, going from
Figure 4.33: Mild Steel / Magnesium Potential Curve: 1D model for a 72 hour simulation. The cathode and anode radius lengths vary, but hold a cathode/anode surface area ratio of 1 with a constant electrolyte solution height of 0.100 cm.

Figure 4.34: Mild Steel / Magnesium Current Density Curve: 1D model for a 72 hour simulation. The cathode and anode radius lengths vary, but hold a cathode/anode surface area ratio of 1 with a constant electrolyte solution height of 0.100 cm.
negative to positive for all cases, due to metal alignment. When looking at the current
densities from the most negative value on the cathodic metal’s outside boundary, the
current density decrease from $-3.218 \times 10^{-3}$, $-2.970 \times 10^{-3}$, and $-2.843 \times 10^{-3} \, \frac{A}{cm^2}$, for each of the overall radius lengths, respectively.

The current density increases and converges to zero as the radius length reaches the radius center, which agrees with the stated “no flux” conditions. When looking at the current densities from the most positive value on the anodic metal’s inner boundary, the current density decreases from $1.588 \times 10^{-2}$, $1.806 \times 10^{-2}$, and $1.936 \times 10^{-2} \, \frac{A}{cm^2}$, for each of the overall radius lengths, respectively. The current density also decreases and converges to zero as the radius length reaches the far-field boundary, which again, agrees with the stated “no flux” conditions. The difference between the current density values on the asymptote with respect to the increasing initial electrolyte solution heights are $1.910 \times 10^{-2}$, $2.102 \times 10^{-2}$, and $2.220 \times 10^{-2} \, \frac{A}{cm^2}$.

Figure 4.35 shows how the damage changes while scaling up the overall radius length while keeping a constant 1:1 ratio and holding a constant electrolyte height of 0.100 cm. Increasing the overall radius length of the cell while holding the cathodic/anodic radius constant, the maximum damage depth at the interface for the anodic mild steel is $-0.2036$, $-0.2248$, and $-0.2371 \, cm$, respectively. Corrosion depth decreases as the distance away from interface increases. As previously explained, the MS/Mg have localized corrosion at the interface. The increase in overall radius length, causes a larger voltage drop. This leads to higher current density values in the larger systems so that the currents balance. Hence, an increase in damage.
Figure 4.35: Mild Steel / Magnesium Damage Curve: 1D model for a 72 hour simulation. The cathode and anode radius lengths vary, but hold a cathode/anode surface area ratio of 1 with a constant electrolyte solution height of 0.100 cm.

4.7.2 Cu/Al System: Scale Up Effects

Figures 4.36 - 4.38 show what effects scaling up the overall radius length has on the potential, current density, and damage over time for the Cu/Al galvanic coupled cell.

Figure 4.36 shows how the potential changes while scaling up the overall radius length while keeping a constant 1:1 cathode/anode ratio and holding a constant height of the electrolyte solution of 0.100 cm after a 72 hour simulation. At the Cu/Al interface for each overall radius length, the potential increases and has the values of $-0.5717$, $-0.5728$, and $-0.5735$ V, respectively. The voltage drop across the cathodic Copper metal allows the potential value to reach $-0.5491$, $-0.5325$, and $-0.5165$ V, respectively, in regards to increasing overall radius length, in the Copper at $r = 0$. The potential value at the outer boundary of Aluminum reaches $-0.5811$, $-0.5906$, $-0.5962$, and $-0.6017$ V, respectively.
Figure 4.36: Copper / Aluminum Potential Curve: 1D model for a 72 hour simulation. The cathode and anode radius lengths vary, but hold a cathode/anode surface area ratio of 1 with a constant electrolyte solution height of 0.100 cm.

and $-0.6002 \, V$, respectively. Figure 4.36 also shows that as overall radius length increases, the potential difference over the entire radius length increases and has the voltage differences of $-0.0320$, $-0.0582$, and $-0.0837 \, V$, respectively.

