Investigations of Crevice Corrosion Scaling Laws Using Microfabrication Techniques and Modeling

A Thesis

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Approval Sheet

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Abstract

The development of a comprehensive, accurate model of the mechanisms and controlling factors of crevice corrosion has been hindered by two primary difficulties: size scale and dimensional variation. Practical crevices have crevice gaps on the order of 0.1-10 µm and lengths of 1-10 mm. It is difficult to reproducibly fabricate crevices on that size scale, and even more challenging to take spatially resolved potential or ion concentration measurements inside the crevice. As a result, it is often necessary to scale up the geometry of the crevice to perform experiments. However, it is still debated how the mechanisms of crevice corrosion scale with geometry so the relevance of results from experiments on large-scale crevices to practical crevices is unclear. Without knowledge of the appropriate scaling law, a model that is developed based on insights from experiments on large-scale crevices is not necessarily applicable to practical crevice corrosion situations.

The other primary difficulty encountered when attempting to model crevice corrosion phenomena is dimensional variation. Computer models, in the interest of reducing coding complexity and increasing computational speed, assume that crevices have ideal dimensions. Practical crevices and crevices fabricated by pressing two pieces of material, however, have many surface irregularities. The subcrevices caused by these surface irregularities can have a significant enough impact on the mechanisms of crevice corrosion to cause scatter in experimental results and make comparisons between models and experiments difficult. Experimental verification, however, is essential to the development of an accurate model.
The semiconductor device industry provides a possible solution to these difficulties. Semiconductor devices are examples of structures on the size scale relevant to crevice corrosion that have rigorously-defined dimensions. In this study, semiconductor device manufacturing techniques were utilized to microfabricate nickel and gold crevices with 7-8 mm lengths and 1-100 \( \mu \text{m} \) crevice gaps. Profilometry measurements indicated that the dimensions of the crevices varied by less than 6\% (e.g., the crevice gap varied from 10.96 \( \mu \text{m} \) to 11.39 \( \mu \text{m} \) across a sample), so the crevices were reasonable approximations of the ideal geometries assumed by models.

The microfabricated gold crevices were utilized for experimental verification of CREVICER, a 2-D spatiotemporal finite element model of occluded region corrosion developed at UVa. Mass transport-limited copper deposition onto a gold crevice substrate was performed experimentally and the system was modeled. The experimentally determined copper deposition profiles were compared to the output of the model. Both profiles were the same shape, but difficulties in obtaining the experimental deposition profiles prohibited a quantitative comparison.

The microfabricated nickel crevices were used in conjunction with CREVICER to investigate the scaling laws that govern crevice corrosion. The system that was studied, nickel in 0.5 M \( \text{H}_2\text{SO}_4 \), is one in which the potential (IR) drop in the crevice is the controlling factor in the initiation and propagation of crevice corrosion. Modeling results indicated that \( x_{\text{crit}}^2/G \), where \( x_{\text{crit}} \) is the distance into the crevice at which corrosion initiates and \( G \) is the crevice gap, is the correct scaling factor for this system. It was found that the \( x_{\text{crit}}^2/G \) dependence is increasingly pronounced for materials that have
electrochemical boundary conditions with thinner, sharper, active noses. Experimental measurements of $x_{\text{crit}}$ for crevices with varying crevice gaps exhibited the same trends as the modeling results, but experimental difficulties caused wide scatter in the data, prohibiting quantitative verification of the scaling law.
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a .................................. proportionality constant varied to fit curve to potentiodynamic data
b .................................. proportionality constant varied to fit curve to potentiodynamic data

\( C_i \) ............................................................... concentration of species i [mol/m³]

\( \nabla C_i \) ................................................ gradient of concentration of species i [mol/m⁴]

\( D_i \) ................................................................. diffusivity of species i [m²/s]

\( E \) .......................................................... electrochemical potential of a reaction across an interface [V]

\( E_{0,an} \) ........................................ Nernst potential for the sum of the anodic reactions [V]

\( E_{0,Cu} \) ................................................ Nernst potential for the copper reduction reaction [V]

\( E_{0,ORR} \) ........................................ Nernst potential for the oxygen reduction reaction [V]

\( E_{\text{hold}} \) ...................................... potential at which crevice mouth is potentiostatically held [V]

\( E_{\text{pass}} \) ................................................ primary passivation potential [V]

\( E_{\text{peak}} \) ........................................ potential at point of maximum current density [V]

\( f_{Cu}(x) \) ...................................................... flux of copper at position x [mol/m²]

\( F \) ......................................................... Faraday’s constant 96,487 [C/eq]

\( G \) .............................................................. crevice gap [m]

\( h \) ........................................................ height of a volume of solution [m]

\( h(x,y) \) ...................................................... height of a crevice at point (x,y) [m]

\( i \) ........................................................ current density across an interface [A/m²]

\( i_{0,an} \) ................................ exchange current density for the sum of the anodic reactions [A/m²]

\( i_{0,Cu} \) ................................ exchange current density for the copper reduction reaction [A/m²]

\( i_{0,ORR} \) ................................ exchange current density for the oxygen reduction reaction [A/m²]
\( i_{\text{lim,Cu}} \) .................................................. limiting current density for copper reduction [A/m\(^2\)]

\( i_{\text{lim,ORR}} \) .................................................. limiting current density for oxygen reduction [A/m\(^2\)]

\( i_{\text{total}} \) .................................................. sum of anodic and cathodic current densities through an interface [A/m\(^2\)]

\( I_m \) ........................................................................................................ mean current [A]

\( \bar{J}_{el} \) .................................................................................................. electrical flux [C/m\(^2\)-s]

\( \bar{J}_i \) .................................................................................................. flux vector of species \( i \) [mol/m\(^2\)-s]

\( J_{\text{walls}} \) .................................................. current perpendicular to crevice walls [A/m\(^2\)]

\( K_1 \) .......................................................... proportionality constant in boundary condition equations

\( K_2 \) .......................................................... vertical shift constant in boundary condition equations

\( l \) ........................................................................................................... length of crevice [m]

\( l_{\text{Cu}} \) .......................................................... lattice constant for copper [m]

\( L \) ........................................................................................................... length of crevice [m]

\( L_p \) .......................................................... distance from mouth of crevice to region of severest attack [m]

\( N \) ............................................................................................................... number of nodes in a finite element mesh

\( N_A \) ......................................................................................................... Avogadro’s number [atoms/mol]

\( Q \) ........................................................................................................... electrical charge [C]

\( t \) ........................................................................................................... time [s]

\( T(x) \) ..................................................................................................... copper deposition thickness at distance \( x \) [m]

\( u_{\text{i}} \) .......................................................... mobility constant for species \( i \) [m\(^2\)-mol/J-s]

\( \bar{v} \) ..................................................................................................... velocity vector of the solution [m/s]

\( w \) ........................................................................................................... crevice gap [m]

\( w_a \) ..................................................................................................... width of region of severe attack [m]

\( x \) ........................................................................................................... distance into the crevice [m]

\( x_0 \) ......................................................................................................... length of the crevice [m]
\(x_{\text{crit}}\) .......................................................... distance from mouth of crevice to region of severest attack [m]

\(x_{\text{pass}}\) .......................................................... distance from mouth of crevice to front of the corrosion band [m]

\(X'\) ................................................................................................... dimensionless length

\(z_i\) ............................................................................ charge number for species \(i\) [eq/mol]

\(\alpha\) .......................................................... constant in boundary condition equations

\(\beta\) .......................................................... constant in boundary condition equations

\(\beta_{\text{an}}\) .......................................................... symmetry factor for sum of anodic reactions

\(\beta_{\text{Cu}}\) .......................................................... symmetry factor for copper reduction reaction

\(\beta_{\text{ORR}}\) .......................................................... symmetry factor for oxygen reduction reaction

\(\phi_s\) .......................................................... solution potential [V]

\(\nabla \phi_s\) .......................................................... gradient in solution potential [V/m]

\(\nabla^2 \phi_s\) .......................................................... Laplacian of the solution potential [V/m²]

\(\gamma\) .......................................................... constant in boundary condition equations

\(\kappa\) .......................................................... solution conductivity [Ω-m]⁻¹

\(\mu\) .......................................................... constant in boundary condition equations

\(\mu_f\) .......................................................... constant in boundary condition equations

\(\mu_e\) .......................................................... constant in boundary condition equations

\(\rho_{\text{Cu}}\) .......................................................... number of atoms per layer of a Cu lattice [atoms/m²]

\(\rho_{\text{el}}\) .......................................................... electric charge density in solution [C/m³]

\(\sigma\) .......................................................... constant in boundary condition equations
Chapter 1: Introduction

Corrosion occurs when metal in an aggressive environment is oxidized. Corrosion causes degradation of the metal substrate, altering the appearance and properties of its surface and possibly resulting in a loss of structural strength and soundness. Localized corrosion is a form of corrosion that occurs over only a small percentage of the total surface area of the metal. Localized corrosion is particularly insidious because although the average mass loss and average corrosion current density of the substrate is small, the regions where the corrosion occurs experience extremely high corrosion rates. These locally accelerated corrosion rates can cause unexpected, premature failures of structures (e.g., perforation of pipes or liquid storage containers).

Crevice corrosion distinguishes itself from other types of localized corrosion, such as pitting, in that it occurs specifically in an occluded region created by a crevice former. The crevice former may be any type of metal or nonmetal that is in close enough proximity to the surface of the metal substrate to create a geometry such that the environment inside the crevice is restricted from freely interacting and mixing with the bulk environment. A classic example of crevice corrosion occurs when a washer is pressed tightly against a metal substrate. A crevice is formed beneath the washer, and accelerated corrosion occurs in this region. This example illustrates another key reason that crevice corrosion is so dangerous; the corrosion occurs underneath the former, making it difficult to identify by visual inspection, which may cause it to be overlooked with potentially disastrous consequences.

Much experimental work has investigated various aspects of the initiation and propagation of crevice corrosion of many metals in a variety of environments. The
results of these experiments have been used in conjunction with fundamental principles of electrochemistry to formulate conceptual models for the mechanisms operating in a particular crevice corrosion system. The two most prominent models for crevice corrosion are the Critical Crevice Solution (CCS) model first formulated by Fontana and Greene[1] and later quantified for stainless steel in seawater by Oldfield and Sutton[2], and the Critical Potential Drop (IR*) model championed by Pickering[3]. In brief, the CCS model places primary importance on the role played by the occluded geometry of the crevice in restricting the solution in the crevice from mixing with the bulk. Eventually a more aggressive chemistry develops within the crevice, which initiates corrosion when it reaches a certain critical level of aggressiveness. The IR* model, on the other hand, maintains that the restricted geometry of the crevice causes the potential to drop inside the crevice from a value at which the metal is passive (on the boldly exposed surface) to a value at which the metal is active (inside the crevice), initiating crevice corrosion.

Variations on these models and others have been expressed using computer programs. The goal of a computer model is to reproduce results seen experimentally, and ultimately to provide a tool for the prediction of crevice corrosion that can be used to guide materials selection, design parameters, and the scheduling of service and replacement of parts. However, there are two primary difficulties that have prevented the construction of a comprehensive, accurate, reliable model for crevice corrosion.

The first challenge is that of experimentation on the relevant size scale. Most practical crevices have crevice gaps on the order of 0.1-10 \( \mu \)m, and lengths of 1-10 mm. It is difficult to reproducibly fabricate crevices on this size scale, and even more challenging to take spatially resolved potential or ion concentration measurements inside
the crevice without introducing a probe that alters the conditions inside the crevice. As a result, it is often necessary to scale up the geometry of the crevice to perform experiments. However, it is still debated how the mechanisms of crevice corrosion scale with geometry so the relevance of results from experiments on large-scale crevices to practical crevices is unclear.

The second primary difficulty encountered when attempting to model crevice corrosion phenomena is dimensional variation within crevices. Computer models, in the interest of reducing coding complexity and increasing computational speed, assume that crevices have ideal dimensions; that is, perfectly vertical side walls and uniform crevice gaps. Practical crevices and crevices fabricated for experiments by pressing two pieces of material together, however, do not have ideal dimensions. Machining marks, uneven distribution of applied force on the crevice former, and irregularities in the surfaces of the crevice walls cause some regions of the crevice to be in intimate contact while others are much farther apart. For example, a standard machining tolerance is 1 mil, or approximately 25 µm. A crevice fabricated from a machined specimen may have surface asperities that create a 25-µm differential in the crevice gap. Often a nominal, or average, gap is determined for experimental crevices using solution volume measurement techniques. This nominal gap is used for modeling purposes. However, the subcrevices created by a irregular crevice wall morphology have been shown to have a significant impact on the ion concentration distributions inside a crevice[^4]. Sridhar and Dunn[^5] have proposed that subcrevices dominated the crevice corrosion behavior of Type 304SS and Alloy 825. Scatter in experimental results caused by effects of surface asperities on the
mechanisms and controlling factors of crevice corrosion makes comparisons between models and experiments difficult.

The semiconductor device industry provides a possible solution to both of these difficulties. Semiconductor devices are examples of structures that are on the size scale relevant to crevice corrosion (µm) and that have rigorously defined geometries. In this work, the fabrication techniques used to make semiconductor devices were adapted to make crevices with ideal dimensions on the relevant size scale. Electrochemical experiments were performed on these crevices for two purposes: comparisons to modeling results and investigations of crevice corrosion scaling laws.

A two-dimensional spatiotemporal finite element model for occluded region corrosion called CREVICER has been developed at UVa. This model is described in detail in Chapter 2. The rigorously dimensioned microfabricated crevices were used to accurately represent the ideal dimensions assumed by CREVICER, and electrochemical experiments on the crevices were used to verify this model. These tests are described in the proof-of-principle sections of Chapters 4, 5, and 6.

Significant improvements and additions were also made to CREVICER. A new finite element solver routine was written that dramatically increased the computational speed of the model as well as reducing the memory allocation requirements of the model. A graphical user interface (GUI) was designed and developed for CREVICER. It provides the user with a point-and-click style interface for defining the parameters for a model. Additional improvements simplified the input process for the model and allowed it to run on multiple platforms, making it more user-friendly and robust.
The small size scale of the microfabricated crevices was utilized to investigate how the mechanisms of an IR*-controlled crevice corrosion system scale with crevice geometry on a dimensional range relevant to practical crevices. Corrosion experiments were performed on microfabricated crevices with varying crevice gaps and the morphologies of the regions of attack were analyzed. CREVICER was used to model these experiments and comparisons between model and experiment were made. CREVICER was also used to extend the scaling law investigations to look at the dependence of the scaling laws on the shape of the electrochemical boundary condition (the current-potential relationship) of the substrate material.
**Chapter 2: Background**

This chapter serves three major functions. First, it describes the tools used in this study. These include CREVICER, the computational model of occluded region corrosion developed at UVa, and the semiconductor device processing facilities used for microfabrication of crevices. Second, this chapter reviews the literature relevant to this work. This includes crevice corrosion models developed by other researchers, prior applications of microfabrication techniques to crevice corrosion studies, and previous investigations of the scaling laws governing the mechanisms of crevice corrosion. Third, this chapter identifies the motivating factors for this study. These factors include the limitations of CREVICER, which motivate improvements to it, and the difficulty in comparing experimental and modeling results due to discrepancies in crevice geometry, which motivate the use of microfabrication techniques for making crevice samples with rigorously-defined dimensions. The difficulty in relating results from experimental work to practical crevice corrosion situations because of the discrepancy in size scale and the lack of well-defined scaling laws motivates the scaling law investigations.

**2.1 Modeling**

This section outlines the motivation for the development of comprehensive models of crevice corrosion, reviews crevice corrosion modeling work in the literature, and describes in detail the scope, structure, prior testing, and limitations of CREVICER, the occluded region corrosion model utilized in this study.
2.1.1 Motivations for Modeling

From both engineering and scientific perspectives, there are many benefits to the development of an accurate, comprehensive model of crevice corrosion.

From the engineering point of view, a model can bridge gaps in experimental data. Because of limitations in measurement instrumentation, experimental data are discrete; measurements can only be made at a finite number of points in time and space. A model can fill in the gaps between points, helping to form a more complete picture of corrosion phenomena. For example, a microsensor could be used to measure the pH at various points inside a crevice. However, a finite amount of time is required to take each measurement, and the measurements can only be taken at discrete points inside the crevice, so the data provides only the framework of the pH distribution inside the crevice. If a mathematical model can be defined which is consistent with both the available experimental data and fundamental principles of electrochemistry, it can be used to develop a more complete pH distribution inside the crevice.

Another benefit an accurate model offers to crevice corrosion engineering is its predictive properties. If it has been proven experimentally that a model is general enough that it is accurate across a spectrum of conditions, that model can be used to predict the occurrence of crevice corrosion for any system within the boundaries of the verified spectrum. For example, experiments could be used to determine the incubation time for corrosion initiation for a 1-cm long 304 stainless steel rectangular slot in seawater. Similar experiments could determine incubation times for slots 2, 3, 4, and 5 cm in length under identical conditions. If the incubation time for a 3.5-cm slot were needed for an engineering application, the experimental data alone would not be able to predict
it. However, if a model was developed that correctly predicted the incubation times for all of the experimentally verified crevice lengths, that model could safely be used to predict the incubation time for a 3.5-cm slot. One must be careful, however, to recognize the limitations of the model; it may not necessarily predict the correct incubation time for a crevice only 1 mm long, a length which is outside the experimentally verified spectrum. This predictive feature of a model is an extremely useful for guiding materials selection, design parameters, and maintenance schedules.

An accurate model can also provide scientific insight into the mechanisms and controlling factors of crevice corrosion. Equations that are found to govern particular corrosion phenomena can provide a link between fundamental electrochemical principles and empirical data. They can pave the way to understanding crevice corrosion from a first-principles point of view.

An aspect of models that is also useful from a scientific perspective is the ability of models to separate experimentally inseparable parameters. This feature can be used perform “virtual experiments” to help identify precisely what influence particular system parameters have on the resulting corrosion phenomena. For example, experimentally it is not possible to change the electrochemical behavior of the substrate metal without changing some other system parameter (e.g., solution composition). However, changing that other parameter may have effects besides the desired one (e.g., it may also change the conductivity of the solution). In a model, however, all of the system parameters can be changed independently of one another, so the effects of each can be monitored separately. This useful aspect of models is utilized in this study to determine the
influence of the shape of the electrochemical boundary condition on the governing scaling law.

2.1.2 Principles of crevice corrosion modeling

Many models for crevice corrosion have been proposed in the literature. These have been categorized and reviewed in detail by Stewart\cite{6}, the developer of CREVICER Version 1, in his Ph.D. dissertation, as well as in several review articles\cite{7-12}. This section provides a brief description of the governing equations commonly used in crevice corrosion models, some of the assumptions often made to simplify the modeling problem, an overview of the options available for solving the equations, and summaries of a few representative examples of prominent crevice corrosion models from the literature.

2.1.2.1 Governing Equations

The corrosion rate of a material is determined by its electrochemical potential and chemical environment. The goal of crevice corrosion models is to characterize these through space and time for an occluded region. This objective is accomplished by determining at each step in time the concentration distributions of the chemical species and the potential distribution inside the crevice. There are three governing equations commonly used to solve for the potential and concentration distributions: one describing the chemical flux inside the crevice, one determining the potential field over the region, and one verifying that charge neutrality is maintained. These are derived and detailed in Stewart’s Ph.D. dissertation\cite{6}. The aim of this section is to provide the reader with a general overview.
The first and foremost governing equation is a mass transport equation that specifies the flux of chemical species in the crevice. This equation is often expressed as:

$$\tilde{J}_i = C_i \tilde{v} - D_i \nabla C_i - z_i F u_i C_i \tilde{\nabla} \phi_i$$  \[1\]

Where:
- $\tilde{J}_i$ is the flux vector of species $i$ [mol/m$^2$-s]
- $C_i$ is the concentration of species $i$ [mol/m$^3$]
- $\tilde{v}$ is the velocity vector of the solution [m/s]
- $D_i$ is the diffusivity of species $i$ [m$^2$/s]
- $\nabla C_i$ is the gradient of concentration of species $i$ [mol/m$^4$]
- $z_i$ is the charge number for species $i$ [eq/mol]
- $F$ is Faraday’s constant 96,487 [C/eq]
- $u_i$ is the mobility constant for species $i$ [m$^2$-mol/J-s]
- $\nabla \phi_i$ is the gradient in solution potential [V/m]

The first term on the right-hand side of this equation represents the movement of chemical species due to convective forces in the solution. Convective transport occurs when chemical species are carried along by a flowing electrolyte. Although this type of transport is easy to visualize, it is rarely included in crevice corrosion models because it is generally assumed that the solution in an occluded region is stagnant due to the restricted geometry. In other words, the contribution of convection is far outweighed by other types of transport.

The second term in the mass transport equation represents movement of chemical species due to diffusion. This type of transport occurs spontaneously when a
concentration gradient exists in the solution. The net flux of the molecules acts to minimize the gradient.

The third and final term in the mass transport equation governs movement of an ionic species due to a potential gradient in solution. This type of transport is called migration. Analogous to diffusion, the charged species in solution will move spontaneously to minimize the potential gradient.

The second governing equation often used in modeling crevice corrosion describes the accumulation of electrical charge in the crevice:

\[
h \frac{\partial \rho_e}{\partial t} = -\mathbf{k} \cdot \nabla \phi - i
\]  \hspace{1cm} [2]

Where:

- \( h \) is the height of the volume [m]
- \( \frac{\partial \rho_e}{\partial t} \) is the time rate of change of the density of electric charge in solution [C/m\(^3\)-sec]
- \( \mathbf{k} \) is the solution conductivity [(Ω-m)\(^{-1}\)]
- \( \nabla \phi \) is the LaPlacian of the solution potential [V/m\(^2\)]
- \( i \) is the current density across an interface [A/m\(^2\)]

The amount of electrical charge in a volume is determined by two quantities: the flux of charge out of the volume and the generation of charge inside the volume. The first term on the right-hand side of the equation describes the flux of electrical charge (current) out of a volume of solution. It is a restatement of Ohm’s law, where the conductivity (\( \mathbf{k} \)) is the reciprocal of the resistivity of the solution and the gradient in the solution potential (\( \nabla \phi \)) is the field. The second term on the right-hand side of the
equation expresses the generation of charge. Charge cannot be created in solution, so
generation is due only to current across an interface (i.e., wall of a crevice). When the
crevise is at steady state, the rate of change of electrical charge (the left-hand side of
Equation 2) is zero, and this equation can be readily used to solve for the potential
distribution in the crevice.

The third and final governing equation often used in crevice corrosion models is a
statement of charge neutrality in the crevice electrolyte:

\[ \sum_i z_i C_i = 0 \]  \[3\]

Where:

- \( z_i \) is the charge number for species \( i \) [eq/mol]
- \( C_i \) is the concentration of species \( i \) [mol/m\(^3\)]

Assumptions made in defining the other two governing equations make some
physically unrealizable situations mathematically feasible. For example, the effects of
the diffusion potential (the potential difference due to variations in diffusion rates among
ions) were not included in the governing equation for electrical flux. As a result,
macroscopic charge separations in solution are mathematically feasible (due to variations
in transport rates among ions), but physically impossible. To combat this type of artifact,
an assumption of charge neutrality in the crevice solution is made. The concentration of
one ionic species is not determined using the governing equation for chemical flux;
instead, it is fixed at a value such that any excess charge created by the other species will
be neutralized.
2.1.2.2 Common Simplifications

In crevice corrosion models, many assumptions are made in order to simplify the governing equations described above. The aim is to eliminate factors that have little influence on the outcome of model in order to make the formulation of the model less complex and to make solving the equations computationally feasible. The danger is oversimplifying to the point that the model no longer represents reality. The common simplifying assumptions are addressed much more thoroughly in Stewart’s Ph.D. dissertation\(^6\); only a few of interest to this work are described here.

The simplifying assumptions commonly made in crevice corrosion models fall into five different categories, as defined by Stewart\(^6\):

1. **Elimination of Thermodynamic Variables:** The effects of changes in temperature and pressure on the conditions in the crevice are often ignored; it is assumed that the crevice remains at a constant temperature and pressure throughout the duration of the run (usually STP). This is a legitimate assumption provided that the real system being modeled does not undergo fluctuations in temperature or pressure.

2. **Simplifying Chemistry Effects:** It is often assumed that the mobility and diffusivity of the chemical species are independent of concentration and that the solution inside the crevice is dilute. These assumptions were used in defining Equation 1. The dependence on chemistry of the generation of a chemical species (by flux through a boundary) is often ignored due to the complexity in developing an electrochemical boundary condition that is dependent on the concentration of species in solution. Homogenous
reactions other than hydrolysis reactions occurring inside the crevice are often ignored, as well as the precipitation of solid products.

3. **Simplifying Potential Effects:** A few models ignore the influence of the potential gradient in solution completely. Most models ignore the diffusion potential, as was done in defining Equation 2. Some use the charge neutrality assumption (Equation 3) in lieu of accounting for potential differences due to the charge separation that results from differences in the diffusivities of ionic species. Many models simplify the representation of the potential-current relationship of the crevice substrate (the electrochemical boundary condition). This simplification is addressed in the context of scaling laws in this work.