Figure 4.37 shows how the current density changes while scaling up the overall radius length while keeping a constant 1:1 cathode/anode ratio and holding a constant height of the electrolyte solution of 0.100 cm after a 72 hour simulation. At the Cu/Al interface for each different overall radius length there is an asymptote, going from negative to positive for all cases, due to metal alignment. When looking at the current densities from the most negative value on the cathodic metal’s outside boundary, the current density decrease from $-3.265 \times 10^{-5}$, $-3.329 \times 10^{-5}$, and $-3.374 \times 10^{-5} \, \frac{A}{cm^2}$, for each of the overall radius lengths, respectively. The current density increases and
Figure 4.37: Copper / Aluminum Current Density Curve: 1D model for a 72 hour simulation. The cathode and anode radius lengths vary, but hold a cathode/anode surface area ratio of 1 with a constant electrolyte solution height of 0.100 cm.

Figure 4.38: Copper / Aluminum Damage Curve: 1D model for a 72 hour simulation. The cathode and anode radius lengths vary, but hold a cathode/anode surface area ratio of 1 with a constant electrolyte solution height of 0.100 cm.
converges to zero as the radius length reaches the radius center, which agrees with
the stated “no flux” conditions. When looking at the current densities from the most
positive value on the anodic metal’s inner boundary, the current density decreases
from $3.048 \times 10^{-5}$, $2.981 \times 10^{-5}$, and $2.936 \times 10^{-5} \ \frac{A}{cm^2}$, for each of the overall radius
lengths, respectively. The current density also decreases and converges to zero as the
radius length reaches the far-field boundary, which again, agrees with the stated “no
flux” conditions. The difference between the current density values on the asymptote
with respect to the increasing initial electrolyte solution heights are $6.313 \times 10^{-5}$,
$6.311 \times 10^{-5}$, and $6.310 \times 10^{-5} \ \frac{A}{cm^2}$.

Figure 4.38 shows how the damage changes while scaling up the overall radius
length while keeping a constant 1:1 cathode/anode ratio and holding a constant height
of the electrolyte solution of 0.100 cm after a 72 hour simulation. For the increasing
overall radius length, the maximum damage depth at the interface for the anodic
Aluminum is $2.726 \times 10^{-4}$, $2.666 \times 10^{-4}$, and $2.625 \times 10^{-4} \ \text{cm}$, respectively. Corro-
sion depth decreases as the distance away from interface increases. Corrosion depth
decreases as the distance away from interface increases. As previously explained, the
Cu/Al have localized corrosion at the interface. The increase in overall radius length,
causes a larger voltage drop. This leads to higher current density values in the larger
systems so that the currents balance. Hence, an increase in damage.

Investigating the scale up of the overall radius length while holding a constant
cathode/anode surface area ratio of 1 gives a few results. The Cu/Al system behaves
differently then the MS/Mg system due to the difference in the polarization curves.
For the Cu/Al system it is still true that voltage drop is larger as the system is scaled up. However, the current density is not higher locally for the larger system. Rather the current density is higher in the smaller system because of the shallower drop in combination with the shape of the polarization curve. Thus, the smaller system sees more damage as shown in Figure 4.38.

4.8 Simulation Limitations

The Wagner relationship, $w << \frac{\Delta \phi}{\Delta i} \kappa$, which is applied to both portions of the polarization curve, must hold throughout this model. The polarization slope values near the open-circuit potential are large, therefore the Wagner relationship holds away from the cathode/anode interface. The Wagner relationship will hold near the interface if the anodic polarization branch has a steep slope, for Magnesium and Aluminum respectively, which are shown in Figures 4.1 and 4.2. In the asymptotic method derivation, an assumption was made that the electrolyte solution thickness and the corrosion depth were of same magnitude. If the corrosion depth advances enough compared to the electrolyte thickness, this assumption would no longer be valid. The electrolyte solution thickness should be small enough to allow $\frac{w}{L} << 1$, for the thin film approximation, to hold true, which it has in all cases investigated. The parameter study for varying electrolyte solution heights show that as the height decreases, the potential drop over the system increases, which would cause computational issues as the potential will go past the open-circuit potential and be calculated using the wrong branch on the polarization curve.
CHAPTER V