4. **Ignoring Temporal Effects:** Although the effects of changes in solution composition due to mass transport are often considered, the dependence of reaction rates on time (due to the dissolution of passive films, etc.) is rarely taken into account. Some models assume the chemical reactions are at equilibrium and solve for the steady-state corrosion condition; they provide no information about how long it takes to reach steady state.

5. **Simplifying Geometry:** These are the simplifications of greatest interest to this work. In the interest of increasing speed, most models only consider one or two dimensions, so a high degree of symmetry is assumed in relating these models to practical crevices. Additionally, as has been mentioned several times before, models assume that a crevice has ideal dimensions, which is
significantly different from most practical and experimental crevices, which contain many surface irregularities.

2.1.2.3 Methods for solving the governing equations

Once the equations governing the concentration and potential distributions in the crevice have been formulated and the appropriate simplifying assumptions have been made so that the equations can be solved reasonably quickly and easily, a method for solving the governing equations over the crevice geometry of interest must be chosen.

One option is to solve the equations analytically. Although this method is the most precise (it yields an exact solution for every point in the crevice), there are enough drawbacks that it is used infrequently. Many simplifications must be made to produce equations that have analytical solutions. In particular, the boundary conditions must be relatively simple, which often places too strict a limitation on the model so that it can no longer be correlated to the practical situation of interest. In addition, unlike numerical methods which, once developed, can be applied to any crevice geometry, analytical solutions require that the governing equations be reformulated for each geometry of interest.

Another option for solving the governing equations to determine the concentration and potential distributions in the crevice is to use a numerical method. Several of these have been applied to crevice corrosion modeling, including finite difference modeling, boundary element modeling, and finite element modeling.

Finite difference modeling involves dividing the region of interest into a grid of points, expressing the governing differential equations as difference equations at each
point, and solving the difference equations to determine an approximate solution of the
governing equations. Finite difference methods are simple to implement, but clumsy
when applied to complex geometries. They are most often used for the time-stepping
aspect of a model.

Boundary element models translate the differential equations across the crevice
volume into integral equations over the surface enclosing the volume and solve these
integral equations by dividing up the surface into elements. The key limitation of
boundary element models is that they are most useful only when the geometry of interest
has a low surface-to-volume ratio. Clearly most occluded regions do not meet this
requirement.

Finite element models divide the region of interest into simple shapes, build
equations for the value of the variable of interest (potential, pH, etc.) at each node on
each shape, and then solve the equations for all of the nodes simultaneously. Finite
element models have the advantage that they can represent complex geometries well.

2.1.2.4 Examples from the literature

Many crevice corrosion models have been developed which incorporate the types
of governing equations, simplifying assumptions, and solution techniques described
above. Rather than review them all comprehensively, which has been done by Stewart[6]
and others[7-12], a few representative examples are presented here which illustrate
variations in modeling techniques and illuminate points for comparison to CREVICER,
the crevice corrosion model used in this study.

Example 1: In a series of papers[13-15], Gartland and coworkers present a
comprehensive model for the crevice corrosion of stainless steel in seawater. A 1-D
finite difference solver is used, and diffusion and migration are the mass transport mechanisms considered. There are several notable characteristics of the model. Linear segment approximations of full polarization curves are used as the electrochemical boundary conditions. Effects of pH on the polarization behavior of the substrate are taken into account through interpolations among a series of polarization curves determined experimentally over a range of pH values. Temperature effects on corrosion rates and transport coefficients are considered, and a salt film is allowed to precipitate from a supersaturated solution, slowing the corrosion rate.

Example 2: In a series of papers\cite{16-18}, Alkire and coworkers present a model of the corrosion of a one-dimensional cylindrical crevice of 99.9% aluminum in 0.05 M NaCl. The model is solved using a finite difference technique. In all applications of the model the diffusive flux of species is considered, but in only one application are the effects of migration on the mass transport of ions considered. Convection is not considered. The electrochemical behavior of the aluminum substrate is given a Tafel representation in the model. The charge neutrality assumption is used, but precipitation of species and hydrolysis reactions are not considered.

Example 3: In a landmark paper\cite{2}, Oldfield and Sutton present the quantified critical crevice solution (CCS) model for crevice corrosion in the form of a predictive tool for the initiation of crevice corrosion of stainless steel in seawater. The model is a one-dimensional numerical model that considers mass transport by diffusion and migration (no convection). The stainless steel substrate is assumed to dissolve at a constant passive current density, meaning that the electrochemical boundary condition is
a constant. Charge neutrality in the crevice is assumed, and homogenous reactions, including an extensive array of hydrolysis reactions, are considered.

**Example 4:** Xu and Pickering[^3] present a model of the IR* mechanism for crevice corrosion initiation, the major competitor of the CCS model. Two environments were considered: iron in an ammoniacal solution and iron in acetate-containing solution. A two-dimensional finite element model is used which encompasses the boldly exposed surface on the exterior of the crevice in addition to the crevice interior. A complex polarization curve is used as the electrochemical boundary condition. Because the premise of the IR* model is that solution chemistry plays no role in crevice corrosion initiation (only potential drop inside the crevice does) no mass transport mechanisms are considered.

These examples from the literature highlight some of the major contributions to the field of crevice corrosion modeling and illustrate how different models incorporate the governing equations, simplifying assumptions, and methods of solution described in the previous sub-sections. However, it should be noted that each model is tailored to a very specific crevice corrosion situation; none can be easily applied to a variety of materials, environments and crevice geometries. For example, the model developed by Xu and Pickering[^3] is only applicable to situations in which the IR drop in the crevice is the controlling mechanism for crevice corrosion. This limitation slows the development of a comprehensive model for crevice corrosion because is necessary to develop a new model from scratch for each new system of interest. Addressing the need for a crevice corrosion model applicable to a wide range of conditions was one of the major motivating factors in the design and development of CREVICER.
2.1.3 CREVICER

CREVICER is the computational model of occluded region corrosion that is utilized in this study. Version 1 of CREVICER was developed and tested by Kevin Stewart at the University of Virginia. A detailed description of the formulation of the model as well as a hard copy of the computer code can be found in his Ph.D. dissertation[6]. This sub-section presents an overview of the structure and scope of the model in the context of the governing equations and common assumptions described in the previous sub-sections. A summary of the prior testing of CREVICER is given. The limitations of Version 1 of CREVICER are pointed out to provide motivation for the improvements and additions made to CREVICER and the additional testing of the model done in this study.

2.1.3.1 Scope

The primary mission of the development of CREVICER was to construct a general model of the aspects and processes common to all types of occluded region corrosion that could easily be specialized to model a particular system. This approach is fundamentally different from the models summarized in Section 2.1.2.4, which are particular to very specific environments (e.g., stainless steel in seawater). In all crevice corrosion systems, the local environment, electrochemical potential, temperature, and pressure determine the reaction rates at any point in the crevice. In order to accurately model crevice corrosion phenomena, the variations in these factors through time and space must be mapped. To develop these maps for a generic crevice system, CREVICER represents the governing equations for transport and generation of species in the crevice in a general format. The coefficients in the equations are set for each particular model run
depending on the environment of interest and the equations are solved. The parameters that are specified for a particular model run are the transport coefficients like the mobility and diffusivity of the species, the heterogeneous reaction rates as a function of chemistry and potential (the electrochemical boundary conditions), and any homogeneous reaction of interest (hydrolysis, etc.).

CREVICER considers two independent spatial dimensions, a temporal dimension, and one dependent spatial dimension, the latter of which is used to specify the crevice gap. It considers mass transport by diffusion and migration only (no convection) and incorporates some of the simplifying assumptions for chemical transport described in Section 2.1.2.2. For example, no diffusion potential is considered, and diffusion is based on the concentration gradient, rather than the activity gradient. CREVICER does not consider effects of pressure, and temperature is only used in calculating the diffusivity. Charge neutrality is enforced as a governing equation and only chromium hydrolysis reactions are considered; no precipitation or other homogeneous chemical reactions are considered. The electrochemical behavior of the substrate material can be represented in any format; constant flux, Tafel dependencies, or higher order polynomial approximations of polarization curves are commonly used.

In CREVICER, the governing equations for the chemical concentration and potential fields in the crevice are written as second-order partial differential equations so they can easily be solved using a finite element method. The equation for a concentration field is:

\[ h(x,y) \frac{\partial C_i}{\partial t} = h(x,y) D_i(x,y) \nabla^2 C_i + h(x,y) \zeta_i F u_i(x,y) \nabla \phi \nabla C_i + J_i(x,y) \]  

[4]
Where:

- $h(x,y)$ is height at point $(x,y)$ [m]
- $C_i$ is the concentration of species $i$ [mol/m$^3$]
- $D_i$ is the diffusivity of species $i$ [m$^2$/s]
- $\nabla C_i$ is the gradient of concentration of species $i$ [mol/m$^4$]
- $z_i$ is the charge number for species $i$ [eq/mol]
- $F$ is Faraday’s constant $96,487$ [C/eq]
- $u_i$ is the mobility constant for species $i$ [m$^2$-mol/J-s]
- $\nabla \phi_s$ is the gradient in solution potential [V/m]
- $\vec{J}_i$ is the flux vector of species $i$ [mol/m$^2$-s]

The equation for the potential field in the crevice is:

$$h(x,y) \frac{\partial Q}{\partial t} = -\kappa h(x,y) \nabla^2 \phi + \vec{J}_{el}(x,y) \tag{5}$$

Where:

- $h(x,y)$ is height at point $(x,y)$ [m]
- $Q$ is charge in Coulombs [C]
- $\kappa$ is the conductivity [(Ω-m)$^{-1}$]
- $\nabla^2 \phi$ is the Laplacian of the solution potential [V/m$^2$]
- $\vec{J}_{el}$ is the electrical flux [C/m$^2$-s]

The charge neutrality assumption is also used in CREVICER. At each timestep, the concentration fields for $n-1$ chemical species are determined using Equation 4 and then the concentration field for the $n^{th}$ species set such that at each point in the crevice charge neutrality is maintained.
2.1.3.2 Structure

The ability of CREVICER to consider the general occluded region corrosion situation is founded in the structure of the model. CREVICER has an object oriented design, which means that it utilizes encapsulation and inheritance, both of which are key to the generality of the program. Encapsulation enables information about the implementation of an aspect of the model to be hidden from the rest of the program. An example of the use of this feature is the representation of the polarization behavior of the metal. When another part of the program calls the procedure that returns the electrical flux, it does not know, and does not need to know, whether that flux is being calculated from a Tafel relationship or a polynomial approximation of a polarization curve. Therefore, the implementation of the electrochemical boundary condition can be tailored to the system of interest without affecting the rest of the program.

Inheritance is the feature of object oriented programming that enables functionality to be shared by objects of the same type. This allows CREVICER to perform the same operations (such as calculating diffusivity), on any type of chemical species in any system being modeled.

Encapsulation and inheritance are implemented in CREVICER through the use of C++ classes. Some of the major classes and their uses are:

TChemistry: Contains a list of chemical species, their concentrations, and booleans that record whether or not the concentrations are fixed. Species can be added to the list, their concentrations altered, or their fixed/not fixed status changed.
**TASpecies:** Contains pertinent information about each aqueous species including charge number, mobility, and chemical potential. Functionality includes calculations of diffusivities.

**TAllSpecies:** Contains all of the TASpecies that are in use. Can be used to calculate solution conductivity, ionic strength, and charge density of a particular solution composition.

**TReaction:** Contains information about electrochemical reactions occurring at an interface. Anodic and cathodic current densities can be calculated, as well as the reversible potential and the flux of a chemical species. The specifics of the implementation of the electrochemical behavior of the substrate (constant, Tafel, or polynomial) are hidden inside this class.

**TMaterial:** Contains the information about each substrate material. Queries the TReaction objects for each reaction occurring on the material to find the total chemical and electrical flux through the substrate.

The information contained in these classes is used to find the terms in Equations 4 and 5. The numerical method used to solve the equations is a finite element method. It solves the 2nd order partial differential equations in two dimensions by dividing the 2-D region into simple shapes (e.g., triangles), or elements, and approximating a value for the parameter of interest at each node, or point, on the shapes by solving the differential equation across each element.

The potential distribution is the first calculation made during each time step in the model. Then the concentration distributions for the species are found using Equation 4, the charge neutrality assumption, and by finding the homogeneous chemical equilibria.
2.1.3.3 Prior testing

A series of analytical tests were performed on CREVICER to verify that it could solve various formulations of the 2\textsuperscript{nd} order partial differential equation properly. In each of the tests a case was used that had an exact analytic solution and the accuracy of the numeric solution from CREVICER was determined relative to the analytic solution. It was verified that CREVICER could accurately determine steady-state potential distributions and handle steady state and time-transient chemical transport. The dimensionality of the model was exercised and a variety of boundary condition formats were used.