CONCLUSION

5.1 Conclusion

The work that is presented in this thesis includes the derivation of a one dimensional model for the damage evolution due to galvanic corrosion in a concentric cylindrical geometry. Two different galvanic cells, Mild Steel and Magnesium coupled together in 1.6% NaCl electrolyte solution, as well as Copper and Aluminum coupled together in 0.1 M NaCl electrolyte solution are investigated.

The Nernst-Planck equation is used to describe the potential in the electrolyte solution. Assuming that the electrolyte solution is well-mixed, has no convection, and obeys electro-neutrality, the Nernst-Planck equation reduces to the Laplace equation for the potential. "No flux" conditions are assumed at the top, left, and right electrolyte boundaries and Ohm’s Law is assumed at the electrolyte/metal boundary.

An asymptotic approach via the thin film assumption is used to reduce the potential equation down to a one-dimensional problem. The thin film assumption of the electrolyte thickness is used to integrate out the vertical dimension of the solution. The governing potential equation is defined when the Wagner relationship and the thin film approximation hold.
The one-dimensional governing potential equation is

\[ \kappa \frac{1}{r} [(w + h)(r\phi_r)]_r = i(\phi). \]

The rate of corrosion is related to Faraday’s Law,

\[ h_t = \frac{i_a(\phi)M_w}{ZF_c\rho} \quad F < r < L. \]

The potential and corrosion rate equations allow the damage evolution of the anode to be solved for iteratively in MATLAB using \textit{bvp4c}, a boundary value problem solver.

5.1.1 Summary of Major Assumptions

The electrolyte is assumed to be well-mixed, which gives no species variation in the electrolyte solution. There is also no flux through the top, left, and right electrolyte boundaries. Ohm’s Law represents the flux through the electrolyte/metal boundary. The damage evolution equation is described by Faraday’s Law. The electrolyte solution is assumed to be a thin film, which implies that \( w \ll L \) or \( \frac{w}{L} \ll 1 \). For the Wagner relationship, \( w \ll \frac{\Delta\phi}{\Delta_i}\kappa \), the electrolyte thickness, \( w \), must be much less than the electrolyte solution conductivity times the anodic polarization slope.

5.1.2 Summary of Contributions

Contributions from this thesis are an iterative numerical approach for simulated corrosion in cylindrical geometries. It calculates a damage profile being directly related to the voltage drop and current density at the Galvanic Corrosion (Operating) Potential. The model accounts for varying the electrolyte solution thickness, varying
the cathode/anode radius length ratios, and scaled up systems, as well as the ability to handle different dual-metal galvanic systems with input of polarization curves.

5.2 Future Implementations

Currently, galvanic corrosion research is investigating higher dimensional models, as well as the ability to track ionic species in the electrolyte solution. Higher ordered models will be able to solve Laplace’s equation without having to assume a thin film approximation for electrolyte solution height. This should allow the potential values to be solved in both the radial and axial directions in terms of a cylindrical model. Due to higher dimensions, more intricate geometries such as washers, fasteners, and bolt heads can be solved, which would be difficult for a one dimensional model. Undercutting of material in some geometries disallow a simple one-dimensional model.

If the electrolyte solution is not well mixed, then it is important to track ionic species in the electrolyte. In this instance, the Nernst-Planck equation must be used to track each ion from the electrochemical reaction as electro-neutrality must be satisfied.