An example of one of the analytical tests is shown in Figure 1. It was taken directly from Stewart\textsuperscript{[6]}. In this case, a simple 1-D rectangular slot is used (Figure 1a). The mouth of the crevice is held potentiostatically and the metal substrate corrodes at a constant rate at every point along the length of the crevice. A flux of zero is the boundary condition at the crevice tip, meaning that there is no corrosion in this region. The steady-state potential distribution in the crevice is determined analytically and numerically and the results are compared (Figure 1b). The analytical solution for this case is given by:

$$\phi_s(x) = -\frac{J_{\text{walls}}}{2\kappa h} x^2 + \frac{J_{\text{walls}} X_0}{\kappa h} x + \phi_0$$  \hfill \text{[6]}$$

Where:

- $\phi_s$ is the potential [V]
- $J_{\text{walls}}$ is the current perpendicular on crevice walls [A/m\textsuperscript{2}]
- $\kappa$ is the solution conductivity [Ω-m\textsuperscript{-1}]
\[ h \] is the crevice height [m]
\[ x \] is the distance into the crevice [m]
\[ x_0 \] is the length of the crevice [m]

a)

b)

![Diagram of crevice geometry and environmental conditions](image)

**Figure 1:** Example of one of the analytical tests of CREVICER performed by Stewart\(^6\). a) Schematic of the crevice geometry and environmental conditions. b) Comparison between analytic and numeric solutions for the potential distribution inside the crevice.

The second set of tests performed on CREVICER utilized the unique “virtual experiment” feature of models that was described in Section 2.1.1 to assist in presenting a plausible explanation for the phenomena of intermediate attack that is commonly seen in crevice corrosion. In many crevice corrosion cases, very little or no attack is seen either at the mouth of the crevice or deep inside the crevice. The region of severe attack is
localized to an intermediate region. Although other widely accepted models\textsuperscript{[2,3]} can explain the lack of attack at the mouth of the crevice, very little has been said about the lack of attack deep inside the crevice. In this set of tests, hypothetical experiments were performed using CREVICER that investigated the effects of turning off and on cathodic reactions inside the crevice. Experimentally, these manipulations would not be possible. The tests showed that the occurrence of cathodic reactions deep inside the crevice could raise the pH of the crevice solution, effectively shutting off corrosion in that region.

2.1.3.4 Limitations

Although Version 1 of CREVICER is a very comprehensive, robust model for occluded region corrosion, there are several aspects of it where improvements were needed. These possible areas of improvement were the motivation for the development of CREVICER Version 2 and CREVICER Version 2-GUI and for the modeling work done in this study. For completeness, this sub-section covers most of the major limitations of CREVICER; not all of these were addressed in this study.

The scope of CREVICER Version 1 is limited to two spatial dimensions, whereas practical crevices occur in 3-D. It does not correct for changes in the morphology of the crevice through time. The only homogeneous reactions considered are chromium hydrolysis, and no consideration is made for the accumulation of precipitates inside the crevice.

Although the structure of the model is object-oriented in design, significant difficulties exist in specifying the parameters for a particular model. Changes must be made deep inside the body of the code, requiring intimate knowledge of the structure of the code and C++ syntax. There is no way to visualize the geometry of the crevice when
defining boundary and initial conditions. After the parameters have been set defining a new model, the code must be recompiled and then run. The finite element solver routine is accurate but slow, making simulations of lengthy experiments or complex geometries computationally infeasible.

The testing of CREVICER has been limited to verification of the accuracy of the numerical solver relative to analytical solutions. No experimental verification has been performed which would investigate the accuracy of the model in representing practical crevice corrosion situations.

2.2 Microfabrication

This section provides an overview of the types of processing techniques that are used in semiconductor device manufacturing and the capabilities of the facilities used in this study. It identifies the reasons microfabrication techniques would be useful in crevice corrosion studies and reviews the literature on the application of microfabrication techniques to corrosion experiments.

2.2.1 Types of techniques used

There are hundreds of different processing techniques utilized in modern semiconductor device manufacturing. The exact order and duration of steps, compositions of chemical baths, and other details of the processes are often proprietary. However, there are basic techniques and principles common to all processes. These are described in this section. The details of the adaptation of these techniques for use in
crevice corrosion experiments are reserved for Chapter 4 and Appendix B. The reference for this background information is a book by Wolf and Tauber\textsuperscript{[19]}.

Although other semiconductors (\textit{e.g.}, gallium arsenide) have found niches in the industry, single-crystal silicon remains the semiconductor of choice for electronic devices. There are six basic techniques utilized in silicon processing that are relevant to this study: wafer cleaning, film growth or deposition, lithography, etching, metal lift-off, and surface characterization. These (with the addition of other techniques such as ion implantation) may be repeated tens to hundreds of times on a single wafer to build a complete device.

1. **Wafer Cleaning:** The first processing step in which organics and other contaminants are removed from the as-received silicon wafers and the surfaces of the wafers are beveled. The cleaning is generally done using a series of chemical baths and rinse steps.

2. **Film growth or deposition:** Thin films layered on the silicon substrate form the structure of silicon devices. These films may be grown or deposited using a variety of methods. Silicon dioxide, an insulating material, is often grown on a silicon substrate using a thermal oxidation process. Silicon dioxide may also be deposited using chemical vapor deposition, the technique commonly used to deposit polysilicon and silicon nitride. Another growth process is epitaxial growth, in which a thin layer of single crystal material is grown on top of a bulk single crystal substrate. This process is most often used to grow thin layers of lightly doped silicon on top of heavily doped silicon regions.
Metals, which are most often used to form the interconnect lines between devices, can be either evaporated or sputtered onto the substrate.

3. Lithography: Perhaps the most pervasive feature of silicon processing, lithography is the method by which the features of the devices are defined. After a thin film is grown or deposited on the substrate, a layer of photoresist is spin-coated onto the wafer. Photoresist is an organic material whose solubility in a developer changes significantly with exposure to ultraviolet radiation. After the photoresist is applied, a mask containing a pattern that defines the features of the device is placed over the wafer and the wafer is exposed to UV radiation. The wafer is rinsed in the developer and the photoresist washes away only in the regions that were exposed to the radiation (because the solubility was increased through exposure). The result is that the pattern is transferred to the photoresist remaining on the substrate. The benefit of this technique is that the entire wafer can be patterned at once, so multiple devices can be fabricated simultaneously.

4. Etching: The next step after a pattern is transferred from the mask to the photoresist is etching of the thin film. There are two types of etching processes, wet etching and dry etching. The goal of both is the same: to place the wafer in an environment where the thin film material is removed at a much faster rate than the masking material (in this example, photoresist). In wet etching, the environment is a chemical bath; in dry etching the environment is a plasma. If the thin film is silicon dioxide, for example, and
the masking layer is photoresist, then the wafer might be placed in a fluoride-containing bath. In that environment, the exposed silicon dioxide is etched away, but the silicon dioxide underneath the photoresist is untouched. Then the photoresist is removed, and the device pattern has been transferred to the silicon dioxide, forming the structure of the devices.

5. **Metal liftoff**: Metal liftoff is a technique used as an alternative to etching. In the etching process, a metal layer is deposited, photoresist is patterned on top of the metal, the unwanted metal is etched in the exposed areas, and the photoresist is removed. In the metal liftoff process, on the other hand, the photoresist is deposited and patterned first, and then the metal is deposited on top. Metal deposition is a blanket process, so the metal covers the photoresist and the exposed substrate. Then the photoresist is removed, lifting off the metal that is on top of it, and leaving the metal pattern on the wafer.

6. **Surface Characterization**: At various stages of processing, measurements are taken to verify the accuracy and reproducibility of techniques. Ellipsometry may be used to measure film thickness, x-ray photoelectron spectroscopy determines surface composition, profilometry can be used to evaluate surface morphology, and SEM or optical microscopy are useful for visual analysis.

The facility used to microfabricate samples for this study was the Semiconductor Device Laboratory (SDL), a class 10000 clean room facility located in the Electrical Engineering Department at the University of Virginia. The SDL is operated on a shared-resources basis; for a flat monthly fee, a user has access to all equipment and
consumables in the clean room. The SDL has the equipment needed to perform many of the processes described above. Wet processing areas are available for wafer cleaning and wet etching, furnaces can be used for wet oxidation, and a photolithography room offers deep and shallow UV exposure capabilities. Metals can be sputtered or evaporated onto the substrate, and some electroplating facilities are available. The SDL also has silicon dioxide deposition, epitaxial growth, and dry etching facilities. A contact profilometer is available for height measurements, several optical microscopes are available inside the clean room, and an SEM is located just outside. There are also two dicing saws adjacent to the clean room for use in separating completed devices that were fabricated together on one wafer. The major capabilities the SDL does not have are ion implantation and polysilicon deposition. Photolithography masks cannot be made on premises, but design software is available in general-use computer labs.

2.2.2 Benefits of application to crevice corrosion studies

There are several characteristics of the silicon processing techniques described in the previous section that make them conducive to use in crevice corrosion studies. The size scale of the semiconductor devices and the stringency of their dimensions offer possible solutions to two major problems experienced by researchers investigating the mechanisms and controlling factors of crevice corrosion.

One of the difficulties that have arisen in attempts to develop an accurate, comprehensive model of crevice corrosion involves the dimensions of the occluded region. As was described in Section 2.1.2.2, in the interest of reducing coding complexity and increasing speed, models assume that crevices have perfectly vertical side walls and a consistent crevice gap. Experimental crevices that are made by pressing two
pieces of material together (e.g., a PTFE washer onto a stainless steel substrate), however, have dimensions that are far from ideal due to the existence of machining marks (1 mil tolerance corresponds to 25 µm surface asperities) and other surface irregularities. In some places the crevice former may be in intimate contact with the substrate, whereas in other places they are quite far apart. In some experiments, a nominal, or average, gap is determined by solution volume measurement techniques and this value is used in modeling the system. However, if it is the tightest region of the crevice that controls the initiation of crevice corrosion, the model will not accurately simulate the experiments. Watson and Postlethwaite showed that variations in the crevice profile can dramatically alter the concentration profiles of ions inside the crevice, even if the average crevice gap is held constant\textsuperscript{[4]}. The nature of the fabrication techniques enables semiconductor devices to have reproducible, rigorously defined dimensions. The resolution of features in the two dimensions in the plane of the silicon wafer is defined by the resolution of the mask used in photolithography, and mask-making techniques are available that can define features accurate to within a few microns. Vertical dimensions are controlled by the selectivity of the etchants. The selectivity varies with etchant, but in general longer etch times yield increases in surface roughness. Etching bulk silicon to a depth of 100 µm results in a surface roughness of approximately 2 µm, whereas etching to a depth of only 10 µm results in surface roughness of about 0.2 µm. If semiconductor device fabrication techniques can be adapted to make crevices with well-defined dimensions, results of experiments performed on those crevices can be more easily correlated to modeling results.
The second major difficulty that has arisen in crevice corrosion investigations is related to the size scale of practical crevice corrosion situations. Most practical crevices have gaps of 0.1-10 µm and lengths of 1-10 mm. It is difficult to reproducibly fabricate experimental crevices on this size scale, however. Additionally, experimental crevices are often scaled up in size in order to allow measurement instrumentation to fit within the crevice gap without disturbing the system. The laws governing the scaling of crevice corrosion mechanisms are still debated, however, as will be discussed in Section 2.3, so the method for relating results from experiments performed on large-scale crevices to practical situations is unclear.

Semiconductor devices are on the size scale relevant to practical crevices. If the techniques used to make these devices are applied to the fabrication of crevices, experiments could be performed on a relevant size scale. It might even be possible to instrument the crevices with pH, chloride, or other types of sensors to attain spatially resolved information about the conditions inside the crevice. Even before this is achieved, however, simple experiments could be performed on the small-scale crevices to help determine the appropriate scaling laws for crevices. These studies would assist in determining the proper technique for relating experimental results from large-scale crevices to practical situations.

In addition to the two major benefits of size scale and rigorousness of dimensions, there are several other characteristics of silicon processing techniques that make them an attractive option for corrosion studies. The nature of the depositing-patterning-etching process enables the simultaneous fabrication of multiple samples on one wafer, speeding the fabrication of multiple samples. There is a high degree of reproducibility among
samples, which is desirable for studies in which the same geometry is used under varying environmental conditions. A variety of substrate metals can be deposited using the same evaporation or sputtering techniques, so no major processing alterations are necessary if the material of interest changes. Finally, the same general processing technique can be applied to a wide variety of applications. For example, subcrevices could be built into a crevice former using the same basic patterning and etching techniques that would be used to make an array of electrodes on the crevice substrates. Only the deposited materials and the etchants would change.