**APPENDIX**

**MATLAB COMPUTER CODE**

% CoCxCyl.m
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Austin Smith %
% ^z 04/25/2013 %
% |----------------------------^---------| %
% | Electrolyte | | %
% | w | %
% __O___________________F________v_________L____>> r %
% | | | %
% | CATHODIC Metal | ANODIC Metal | %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

function CoCxCyl
clc % Clears Command Window
close all % Closes all figures
clear all % Clears variables
StartTime = cputime; % Starts Program Timer

% Defined Values -----------------------------------------------------------
hrs = 72; % Pick simulation time in hours
dt = 900; % 15 min 300=5min time step [Large Steps, 1000]
data = 08; % 2 hours : dtndata, Record data
nfigure = 08; % 2 hours : dt*nfigure, Updates figures
nmax = (hrs*60*60)/dt+1; % Total Number of Time Steps
dr = 1.0e-03; % [Originally at 1.0e-03]
tol = 1.0e-12; % [Originally at 1.0e-12]
Faraday = 96485.3365; % Faraday’s constant (C/mol)

for RC = 1:1:26;
clearvars -except StartTime hrs dt ndata nfigure nmax dr tol Faraday RC
%MAGNESIUM / MILD STEEL -- RC 01,03,05,11 Equivalent
% Base Case
if (RC==01), mcase=1; gcase=1; wcase=2; zinit = [-1.3107; 0];
% Vary Electrolyte Height with Base Case Geometry
elseif (RC==02), mcase=1; gcase=1; wcase=1; zinit = [-1.3076; 0];
elseif (RC==03), mcase=1; gcase=1; wcase=2; zinit = [-1.3107; 0];
elseif (RC==04), mcase=1; gcase=1; wcase=3; zinit = [-1.3138; 0];
% Increase Anode, Constant Cathode
elseif (RC==05), mcase=1; gcase=1; wcase=2; zinit = [-1.3107; 0];
elseif (RC==06), mcase=1; gcase=2; wcase=2; zinit = [-1.3126; 0];
elseif (RC==07), mcase=1; gcase=3; wcase=2; zinit = [-1.3134; 0];
end

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% Increase Cathode, Constant Overall
elseif (RC==08), mcase=1; gcase=4; wcase=2; zinit = [-1.3145; 0];
elseif (RC==09), mcase=1; gcase=5; wcase=2; zinit = [-1.3115; 0];
elseif (RC==10), mcase=1; gcase=6; wcase=2; zinit = [-1.3091; 0];
% Geometries: Scale Up keeping a 1:1 Surface Area Ratio
elseif (RC==11), mcase=1; gcase=7; wcase=2; zinit = [-1.3107; 0];
elseif (RC==12), mcase=1; gcase=8; wcase=2; zinit = [-1.3088; 0];
elseif (RC==13), mcase=1; gcase=9; wcase=2; zinit = [-1.3076; 0];
end

% Geometries: Scale Up keeping a 1:1 Surface Area Ratio
elseif (RC==14), mcase=2; gcase=1; wcase=2; zinit = [-0.5718; 0];
elseif (RC==15), mcase=2; gcase=1; wcase=1; zinit = [-0.5735; 0];
elseif (RC==16), mcase=2; gcase=1; wcase=2; zinit = [-0.5718; 0];
elseif (RC==17), mcase=2; gcase=1; wcase=3; zinit = [-0.5705; 0];
elseif (RC==18), mcase=2; gcase=1; wcase=2; zinit = [-0.5718; 0];
elseif (RC==19), mcase=2; gcase=2; wcase=2; zinit = [-0.5864; 0];
elseif (RC==20), mcase=2; gcase=2; wcase=2; zinit = [-0.5985; 0];
% Increase Cathode, Constant Overall
elseif (RC==21), mcase=2; gcase=4; wcase=2; zinit = [-0.5994; 0];
elseif (RC==22), mcase=2; gcase=5; wcase=2; zinit = [-0.5882; 0];
elseif (RC==23), mcase=2; gcase=6; wcase=2; zinit = [-0.5727; 0];
elseif (RC==24), mcase=2; gcase=7; wcase=2; zinit = [-0.5718; 0];
elseif (RC==25), mcase=2; gcase=8; wcase=2; zinit = [-0.5728; 0];
elseif (RC==26), mcase=2; gcase=9; wcase=2; zinit = [-0.5769; 0];
end