2.2.3 Literature review

A few other researchers have taken advantage of the benefits of semiconductor device manufacturing techniques in their corrosion studies. Alkire and coworkers have used photolithographic techniques in two related studies\cite{20,21}. They first used lithography to create single pits on a stainless steel substrate. The work was motivated by the difficulty of directly observing the behavior of a single pit on a large specimen undergoing corrosion at many pit sites. The difficulty arises owing to the small size of the pits and the unpredictability in the time and location of their nucleation. Observation of a single pit is necessary for increased understanding of pitting corrosion phenomena, however, because many measurements taken on the entire specimen (e.g., current measurements) are not representative of the local behavior inside a pit. In this study\cite{20}, photolithography was used to specify the exact location of a pit on a stainless steel substrate so that it could be monitored. 2.2-cm diameter disks of 304 austenitic stainless steel were cut from rod stock and mechanically polished to 0.05 \( \mu \)m. These disks were spin-coated with photoresist and a chrome-plated glass photomask was used to expose a
single circular region (100-µm diameter) approximately in the center of each disk. The photoresist was developed, revealing the underlying steel in the exposed region. When the specimens were exposed to 0.1 N NaCl, corrosion occurred only at a single pit in the exposed region of the substrate, making localized measurements possible.

In a related study\textsuperscript{[21]}, Alkire and coworkers applied photolithographic techniques to the investigation of corrosion pits initiated at MnS inclusions in 304 stainless steel. 1.48-cm diameter disks were cut from rod stock, polished to 0.05 µm, and spin-coated with photoresist. To expose a group MnS inclusions, a chrome-plate glass mask was used to make a grid of 121 square regions 100 µm on a side on the specimen. By using the grid for reference, inclusions could be identified before and after exposure to a corrosive environment. A single inclusion could be studied by utilizing a second mask containing only a single square opening (50 x 50 µm). By overlaying the two masks, a region containing a single inclusion could be exposed and studied.

In a recent study of the influence of copper defects on pitting initiation of aluminum\textsuperscript{[22]}, Wall and coworkers at Sandia National Laboratories utilized semiconductor device manufacturing techniques in their specimen preparation. Aluminum thin films, 150-200 nm thick, were deposited using electron-beam evaporation onto silicon substrates. The films were exposed to an O\textsubscript{2} plasma to form a 3-nm thick protective alumina film. A metal liftoff process was used to create copper islands on the aluminum substrate. The specimens were spin-coated with photoresist and arrays of hexagonal shaped openings of variable size and spacing were defined using photolithography. The alumina was etched in the exposed regions and copper was evaporated onto the freshly exposed aluminum as well as the surrounding photoresist.
The photoresist was removed, lifting off the metal on top of it, and leaving behind a well-defined grid of copper islands on an aluminum substrate. The grid was used to investigate the impact of noble particle defects on the initiation of metastable pitting of aluminum.

Although these studies have demonstrated the utility of lithographic and metal lift-off techniques for corrosion research, none have used microfabrication techniques to form three-dimensional structures on a micron size scale. 3-D crevice structures with rigorously defined dimensions are needed to investigate crevice corrosion on a size scale relevant to practical crevices and to perform experimental verification of a crevice corrosion model. An area of research in which semiconductor device fabrication techniques have been applied to the formation of 3-D structures is microelectromechanical systems (MEMS)\textsuperscript{[23-28]}. MEMS are systems in which electrical and mechanical capabilities are combined on a micron size scale. Examples of MEMS are pressure sensors and accelerometers. Valves, pumps, motors, and many other devices with moving parts have been fabricated on a micron size scale utilizing MEMS techniques. A standard MEMS device is fabricated by depositing, patterning, and etching several layers of structural and sacrificial material utilizing the processes described in Section 2.2.1. In addition, several techniques have been developed specifically for MEMS applications. These include LIGA\textsuperscript{[27,28]} and silicon macropore formation\textsuperscript{[26]}, two techniques aimed at producing well-defined structures with aspect ratios on the order of 25:1, much larger than the aspect ratio of a standard semiconductor device.

The prior applications of microfabrication techniques to corrosion studies and to the formation of well-defined, high-aspect ratio 3-D structures suggests that these
techniques offer a viable method for fabricating crevices with rigorously defined dimensions on a size scale relevant to practical crevices. The ideal dimensions of these crevices would make them useful for performing experimental verification of crevice corrosion models. The size scale of the crevices would make them useful for investigating the scaling laws governing crevice corrosion.

2.3 Crevice Corrosion Scaling Laws

As has been mentioned previously, the dimensions of crevices in naturally occurring crevice corrosion instances are on the order of millimeters in length and microns in gap. Reproducibly fabricating crevices on this size scale and fitting measurement instrumentation inside the crevices to attain spatially resolved experimental data is a challenge to researchers. As a result, it is often desirable to scale up the dimensions of experimental crevices. However, it is still debated how the mechanisms of crevice corrosion scale with geometry. This makes it unclear how to relate results attained from large-scale crevices to practical situations. Use of the incorrect scaling law could lead to unreliable design guidelines, which could result in a premature failure due to unexpected occurrences of crevice corrosion.

Semiconductor device fabrication techniques suggest a possible method for fabricating crevice samples on the size scale relevant to crevice corrosion. These small-scale crevices could be used to investigate the scaling laws applicable to crevice corrosion. Modeling work using CREVICER could also be used to augment and extend the experimental results. Knowledge of these scaling laws would enable the application of experimental results attained on instrumented, large-scale crevices to practical crevice
corrosion situations. The utility of that knowledge motivated the investigations of crevice corrosion scaling laws in this study.

This section explains the premise of a scaling factor and how it relates to a scaling law, reviews the discussion of scaling factors in the literature, and explains the reasoning behind the choice of the crevice corrosion system for the scaling law investigations in this study.

2.3.1 Premise of a scaling factor

The local environment, electrochemical potential, temperature, and pressure determine corrosion rates. In most crevice corrosion cases the latter two are constant, so it is primarily the spatial and temporal distributions of chemistry and potential that determine the corrosion attack morphology. If the potential and concentration distributions remain constant, the corrosion rates will also remain constant.

A scaling law is a statement of how the geometry of a crevice must be scaled in order that the potential and concentration distributions (and therefore the corrosion attack) remain constant on a relative length scale. For example, suppose the region of severest attack in a 1-cm crevice is 0.3 cm from the crevice mouth. If the correct scaling law is used to make a 10-cm crevice, the region of severest attack on the large-scale crevice will be 3 cm from the crevice mouth.

A scaling factor is a geometrical relationship that must remain constant in order that the concentration and potential distributions in a crevice remain constant on a normalized length scale. The two most common scaling factors discussed in relation to crevice corrosion are $L/G$, and $L^2/G$, where $L =$ either the length of the crevice or the distance from the mouth of the crevice to the region of severest attack, and $G =$ the
crevice gap. The crevice corrosion conditions under which these factors have appeared in
the literature are described in the following sections.

2.3.2 \( L^2/G \) in literature

The earliest mention of the \( L^2/G \) scaling factor for crevice corrosion is in a paper
by Turnbull\[29\] in which a model of crack electrochemistry for steel in the active state is
presented. Mass transport by diffusion and migration are considered in the model. The
basis for the scaling factor is the non-dimensional representation of the transport
equations. Turnbull states that “when the mass transport equations are expressed in non-
dimensional form the length and width always appear as the combined parameter \( L^2/w \)
except in the boundary conditions at the crack tip…” (p.1417). Modeling results are
presented which show that for the system of interest to the study the contributions of the
flux at the crack tip to the concentration and potential profiles in the crevice are
negligible. This lack of contribution is primarily because the entire side of the crevice is
assumed to be actively corroding and the surface area of the side is much larger than the
surface area of the tip. Once the flux at the tip is assumed negligible, it is set to zero, and
the scaling factor is applicable. Turnbull is careful to note that the scaling factor is
relevant only to a rectangular crevice geometry; if a wedge-shaped crack geometry was
used the scaling factor would no longer be valid.

Walton\[30\] presents the dimensionless analysis of the mass transport equations that
give rise to the \( L^2/G \) scaling factor. In his analysis all parameters are expressed in non-
dimensional form and the transport equations are reformulated. An example of a non-
dimensional parameter is \( X' \), the dimensionless length, which is equal to \( x/l \) where \( x \) is
some distance into the crevice and \( l \) is the total length of the crevice. Walton includes in
his analysis a dimensionless representation of the rates of chemical reaction in solution. The influence of geometry on these rates is $l^2$ rather than $l^2/h$. This means that a further assumption is necessary for the $l^2/h$ scaling law to be applicable; namely, that the time scale of the reactions in solution is fast relative to transport time (i.e., the reactions are at equilibrium). Unlike Turnbull, who assumes that the sides of the crevice are actively corroding at a constant rate, Walton utilizes linear segment approximations of polarization curves to simulate the electrochemical behavior of the crevice substrate. However, like Turnbull, he notes that the flux at the crack tip must be negligible (small relative to the flux through the sides) for the scaling factor to apply.

Psaila-Dombrowski uses a model of crack and crevice chemistry in light water reactor environments to verify the $L^2/G$ scaling law. The system modeled is a 1-D rectangular slot with 304 stainless steel as the active substrate material. The environment is that of normal boiling water reactor (BWR) water chemistry. The time evolution of the crevice chemistry is modeled for two crevices of different sizes, but with equal $L^2/G$ factors, in identical environments. The results show that the concentration profiles for the two cases are identical, provided they are plotted on a normalized length scale.

The $L^2/G$ scaling factor also appears in modeling work by Alkire. In addition to theoretical work, results from experimental investigations of the critical geometry for crevice corrosion initiation of aluminum in 0.05 M NaCl are presented. Although no direct experimental verification of the scaling factor is given, some correlation can be derived from the experimental data. Incubation times for corrosion initiation in crevices with varying dimensions are given. If the $L^2/G$ scaling factor is correct, the incubation times should be the same for crevices with similar values for $L^2/G$. Table 1 shows the
crevice lengths, crevice gaps, $L^2/G$ factors, and corrosion incubation times for some of the experiments (reproduced from the literature[16]). Although the overall trends are consistent (crevices with smaller scaling factors generally had longer incubation times), the direct correlation is not very good. Two crevices had scaling factors almost exactly equal to 403, but their incubation times varied by several hours. These results may mean that the $L^2/G$ scaling factor is not applicable to this system, but there is not enough data to draw any definite conclusions.

Table 1: Scaling factors and crevice corrosion incubation times from experiments performed by Alkire[16].

<table>
<thead>
<tr>
<th>Crevice length (mm)</th>
<th>Crevice gap (mm)</th>
<th>Scaling factor $L^2/G$</th>
<th>Incubation time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.35</td>
<td>0.10</td>
<td>403.225</td>
<td>2-3</td>
</tr>
<tr>
<td>6.35</td>
<td>0.16</td>
<td>252.0156</td>
<td>4</td>
</tr>
<tr>
<td>6.35</td>
<td>0.17</td>
<td>237.1912</td>
<td>5</td>
</tr>
<tr>
<td>6.35</td>
<td>0.19</td>
<td>212.2237</td>
<td>6</td>
</tr>
<tr>
<td>6.35</td>
<td>0.20</td>
<td>201.6125</td>
<td>8</td>
</tr>
<tr>
<td>6.35</td>
<td>0.22</td>
<td>183.2841</td>
<td>Never occurred</td>
</tr>
<tr>
<td>6.35</td>
<td>0.30</td>
<td>134.4083</td>
<td>Never occurred</td>
</tr>
<tr>
<td>9.52</td>
<td>0.22</td>
<td>411.9564</td>
<td>4-5</td>
</tr>
<tr>
<td>9.52</td>
<td>0.30</td>
<td>302.1013</td>
<td>5-6</td>
</tr>
<tr>
<td>9.52</td>
<td>0.40</td>
<td>226.576</td>
<td>Never occurred</td>
</tr>
<tr>
<td>9.52</td>
<td>0.50</td>
<td>181.2608</td>
<td>Never occurred</td>
</tr>
<tr>
<td>11.11</td>
<td>0.10</td>
<td>1234.321</td>
<td>3-4</td>
</tr>
<tr>
<td>11.11</td>
<td>0.30</td>
<td>411.4403</td>
<td>4-5</td>
</tr>
<tr>
<td>11.11</td>
<td>0.50</td>
<td>246.8642</td>
<td>Never occurred</td>
</tr>
<tr>
<td>12.70</td>
<td>0.40</td>
<td>403.225</td>
<td>6-7</td>
</tr>
<tr>
<td>12.70</td>
<td>0.60</td>
<td>268.8167</td>
<td>Never occurred</td>
</tr>
</tbody>
</table>

Gartland[32] introduced a slightly different scaling factor in his modeling work. The initiation and propagation of crevice corrosion in a 1-D stainless steel rectangular slot in seawater were modeled. A CCS criterion was used to determine the initiation time. The polarization behavior of the substrate material was approximated using a square wave, so the flux was zero everywhere except in the active region. Corrosion initiated at a particular distance into the crevice, $L_p$. The scaling factor that appears in the
model was \( L_p^2/G \) where \( L_p \) is the length of the passive region at the mouth of the crevice rather than the entire length of the crevice. \( G \) is the crevice gap.