% Geometry Case Choices for Parameter Study
% Geometries: Constant Cathode, Increased Anode Layer
if (gcase==1), gflag = 'g01_'; F = 2.000; L = 2.828; %BaseCase
elseif (gcase==2), gflag = 'g02_'; F = 2.000; L = 3.464;
elseif (gcase==3), gflag = 'g03_'; F = 2.000; L = 4.472;
% Geometries: Increase Cathode SA, Constant Overall SA
elseif (gcase==4), gflag = 'g04_'; F = 1.789; L = 4.000;
elseif (gcase==5), gflag = 'g05_'; F = 2.309; L = 4.000;
elseif (gcase==6), gflag = 'g06_'; F = 2.828; L = 4.000;
% Geometries: Scale Up keeping a 1:1 Surface Area Ratio
elseif (gcase==7), gflag = 'g07_'; F = 2.000; L = 2.828;
elseif (gcase==8), gflag = 'g08_'; F = 3.000; L = 4.243;
elseif (gcase==9), gflag = 'g09_'; F = 4.000; L = 5.657;
end

% w, Electrolyte Height Case Choices for Parameter Study ----------------
if (wcase==1), wflag = 'w1_'; w = 0.025; % 25% of w3 w/L=0.00625
elseif (wcase==2), wflag = 'w2_'; w = 0.100; % * Original w/L=0.02500
elseif (wcase==3), wflag = 'w3_'; w = 0.400; % 400% of w3 w/L=0.10000
end
% Metal Properties Case Choices for Parameter Study -------------------------
if (mcase==1)
    mflag = 'MgMs_'; % MAGNESIUM & MILD STEEL
    Density = 1.74; % Density (gr/cm^3)
    MW = 24.31; % Molecular Weight (gr/mole)
    kappa = 0.0271; % Electrolyte Conductivity
    VE = 2; % Valence Electrons (Mg)
elseif (mcase==2)
    mflag = 'AlCu_'; % ALUMINIUM & COPPER
    Density = 2.7; % Density (gr/cm^3)
    MW = 26.98; % Molecular Weight (gr/mole)
    kappa = 0.0105; % Electrolyte Conductivity
    VE = 3; % Valence Electrons (Al)
end
Cmetal = Density/MW;

% Points for the Bisection Method
D = L-F;
M = 1.0e-6; % {Coding Issues} Get off of integer
rinitL = [0 .2*F .4*F .6*F .8*F F+M];
rinitR = [F+M F+.2*D F+.4*D F+.6*D F+.8*D L];
rinit = [rinitL'; rinitR'];

% ------------------ Galvanic Corrosion Program Code -------------------
StartCaseTime = cputime;
fprintf('
RC = %g
',RC);
fprintf('mcase = %g	Density = %g	',mcase,Density);
fprintf('MW = %g	kappa = %g
',MW,kappa);
fprintf('wcase = %g	w = %g
',wcase,w);
fprintf('gcase = %g	F = %g	L = %g	
',gcase,F,L);
fprintf('dr = %g
',dr);
fprintf('rinit = ');fprintf('%g ',rinit');

% Physical Lengths/Ranges -----------------------------------------------
r1 = 0:dr:F;
N1 = length(r1); % Length of Inner/Left Material
r2 = F:dr:L;
N2 = length(r2); % Length of Outer/Right Material
rtot = [r1(1:N1-1) r2];
rplot = 0:dr:L;

% Initial Time (t = 0 hours) --------------------------------------------
fprintf('

----- Solving for Initial Time -----
')
Hvec = zeros(1,length(rtot));
Hpvec = zeros(1,length(rtot));

PHIPHI = -1.800:0.001:0.000;
for i=1:length(PHIPHI),
    sa(i) = ia(PHIPHI(i));
    sc(i) = ic(PHIPHI(i));
end
% Find Initial Potential
options = bvpset('RelTol',tol);
solint = bvpinit(rinit,zinit); % Initial Guess
z1 = bvp4c(@bvpode,@bvpbc,solint,options); % BVP4C, Boundary Value Prbm.
Zint = deval(z1,rplot);
PHI = Zint(1,:); % Phi from output
PHIp = Zint(2,:); % Phi_r from output

% Assigning Anodic/Cathodic (Current) Sides to Geometry
for i=1:length(rplot)
    if (rplot(i)<F), s(i) = -ic(PHI(i)); % Cathodic Inside F
    else s(i) = ia(PHI(i)); % Anodic Outside F
    end
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%figure(RC) % Potential
%plot(rplot,PHI), title('Potential vs Radius Length')
%xlabel('Radius Length (cm)'), ylabel('Potential (Volts, V)')
%hold on
%fprintf('
Initial Time ... Check Calibration
--- Break ---
')
%break
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Write Initial Time to Files -------------------------------------------
jj = '000';
filename1 = [ mflag gflag wflag 'Pot' jj ];
filename2 = [ mflag gflag wflag 'Dam' jj ];
filename3 = [ mflag gflag wflag 'Cur' jj ];
filename4 = [ mflag gflag wflag 'Cde' jj ];
fid1 = fopen(filename1,'w');
fid2 = fopen(filename2,'w');
fid3 = fopen(filename3,'w');
fid4 = fopen(filename4,'w');
for i=1:length(rplot),
    fprintf(fid1,'%e %e
',rplot(i),PHI(i));
end
for i=1:length(rplot),
    fprintf(fid2,'%e %e
',rplot(i),-Hvec(i));
end
for i=1:length(rplot),
    fprintf(fid3,'%e %e
',rplot(i),PHIp(i));
end
for i=1:length(rplot),
    fprintf(fid4,'%e %e
',rplot(i),s(i));
end
fclose(fid1);
fclose(fid2);
fclose(fid3);
fclose(fid4);
% Plotting Figures for First Time -----------------------------------------
% Figure Naming Convention
fn = mc\textbullet{}10000 + gc\textbullet{}100 + wc\textbullet{}10;

% Polarization curve (Potential vs. Current Density)
\texttt{figure(fn + 1)}
\texttt{plot(sa,PHIPHI,sc,PHIPHI), title('Polarization Curves: Cylindrical')}
\texttt{xlabel('Current Density (A/cm^2)'), ylabel('Potential (Volts, V)')}
\texttt{legend('Anodic','Cathodic')}

\texttt{figure(fn + 2)}
\texttt{semilogx(sa,PHIPHI,sc,PHIPHI), title('Polarization Curves: Semilog')}
\texttt{xlabel('Current Density (A/cm^2)'), ylabel('Potential (Volts, V)')}
\texttt{legend('Anodic','Cathodic')}

\texttt{figure(fn + 3)} % Potential
\texttt{plot(rplot,PHI), title('Potential vs Radius Length')}
\texttt{xlabel('Radius Length (cm)'), ylabel('Potential (Volts, V)')}
\texttt{hold on}

\texttt{figure(fn + 4)} % Current
\texttt{plot(rplot,PHIp), title('Current vs Radius Length')}
\texttt{xlabel('Radius Length (cm)'), ylabel('Current (Ampere, A)')}
\texttt{hold on}

\texttt{figure(fn + 5)} % Current Density
\texttt{plot(rplot,s), title('Current Density vs Radius Length')}
\texttt{xlabel('Radius Length (cm)'), ylabel('Current Density (A/cm^2)')}
\texttt{hold on}
\texttt{drawnow}

\texttt{filename5 = [ RCflag mflag 'polarization'];}
\texttt{fid5 = fopen(filename5,'w');}
\texttt{for i=1:length(rplot)}
\hspace{1em} \texttt{fprintf(fid1,'%g %g %g\n',sa,sc,PHIPHI);}
\texttt{end}
\texttt{fclose(fid5);}