The \( L_p^2/G \) scaling factor also appeared in modeling work by Pickering\(^3\). The most significant feature of this model is that it utilizes the IR* condition for the initiation of crevice corrosion rather than the CCS condition. The potential drop inside the crevice is the only mechanism considered in this model. The geometry of the crevice is a 1-D rectangular slot. The polarization behavior of the metal has an active-passive transition. Pickering derives a theoretical expression for the distance into the crevice at which corrosion initiates \( (L_p \text{ or } x_{\text{pass}}, \text{ as he defines it}) \) as a result of a drop in potential that places the metal in its active regime. The \( L_p^2/G \) scaling factor appears in this expression. However, Pickering uses several assumptions to simplify the expression. A different scaling factor, \( L_p/G \) appears in the simplified version. This scaling factor is described in more detail in the next section.

2.3.3 \( L/G \) in literature

As was described in the previous section, theoretical work by Pickering\(^3\) initially suggested the correct scaling factor for IR* controlled crevice corrosion is \( L_p^2/G \), where \( L_p \) is the distance into the crevice where corrosion initiates and \( G \) is the crevice gap. However, further simplifications of the expression lead to a scaling factor of \( L_p/G \). The primary assumption used to reach the simplified expression is that the passive current density of the metal is negligible. Experimental data for iron in an ammoniacal and an acetic acid solution (IR* controlled systems) are compared to modeling results. Both indicate linear relationships between \( L_p \) and applied potential for constant crevice gap. These linear relationships suggest that \( L_p/G \) is the correct scaling factor. However,
the crevice gaps considered in these experiments are 100 and 500 µm, at least an order of magnitude larger than practical crevice gaps.

Pickering\cite{33} addressed the \( L_p/G \) scaling factor in other experimental work. Another IR* controlled system, nickel in 0.5 M sulfuric acid, was the environment of interest. The simplified expression for \( L_p \) was used to calculate the expected value for \( L_p \) given values for crevice gap and applied potential. The crevice gap was fixed at 300 µm and the applied potential was varied. The calculated values were compared to experimental values for \( L_p \). A rough correlation was made, but not enough data were available to conclude that \( L_p/G \) is definitely the appropriate scaling factor.

The crevice corrosion system used by Pickering in the aforementioned experimental work (nickel in 0.5-M sulfuric acid) was chosen for the scaling law investigations in this study. Several factors motivated the choice of that system. First, there is a clear debate between two possible scaling laws: \( L_p^2/G \) and \( L_p/G \). Are the assumptions that were made in deriving the \( L_p/G \) scaling factor valid? Second, experimental data are available in the literature for comparison. The crevice gaps used in the literature are larger than practical crevice gaps, but are close enough to be useful in determining the governing scaling laws. Finally, the IR* mechanism provides an easily measurable parameter that can be used to determine the scaling law: the clearly delineated line of attack at a distance \( L_p \) into the crevice.
Chapter 3: Objectives

The objectives of this work fall into three categories: improvements to CREVICER, proof-of-principle of the use of semiconductor fabrication techniques to make crevices with ideal dimensions for model verification, and the utilization of corrosion experiments on microfabricated crevices combined with modeling for the investigation of crevice corrosion scaling laws. The motivations for the improvements to CREVICER were the limitations of the model as described in Section 2.1.3.4. The motivation for the proof-of-principle work for applying semiconductor fabrication techniques to crevice corrosion studies was the difficulty experienced by researchers\cite{5} in comparing experimental and modeling results because the dimensions of the experimental crevices are not rigorously defined. The motivation for the investigation of crevice corrosion scaling laws was the difficulty in relating results of experiments performed on scaled-up crevices (which are scaled-up so that measurement instrumentation can fit within the crevice gap) to practical crevice corrosion situations, which occur on a much smaller size scale.

3.1 Improvements and Additions to CREVICER

The focus of the work on CREVICER was to make it less of a project under development, understood and usable only by those intimately familiar with the code, and more of a tool employable by anyone familiar with corrosion principles and comfortable with computers. The following improvements and additions to CREVICER were steps toward achieving this goal:

1. Increase the speed of CREVICER. This improvement will make runs through more real-time time steps feasible, enabling the simulation of longer experiments.
Increasing the computational speed will also enable the use of many more finite elements, making possible models of more complex crevice geometries.

2. **Implement a graphical user interface (GUI).** Currently the user must make changes to the source code of CREVICER and recompile it before running a model. A GUI will provide the user with a visual representation of the crevice and finite element mesh and will enable the user to input all system parameters utilizing point-and-click methods. No recompilation of the code will be necessary to run a model.

3. **Make CREVICER usable on a Windows platform.** CREVICER Version 1 runs only on a UNIX platform. Enabling it to run in Windows\textsuperscript{TM} will significantly widen the pool of potential users.

4. **Add aluminum hydrolysis to CREVICER’s capabilities.** The current version of CREVICER can account for chromium hydrolysis reactions in the solution inside the crevice, but no other homogenous reactions. Adding aluminum hydrolysis capabilities would widen CREVICER’s applicability to include systems involving aluminum alloys.

5. **Investigate the variability in the results and the convergence limits of CREVICER.** Knowledge of how sensitive the results of the model are to mesh density and initial conditions and knowledge of the relationship between mesh density, time step length, and convergence of CREVICER would provide users with guidelines as to what types of mesh parameters and initial conditions they should use to best model their system.
3.2 Proof-of-Principle of Microfabrication Applied to Crevice Corrosion

The focus of this work was to identify whether or not semiconductor device manufacturing techniques can be utilized to make crevices that have rigorously-defined dimensions so that results from experiments performed on them can be compared to results from models, which assume ideal crevice dimensions. If successful, this work will assist in surmounting one of the major hurdles to modeling the mechanisms of crevice corrosion: lack of agreement between experimental and modeling results due to the discrepancy between the ideal geometries of modeled crevices and the irregular geometries of most experimental crevices. The steps necessary to achieve these goals were:

1. **Fabricate crevices utilizing semiconductor device fabrication techniques.** The first step was to adapt the necessary microfabrication processes to crevice applications.

2. **Measure the variability and reproducibility of the crevice dimensions.** This task identified how well defined the dimensions of the crevices are and how close they come to matching the ideal dimensions assumed by CREVICER.

3. **Perform electrochemical experiments on the crevices using a well-known system.**

   This task aimed to verify the applicability of the microfabricated crevices to crevice corrosion experiments and provide straightforward, predictable experimental results for model comparisons.
4. **Model the experiments using CREVICER.** This task provided results of simulations of the electrochemical experiments for comparison to the experimental results. The simulations assume that the dimensions of the crevices are ideal.

5. **Compare the experimental and modeling results.** This task provided experimental verification of CREVICER and identified the degree of agreement that can be expected between results of the model and results of experiments on the microfabricated crevices.

### 3.3 Scaling Law Investigations through Modeling and Experiments

The goals of this section were to utilize the size scale of the microfabricated crevices to investigate how the mechanisms of crevice corrosion scale with geometry and to utilize CREVICER to corroborate the experimental results and identify the influence of particular environmental parameters on the relevant scaling law. This work will assist in overcoming the second major hurdle to the development of an accurate, comprehensive model of crevice corrosion phenomena: the fact that most crevices used in experiments must be much larger than practical crevices in order to fit measurement instrumentation inside the crevice combined with the fact that the relationship between crevice corrosion mechanisms and geometry is still debated. Knowledge of the scaling laws governing crevice corrosion would enable accurate application of experimental results from large-scale crevices to practical crevice corrosion situations, which generally occur on much smaller size scales. The steps necessary to achieve these goals were:

1. **Microfabricate crevices with varying crevice gaps on a size scale relevant to practical crevices.** The semiconductor device fabrication techniques used for the proof-of-
principle experiments were utilized to make these crevices. The dimensions of the crevices, particularly the crevice gaps, were monitored closely for use in modeling and determining scaling law relationships.

2. **Perform corrosion experiments on the microfabricated crevices.** A system in which the controlling mechanisms of crevice corrosion are well known was used so the relationship between geometry and mechanism is clear.

3. **Determine the relationship between the corrosion attack morphology on the crevice substrate and the crevice geometry.** This relationship provided information about how the mechanisms controlling the corrosion attack scale with geometry.

4. **Model the corrosion experiments using CREVICER.** This comparison assisted in verifying the experimental results as well as filling in gaps between data points to form a more complete picture of the mechanism/geometry relationship.

5. **Use CREVICER to investigate the influence of specific environmental parameters on the applicable scaling law.** One of the huge benefits of a model is its ability to separate variables that experimentally are inseparable. CREVICER was used in this capacity to identify precisely which parameters in the crevice corrosion system determine the relevant scaling law.
Chapter 4: Experimental

4.1 Improvements and additions to CREVICER

Several significant improvements were made to CREVICER during this study. Each change addressed one of the limitations of Version 1 of CREVICER. For example, one limitation of Version 1 of CREVICER is its speed. Approximately 95% of the computational time in CREVICER is spent solving the matrix of equations used in the finite element method. In an attempt to increase the speed of the model, a new \textit{Solve} routine was implemented. Another improvement made to CREVICER was the addition of the aluminum hydrolysis reactions to the list of homogeneous reactions considered by the model. A major addition to CREVICER was a new graphical user interface (GUI) designed to simplify the process for setting up a new model. Appropriate changes were also made to CREVICER to interact with the GUI. The implementation of these improvements is detailed in this section.

4.1.1 Implementation of a new solver routine

The \textit{Solve} algorithm in the CREVICER model is the routine in which the two-dimensional array, or matrix, used in the finite element method is solved numerically. The matrix is \( N \times N \) in size, where \( N \) is equal to the number of nodes in the finite element mesh. Each row in the matrix represents the equation relating a particular node to all of the nodes surrounding it in the mesh. Each row only has non-zero entries in the columns corresponding to the surrounding nodes. Because the number of nodes surrounding a particular node is much smaller than the total number of nodes in a mesh, the vast majority of entries in each row of the matrix are zeroes. In Version 1 of CREVICER, this
matrix was stored in a static NxN array and solved using Gaussian elimination and back substitution, standard linear algebra techniques. Although this method is easy to understand and straightforward to implement, it is computationally slow because it performs many unnecessary comparisons of array elements; namely, all of the zero elements. It also requires the static (at compile-time) allocation of large blocks of memory, which can be a problem for some compilers, especially when fine, dense meshes are used.

The improvements made in Version 2 of CREVICER included the implementation of a new Solve algorithm, in which a sparse-matrix notation is used to represent the two-dimensional array. In this implementation, a one-dimensional array of pointers to N doubly linked lists is statically allocated. Each doubly linked list represents a row of the matrix and only contains the non-zero elements of the row, identifying them by their column numbers (which correspond to nodes in the mesh). Once assembled, the sparse matrix is solved using Gaussian elimination and back substitution. During this process elements in the doubly linked lists are added or deleted when they become non-zero or zero, respectively.

The new Solve algorithm was tested against the old routine for accuracy and speed. The tests were performed by modeling the first ten pseudo-timesteps for calculating the initial potential distribution inside a gold crevice when a potential of –0.16 V (NHE) is applied to the mouth of the crevice. The crevice environment was a copper plating solution (0.05 M H₂SO₄ + 0.005 M CuSO₄) and the potential was held in the diffusion limited regime of the copper deposition reaction. Models were run under identical environments; the only difference was the Solve routine. A stopwatch was used
to measure the speed of the models. A character by character comparison of the output files was used to test the accuracy.

4.1.2 Addition of Aluminum hydrolysis reactions

Version 1 of CREVICER includes a routine that accounts for the chromium hydrolysis reactions in the crevice solution. This routine outputs concentrations of Cr$^{3+}$, CrOH$^+$, CrOH$_2^+$, CrOH$_3^-$, and CrOH$_4^-$, based on their input concentrations and reaction constants for the hydrolysis reactions from the literature$^{[34]}$. The final concentrations are found using a recursive guess-and-check method, which is described in detail by Stewart$^{[6]}$. First, an estimate for the CrOH$^+$ concentration is set based on the initial concentration of Cr$^{3+}$. Then, the concentrations of the other ions are calculated relative to CrOH$^+$ using their reaction constants. Finally, the concentrations of the hydrolysis ions are summed to find the total Cr used and this amount is compared to the total Cr available (from the initial ion concentrations). The initial estimate for the concentration of CrOH$^+$ is revised and the process is repeated until the quantities of Cr used and Cr available converge within an allowable margin.