% Start Time Loop for Damage Evolution ================================
\texttt{fprintf('----- Start of Time Loop -----')}
\texttt{for n=1:nmax-1}
\hspace{1em} % Update Hvec - Damage ----------------------------------------
\hspace{2em} \texttt{for i=N1:(N1+N2-1)}
\hspace{3em} \texttt{Hvec(i) = Hvec(i) + dt*ia(PHI(i))/(VE*Faraday*Cmetal);}
\hspace{2em} \texttt{end}
\hspace{1em} \texttt{fprintf('\n%d of %d : max H = \%e\n',n,nmax-1,max(Hvec))}
\texttt{end}
% Update Hpvec - Damage Slope ----------------------------------------
Hpvec(N1) = (-3*Hvec(N1)+4*Hvec(N1+1)-Hvec(N1+2))/(2*dr);
for i=(N1+1):(N1+N2-2)
    Hpvec(i) = (Hvec(i+1)-Hvec(i-1))/(2*dr);
end
Hpvec(N1+N2-1) = (3*Hvec(N1+N2-1)-4*Hvec(N1+N2-2)+Hvec(N1+N2-3))/(2*dr);
% Update Potential ---------------------------------------------------
options = bvpset('RelTol',tol);
solint = bvpinit(rinit,zinit);
z1 = bvp4c(@bvpode,@bvpbc,solint,options);
Zint = deval(z1,rplot);
PHI = Zint(1,:); % Potential , Phi
PHIp = Zint(2,:); % Current , Phi_r
% Update Files -------------------------------------------------------
if (mod(n,ndata)==0)
    jj = num2str(n/ndata);
    if (length(jj)==1), jj = ['00' jj]; end
    if (length(jj)==2), jj = ['0' jj]; end
    filename1 = [ mflag gflag wflag 'Pot' jj ];
    filename2 = [ mflag gflag wflag 'Dam' jj ];
    filename3 = [ mflag gflag wflag 'Cur' jj ];
    filename4 = [ mflag gflag wflag 'Cde' jj ];
    fid1 = fopen(filename1,'w');
    fid2 = fopen(filename2,'w');
    fid3 = fopen(filename3,'w');
    fid4 = fopen(filename4,'w');
    for i=1:length(rplot)
        fprintf(fid1,'%e %e
',rplot(i),PHI(i));
    end
    for i=1:length(rplot)
        fprintf(fid2,'%e %e
',rplot(i),-Hvec(i));
    end
    for i=1:length(rplot)
        fprintf(fid3,'%e %e
',rplot(i),PHIp(i));
    end
    for i=1:length(rplot)
        fprintf(fid4,'%e %e
',rplot(i),s(i));
    end
    fclose(fid1);
    fclose(fid2);
    fclose(fid3);
    fclose(fid4);
end
% Update the Current Density Data ------------------------------------
for i=1:length(rplot)
    if (rplot(i)<F), s(i) = -ic(PHI(i)); %Cathodic Inner
    else
        s(i) = ia(PHI(i)); %Anodic Outer
    end
end
if (mod(n,nfigure)==0)
    figure(fn + 3) % Potential
    plot(rplot,PHI), title('Potential vs Radius Length')
    xlabel('Radius Length (cm)'), ylabel('Potential (Volts, V)')
    hold on

figure(fn + 4) % Current
    plot(rplot,PHIp), title('Current vs Radius Length')
    xlabel('Radius Length (cm)'), ylabel('Current (Ampere, A)')
    hold on

figure(fn + 5) % Current Density
    plot(rplot,s), title('Current Density vs Radius Length')
    xlabel('Radius Length (cm)'), ylabel('Current Density (A/cm^2)')
    hold on

figure(fn + 6) % Damage Profile
    plot(rplot,-Hvec), title('Damage Profile vs Radius Length')
    xlabel('Radius Length (cm)'), ylabel('Height (cm)')
    hold on
drawnow
end