The improvements in Version 2 of CREVICER included the implementation of a new routine to account for the hydrolysis reactions of aluminum. This routine was added to broaden the applicability of CREVICER to include crevice corrosion systems involving aluminum alloys. The routine uses a recursive guess-and-check process similar to that in the chromium hydrolysis routine. The only differences are that the reaction constants are those for aluminum$^{[34]}$ and the output is the concentrations of Al$^{3+}$, AlOH$^+$, AlOH$_2^+$, AlOH$_3^-$, and AlOH$_4^-$. The accuracy of the new aluminum hydrolysis routine was checked by varying the pH of the crevice solution from 3.26 to 10 and
comparing the resulting proportions of hydrolysis products to those reported in the literature\textsuperscript{[35]}.

4.1.3 Implementation of a Graphical User Interface (GUI)

Utilizing Version 1 of CREVICER to model a new crevice corrosion system requires making changes to the C++ source code, recompiling it, and then running it. Changing the concentration of an ionic species, the crevice gap, or the parameters involved with time-stepping involves minor alterations to the main procedure, but adding a new chemical species, substrate material, or heterogeneous reaction requires defining a new C++ class. Any changes require some knowledge of C++ syntax, and the more complex alterations require an intimate familiarity with the structure of the model. These requirements can make modeling utilizing Version 1 of CREVICER a difficult and time-consuming chore for the average user.

One of the major additions made to CREVICER in Version 2-GUI was the design and implementation of a graphical user interface (GUI). The goal of the GUI is to provide a point-and-click style interface that offers the user a straightforward, visual method to define the parameters for a new model. The complete specifications for the GUI are found in Appendix A, but they can be summarized as follows:

**Step 1:** The GUI reads in a user-provided data file containing the finite element mesh information (node and element sizes and locations) and displays a graphical representation of the mesh on the screen.

**Step 2:** The user utilizes windows with input fields to define the necessary parameters for any chemical species, materials, or reactions relevant to the system to be modeled that are not already present in the GUI libraries.
Step 3: The user selects “all nodes”, “all elements”, or “all edges” to input global system parameters such as chemical species and their initial concentrations, substrate materials, relevant electrochemical reactions, and crevice gap.

Step 4: Through the use of a zoom box, the user selects particular nodes, elements, or edges to set localized conditions. For example, by selecting the nodes along the front edge of the mesh, the user can fix the concentrations of ionic species to their bulk values at the mouth of the crevice. The substrate material of a single element can be changed to mimic an inclusion or the crevice gap can be decreased in one area to simulate the effect of a subcrevice.

Step 5: The user advances to the final input window where he/she sets global time-stepping parameters and selects the desired output information.

Step 6: Once all of the parameters for the model have been set, the GUI saves the information to a file.

Step 7: The user exits the GUI and launches CREVICER Version 2-GUI, which reads in the file from the GUI and models the system.

Once specifications for the GUI were defined, they were turned over to Jonathan Howse, an undergraduate computer science major at UVa, who developed the GUI using Microsoft Visual C++™. The details of the implementation of the GUI as well as a complete listing of the code can be found in his senior thesis[36]. Robert Koehl, another undergraduate computer science major at UVa, is currently making improvements and additions to the input GUI. He is also working on an output GUI that will offer the user a visual representation of the concentration and potential distributions in the occluded region after CREVICER outputs them.
4.1.4 Implementation of changes to CREVICER to interact with the GUI

Development of a GUI-compatible version of CREVICER required several alterations and additions to the source code. The *setup* routine, which is the first function called from the *main* procedure and which is the routine in which all of the environmental parameters for the model are set, was completely rewritten to read from the output file of the GUI. Generic C++ classes for chemical species, materials, and reactions were defined to incorporate user-defined species, materials, and reactions from the GUI. Dynamic list types were also defined to hold a variable number of objects of these generic classes. This use of dynamic list types was necessary because it is unknown at compile-time of CREVICER Version 2-GUI how many species in solution, substrate materials, or electrochemical reactions the user will define and utilize in the GUI. CREVICER Version 2-GUI was also debugged so it would compile and run in Visual C++™ on a PC, the same platform on which the GUI was developed.

4.2 Investigating the capabilities of CREVICER

Limited tests were run on CREVICER to assess the variability of the results of the model and its convergence limits. The effect of the density of the finite element mesh on the model output was investigated. The influence of the user-defined initial potential distribution on the results of the model was also considered. The roles of time step length, mesh density, and concentration and potential gradients in the achievement of numerical convergence of CREVICER were investigated. These tests were motivated by the need to define basic guidelines for CREVICER users regarding the selection of an appropriate mesh and time stepping parameters.
4.2.1 Assessing the variability of the results

Tests were run on CREVICER to assess how the results of the model varied with finite element mesh density and initial potential distribution. For the mesh density tests, two models with meshes that had the same geometry, but different numbers of nodes, were run under identical conditions and the results were compared. Both meshes represented a 1-D crevice 0.7 cm in length, but one mesh had 100 nodes along the crevice length (one every 70 µm) whereas the other had 400 nodes along the crevice length (one every 17.5 µm). The system modeled was nickel in sulfuric acid. The nickel was held potentiostatically in the passive region and the initial potential distribution in the crevice was determined.

CREVICER solves for the potential distribution in a crevice by pseudotimestepping until a solution is reached that satisfies the given boundary conditions. Stewart\[6\] explains the details of this method. The initial potential distribution tests investigated whether or not the user-defined initial potential distribution in the crevice has an impact on the potential distribution to which CREVICER converges. In these tests, two models with the same boundary conditions but considerably different user-defined initial potential distributions were run under identical environmental conditions and the results were compared. In one model, the initial potential distribution was set to –0.290 V (SCE) everywhere except at the mouth of the crevice, where it was fixed at +0.3 V (SCE) (a boundary condition). In the other model, the potential at the mouth was also fixed at +0.3 V (SCE), but set to –0.1 V (SCE) at all other points in the crevice. CREVICER was used to determine the steady-state potential distributions for the two cases and the results were compared.
4.2.2 Determining the convergence limits

The method by which CREVICER solves for potential and concentration distributions in a crevice, optimizing polynomial approximations for the analytical solution at each node in the finite element mesh, introduces limitations into the model. In order for the solutions to converge numerically, the changes from element to element in the mesh must not be too drastic. A balance must be struck among the time and length scales and the conditions of the model. For example, models with steep potential or concentration gradients require a higher density mesh so that the differential from node to node is manageable. Models with high fluxes require shorter time steps so that the concentration distribution does not vary drastically from one time step to the next.

During the portion of this study focused on investigating the scaling laws of crevice corrosion, which will be described in detail in Section 4.6, a series of models were run that provided insight into the practical convergence capabilities of CREVICER. Knowledge of the convergence capabilities can be used to provide novice CREVICER users with general guidelines for the selection of a mesh density and chemical and potential time step lengths that are appropriate for their system. The series of models run for the scaling law experiments were not specifically designed to quantify the convergence limits of CREVICER, but certain characteristics of the models made them useful for making observations about the convergence limits.

All thirty-six models were run under identical conditions except for two parameters that were varied: the crevice gap and the shape of the electrochemical boundary condition. Two types of mathematical instabilities were observed: one relating to the convergence of the potential distribution inside the crevice and one relating to the
convergence of the concentration distribution of nickel ions inside the crevice. Because only two parameters in the models were varied, observations could be made about the relationship between these parameters and the convergence of the model under the specific mesh and time step conditions used. In this series of models, the crevice gap was varied from $1.5 \mu m$ to $150 \mu m$.

All of the electrochemical boundary conditions were mathematical representations of potentiodynamic behavior exhibiting an active/passive transition (Figure 6). The shape of the active nose varied from Double Bump, which had a nose width of 400 mV to Skinny, which had a nose width of less than 200 mV. In all cases except for $I_{\text{pass}} \uparrow$ the current density at the peak of the active nose was three orders of magnitude larger than the passive current density. The length of the chemical (real-time) time steps was 0.1 sec. The length of the potential (pseudo) time steps was $10^{-8}$ sec. The finite element mesh had 350 nodes along the crevice length (0.7 cm). The density of the nodes was distributed so that the nodes at the mouth of the crevice, where the steep potential and concentration gradients were expected to occur, were 100 times closer together than the nodes at the tip of the crevice. There was approximately $1 \mu m$ between nodes at the mouth of the crevice and $100 \mu m$ between nodes at the tip. The criteria for the convergence of the potential distribution was a residual of less than 0.002. The residual, which is defined in detail in Stewart\(^6\), is a measure of the deviation of the numerical solution from the true analytical solution.

During the modeling study, it was noted which models converged under which conditions. The type of instability (potential or chemical) was also observed. The intent
is that these results be used to provide general guidelines for mesh and time step length selections.

4.3 Microfabrication

As was described in Section 2.2, semiconductor device manufacturing techniques were used to fabricate the samples used in this study. The microfabricated crevices were made in the Semiconductor Device Laboratory, a class 10,000 clean room facility located in the Department of Electrical Engineering at the University of Virginia. The crevices were fabricated in two independent pieces: the former, which defines the vertical geometric characteristics of the crevice including the crevice gap, and the substrate, which contains the metal electrode used in the corrosion experiments. After fabrication, the formers and substrates were pressed together to form the complete crevices. Detailed processing sheets for the steps involved in the microfabrication of the crevice substrates and formers can be found in Appendix B; this section contains a summary of the process.

4.3.1 Crevice Formers

One-inch diameter silicon wafers from Virginia Semiconductor (Fredericksburg, VA) were used to make the crevice formers. Four to six formers were fabricated simultaneously on each wafer, which were diced in the last processing step to separate the samples. The wafers were 400-500 µm thick so that they could be etched to depths up to 100 µm without becoming overly fragile. A <110> orientation was chosen so that (111) planes would be perpendicular to the surface of the wafer. Then an etchant that preferentially etches along the (100) and (110) planes could be used to etch the bulk silicon, forming vertical side walls. The doping and resistivity of the formers was
unimportant because they were used only to form the structure of the crevice, not as metal electrodes. The process for making the crevice formers is outlined in Figure 2.

**Step 1: Wafer cleaning:** The wafers were first cleaned using an RCA clean, a standard cleaning process used for silicon wafers in the semiconductor device industry\textsuperscript{[19]}. The RCA clean involves dipping the wafer in six different chemical baths for specific amounts of time (see Appendix B). The baths include acetone, trichloroethane (TCA), methanol, buffered oxide etchant (a dilute hydrofluoric acid mixture), a hydrogen peroxide/ammonium hydroxide/water mixture, and a hydrogen peroxide/hydrochloric acid/water mixture. The purpose of the baths is to remove organic and other impurities from the surface of the wafer and remove the native oxide from the silicon.

**Step 2: Wet oxidation:** After the RCA clean, the wafers were placed in a wet oxidation furnace to grow a layer of silicon dioxide on the surface (Figure 2a). The furnace was heated to 1160 °C and oxygen was flowed through a bubbler containing 95 °C deionized water and then through the furnace. The thickness of the oxide layer was determined by the amount of time the wafers remained in the furnace. Approximately 1 hour of heating was required to grow an oxide 0.5 µm thick, while about 4 hours was necessary to grow a 1 µm oxide.

**Step 3: Photoresist application, patterning, and developing:** After being removed from the furnace and allowed to cool, a photoresist primer was applied to the wafers and they were spin-coated with AZP4110 photoresist (Clariant International, Ltd., Muttenz, Switzerland) for 30 sec at 6000 rpm. A Mylar mask containing a pattern depicting the geometry of the crevice formers was placed over each wafer and the wafer was exposed to UV radiation for 20 seconds. The wafer was rinsed in AZ Developer for 1.5 minutes,
during which time the photoresist that had been exposed to the UV radiation dissolved away due to its increased solubility. The photoresist that was blocked from the UV radiation by the pattern on the mask did not dissolve, transferring the pattern from the mask onto the wafer (Figure 2b). Designs for the Mylar masks used to pattern the wafers were drawn using Micrografx Designer 4.0. The designs were drawn 200% scale, printed onto glossy paper using a 1200 dpi laser printer, and were taken to T&N Printing (205 12th St. NE, Charlottesville, VA) where they were reduced and transferred to Mylar sheets, a material similar to a heavy-duty transparency.