% Write Final Loop Data File for input to excel (if needed) -----------
if (mod(n,nmax-1)==0)
    filename5 = ['_DONE_' mflag gflag wflag ];
    fid5 = fopen(filename5,'w');
    fprintf(fid5,'F L w
');
    fprintf(fid5,'%e %e %e
',F,L,w');
    fprintf(fid5,'Length Potential Current CurDens Damage
');
    for i=1:length(rplot)
        if (rplot(i)<F), Hvec(i) = 0; end
        A = rplot(i); B = PHI(i); C = PHIp(i); D = s(i); E = -Hvec(i);
        fprintf(fid5,'%e %e %e %e %e
', A, B, C, D, E);
    end
    fclose(fid5);
end

% Loop Timer -----------------------------
done = n/(nmax-1)*100;
conttimer = cputime;
ct = (conttimer - StartCaseTime)/60;
fprintf('%g percent complete after %g minutes
',done,ct)
end % Damage Loop
end % RC Loop

EndTime = cputime; % Ends Program Timer
RunTime = (EndTime - StartTime)/60;
fprintf('\n--- Program Completed ---
');
fprintf('\n--- Run Time = %f minutes
---
',RunTime);

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% Subprograms and Functions

% Boundary Value Problem:

```matlab
function j = bvpbc(zl,zr)
j = [ zl(2,1)-0 % zl(2,1)=0 -> PHI(0)=0, no flux
     zr(1,1)-zl(1,2) % zr(1,1)=zl(1,2) -> PHI(F+) = PHI(F-), current
     zr(2,1)-zl(2,2) % zr(2,1)=zl(2,2) -> PHI(F+) = PHI(F-), cur dens
     zr(2,end)-0 ]; % zl(2,1)=0 -> PHI(L)=0, no flux
end
```

% Governing Equation

```matlab
function dzdr = bvpode(r,z,region)
dzdr = zeros(2,1);
dzdr(1) = z(2);
HH = interp1q(rtot',Hvec',r);
HHp = interp1q(rtot',Hpvec',r);
K = kappa;
E = 1.0e-12; % {Coding Issues} Divide by 0
switch region
  case 1
    dzdr(2) = -ic(z(1)) - ((1/(r+E))*K*z(2)*(w+HH+r*HHp))/(K*(w+HH));
  case 2
    dzdr(2) = ia(z(1)) - ((1/(r+E))*K*z(2)*(w+HH+r*HHp))/(K*(w+HH));
end
```

% ANODIC METAL Polarization Curves

```matlab
function y = ia(PHI)
% Magnesium Polarization Curves [Despande], Linear Approx. OCP = -1.60
if (mcase==1)
  if (PHI>-1.60)
    y = -5.00 + (4.00/0.40)*(PHI+1.60);
  else
    y = -5.00 - (4.00/0.40)*(PHI+1.60);
  end
  y = 10^-y*0.85;
end
% Aluminum Polarization Curves [Lillard], Linear Approx. OCP = -0.95
if (mcase==2)
  if (PHI>-0.95)
    y = -8.00 + (7.00/0.76)*(PHI+0.95);
  else
    y = -8.00 - (7.00/0.76)*(PHI+0.95);
  end
  y = 10^-y;
end
```

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function y = ic(PHI)
    if (mcase==1)
        if (PHI<-0.70)
            y = -6.00 - (5.00/0.80)*(PHI+0.70);
        else
            y = -6.00 + (5.00/0.80)*(PHI+0.70);
        end
        y = 10^y*0.85;
    end
    if (mcase==2)
        if (PHI<-0.14)
            y = -8.00 - (7.00/0.86)*(PHI+0.14);
        else
            y = -8.00 + (7.00/0.86)*(PHI+0.14);
        end
        y = 10^y;
    end
end

% CATHODIC METAL Polarization Curves ---------------------------------------
% Mild Steel Polarization Curves [Despande], Linear Approx. OCP = -0.70
% Copper Polarization Curves [Lillard], Linear Approx. OCP = -0.14

end % End of Function CoCxCyl