**Step 4: Oxide Etch:** After the photoresist was applied, patterned, and developed, the wafers were placed in Particu-Lo LTM Superwet Buffered Oxide Etchant 10-1 (General Chemical Corp., Parsippany, NJ), an ammonium fluoride/hydrofluoric acid mixture (10 parts by volume NH$_4$F (40%), 1 part by volume HF (49%)) that preferentially etches silicon dioxide. In this thesis, this etchant will be referred to as 10:1 BOE. In the regions where the oxide was protected by the photoresist pattern it remained intact, while all exposed oxide was etched away, revealing the underlying silicon (Figure 2c). Thus, the pattern for the crevice formers was transferred from the photoresist to the silicon dioxide.

**Step 5: Photoresist Removal:** After the pattern was transferred to the oxide, the remaining photoresist was removed by soaking the wafers in acetone for ten minutes (Figure 2d).

**Step 6: Silicon Etching:** Once the photoresist was removed, the wafers were placed in a bath containing potassium hydroxide and isopropyl alcohol. Potassium hydroxide readily attacks silicon, but not silicon dioxide, and etches silicon (100) planes
100 times faster than silicon (111) planes\textsuperscript{[19]}. \(\langle 110\rangle\) wafers were used so that (111) planes were perpendicular to the surface of the wafer. Thus the wafers were etched vertically in the regions not covered by oxide, deepening the features of the pattern defined by the oxide (Figure 2e). The wafers were intermittently removed from the bath and the etch depth was measured using a Tencor Alpha-Step 200 contact profilometer. This etch depth determined the gap, or vertical dimension, of the assembled crevice.

**Step 7: Dicing:** Once the formers were etched to the desired depth, the wafers were diced using a Disco DAD-2H/6T automatic dicing saw to separate the individual samples.

**Step 8: Final cleaning:** After dicing, each individual former was spin-cleaned using ethanol, trichloroethylene (TCE), and methanol.

![Diagram](image_url)

*Figure 2: Process for fabricating crevice formers. a) Step 2, wet oxidation. b) Step 3, photolithography. c) Step 4, oxide etch. d) Step 5, photoresist removal. e) Step 6, silicon etching.*
4.3.2 Crevice Substrates

The crevice substrates were also made from one-inch diameter silicon wafers from Virginia Semiconductor. Three or four substrates were fabricated on each wafer, which were diced in the final step of processing to separate the samples. The wafers used for the substrates were also 400-500 µm thick to minimize losses due to breakage. No bulk silicon etching was performed on the substrates so standard <100> orientation wafers were chosen. The wafers were doped with boron (a p-type dopant) to achieve a resistivity less than 0.01 Ω-cm. This low resistivity silicon was needed to make an electrical connection between the metal electrode on the surface of the silicon and a platinum wire attached to the back of the wafer. The process for fabricating the crevice substrates is outlined in Figure 3.

Step 1: Wafer Cleaning: As was the case with the crevice formers, the first step in the crevice substrate processing was an RCA clean of the silicon wafers.

Step 2: Wet Oxidation: A layer of silicon dioxide was also grown on the substrate wafers using the wet oxidation process (Figure 3a), but usually to a different thickness.

Step 3: Photoresist application and exposure, Layer 1: After oxide growth, a photoresist primer was applied to the substrate wafers and AZ 4110 photoresist was spin-coated onto the wafers for 30 sec at 6000 rpm. The wafers were exposed to UV radiation for twenty seconds. No patterned Mylar mask was placed over the wafers during the exposure; they were flood exposed to UV radiation.

Step 4: Photoresist application, patterning, and developing, Layer 2: After the flood exposure of the first layer of photoresist, the substrate wafers were placed back on the spin-coater and a second layer of photoresist, AZ 4210, was applied to the wafers for
30 sec at 6000 rpm. This time a Mylar mask patterned with the geometry of the crevice substrates was placed over the wafers and they were exposed to UV radiation for 30 seconds. The wafers were rinsed in AZ Developer for three minutes. In the early stages of developing, the regions of the top layer of photoresist that were not masked from the UV radiation were washed away by the developer, exposing the bottom layer of photoresist in those areas. Because the entire bottom layer of photoresist was UV-exposed, it rinsed away in the regions below the unmasked portions of the top layer (exposing the underlying oxide), and then began to wash away at the edges of the regions below the masked portions of the top layer of photoresist, forming an overhang (Figure 3b). This overhang was critical to the success of later processing steps.

**Step 5: Oxide etch:** After the double layer of photoresist was applied and developed, the oxide was etched away in the unmasked regions of the wafers, as was done with the crevice formers (Figure 3c).

**Step 6: Metal evaporation:** Without removing the photoresist, the substrate wafers were placed in a Temescal BJD-1800 electron beam evaporator and the material for the metal crevice electrodes was evaporated onto the wafers. A thin layer of chromium (~500 Å) was evaporated first to serve as an adhesion layer between the silicon and the electrode metal. 0.3-0.6 μm layers of gold or nickel were evaporated on top of the chrome and were used as the electrode metals. Metal evaporation is a blanket deposition process; the metal was deposited both on the exposed silicon and on top of the photoresist pattern (Figure 3d).

**Step 7: Metal lift-off/removal of photoresist:** After the substrate wafers were removed from the evaporator they were rinsed in acetone for 5-10 minutes to dissolve the
photoresist. This dissolution was possible because the overhang created by the two-step photoresist application process formed a clean break between the metal on the silicon and the metal on top of the photoresist, exposing the sides of the layers of photoresist. As the photoresist dissolved, it lifted off the metal that was deposited on top of it. The result was a metal electrode on the silicon, bounded by oxide to define the crevice substrate geometry (Figure 3e).

Step 8: Dicing: As was the case with the formers, after the crevice substrates were fabricated the wafers were diced to separate the individual substrates.

Step 9: Final cleaning: The final step in the crevice substrate processing was a thorough spin cleaning with ethanol, TCE, and methanol.

![Figure 3: Process for fabricating crevice substrates. a) Step 2, wet oxidation. b) Step 3 and Step 4, two-layer photolithography. c) Step 5, oxide etch. d) Step 6, metal evaporation. e) Step 7, metal lift-off.](image-url)
4.4 Experimental Setup

The details of the apparatuses and equipment used for electrochemical experiments are given in this section. The method used to assemble complete crevices from the microfabricated substrates and formers is detailed. The equipment used to take electrochemical, pH, and conductivity measurements is also described.

4.4.1 Crevice Assembly

After fabrication, dicing, and cleaning, the crevice substrates and formers were taken from the clean room back to the electrochemistry lab. Electrical connection to the metal electrodes on the crevice substrates was made by affixing approximately eight inches of 0.1 mm diameter Premion (99.998% pure) platinum wire to the back side of the substrates with silver conductive adhesive made by Electron Microscopy Sciences. After drying, the substrates were prepared for corrosion testing in one of two ways. In early experiments, the substrates were directly affixed to the center of a 3x3 inch piece of Plexiglas with Dow Corning high vacuum grease. The vacuum grease served a dual purpose: sealing the silver paint off from the solution, and easing alignment of the crevice substrate. In later experiments, the back of the substrate was covered with Microstop lacquer and mounted on a piece of glass slide slightly larger than the substrate. Additional lacquer was applied to seal the edges of the substrate to keep solution from reaching the silver paint. Then the glass slide was attached to the Plexiglas with vacuum grease.

When performing a corrosion experiment, a crevice former was attached to a small piece of Plexiglas with double-stick tape. The former was flipped over, aligned,
and pressed against the substrate to form a complete crevice. The assembly was held in place with nylon screws connecting the two pieces of Plexiglas. The entire assembly was placed vertically in the corrosion-testing cell so that the solution level just reached the top of the crevice. A schematic of the crevice assembly is shown in Figure 4. The platinum wire extended out of the cell and was attached to the working electrode lead of the potentiostat. Before performing a corrosion test, the open circuit potential of the crevice electrode was monitored until it stabilized. During this time, the crevice former was only loosely attached to the substrate; it was held on with the nylon screws approximately a centimeter above the substrate surface. After the open circuit stabilized, the crevice former was pressed against the substrate. In earlier experiments the assembly was removed from the solution, the crevice was filled with solution using a pipette, and the crevice former was clamped firmly down on the substrate. In later experiments the crevice former was aligned and clamped down with the assembly still in solution to avoid the introduction of air bubbles inside the crevice.

Figure 4: Schematic of the crevice assembly.
4.4.2 Equipment

All electrochemical experiments were performed on either an EG&G Versastat or an EG&G model 273 potentiostat. Gateway 486-33 MHz computers controlled the Versastat and the 273. EG&G’s corrosion analysis software Model 352/252 Version 2.30 was used to set up and run experiments on both stations. In all experiments a saturated calomel electrode (SCE) was used as a reference electrode and a platinum mesh served as the counter electrode.

Solution conductivity measurements were made using a Yellow Springs Inc. (YSI) Model 32 benchtop conductance meter with a YSI Model 3403 conductivity cell with a cell constant \( K = 1.0 \text{ cm}^{-1} \). To take a measurement, the cell was removed from its deionized water-filled storage container and placed in the beaker or bottle containing the solution to be used in the crevice corrosion experiments. The bottom 2-3 inches of the conductivity cell were submerged in the solution for several minutes, until the conductivity reading stabilized. The cell was then removed from the solution, rinsed in DI water, and returned to its storage container. The conductivity measurements were not made directly in the corrosion cell because the solution level was too shallow to acquire a stable reading.

Solution pH measurements were made using either Fisher Scientific short-range alkacid pH paper (range 0.0 – 3.0 in 0.5 pH steps) or a Corning (range 0-14) hand-held pH meter. Measurements using the pH paper were made by submerging half of a four-to-five inch long strip of paper directly in the corrosion cell for five seconds. The paper was then removed from the solution and the color of the submerged portion was compared with the pH standards to find the closest match. Before the hand-held pH meter was
used, it was calibrated using buffer solutions of pH 2 and pH 3. The tip of the meter was then submerged in a beaker containing the corrosion cell solution and held there until the pH stabilized, which generally took ten to fifteen minutes.

4.5 Proof-of-principle experiments and modeling

Proof-of-principle experiments were performed to demonstrate the use of semiconductor device manufacturing techniques for the fabrication of crevices with rigorously defined dimensions and to illustrate the crevices’ applicability to performing experimental verification of CREVICER. In these experiments, a potentiostatic hold technique was used to plate copper from a copper sulfate solution onto a gold substrate inside of a microfabricated crevice. The system was modeled using CREVICER and the resulting deposition profile inside the crevice was compared to the experimental results.

4.5.1 Microfabrication processing specifics

Crevice substrates and formers were fabricated utilizing the processing methods described in Section 4.3 and detailed in Appendix B. Four wafers were used to make each type of sample. Four samples were fabricated on each wafer, so the total yield was sixteen crevice formers and sixteen substrates. The crevices were rectangular slots 8-mm long and 4-mm wide. The crevice gap varied; it was determined by the etch depth of the crevice former. The fabrication details specific to this set of experiments are outlined Tables 2 and 3.
Table 2: Processing specifics for the crevice formers used in the proof-of-principle experiments.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Former</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of wafers processed</td>
<td>4</td>
</tr>
<tr>
<td>Number of samples per wafer</td>
<td>4</td>
</tr>
<tr>
<td>Oxidation furnace time</td>
<td>5 hours</td>
</tr>
<tr>
<td>Total oxide thickness</td>
<td>1.26 µm</td>
</tr>
<tr>
<td>Oxide etch time in 10:1 BOE</td>
<td>24 min</td>
</tr>
<tr>
<td>Final heights after bulk etch</td>
<td>Wafer 2-F-1: 1.01 ± 0.05 µm</td>
</tr>
<tr>
<td></td>
<td>Wafer 2-F-2: 5.04 ± 0.24 µm</td>
</tr>
<tr>
<td></td>
<td>Wafer 2-F-3: 12.09 ± 0.69 µm</td>
</tr>
<tr>
<td></td>
<td>Wafer 2-F-4: 67.10 ± 1.53 µm</td>
</tr>
</tbody>
</table>

Table 3: Processing specifics for the crevice substrates used in the proof-of-principle experiments.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of wafers processed</td>
<td>4</td>
</tr>
<tr>
<td>Number of samples per wafer</td>
<td>4</td>
</tr>
<tr>
<td>Oxidation furnace time</td>
<td>1 hour</td>
</tr>
<tr>
<td>Total oxide thickness</td>
<td>0.55 µm</td>
</tr>
<tr>
<td>Photoresist thickness (two layers)</td>
<td>2.69 µm</td>
</tr>
<tr>
<td>Oxide etch time in 10:1 BOE</td>
<td>12 min</td>
</tr>
<tr>
<td>Thickness of chrome adhesion layer</td>
<td>250 Å</td>
</tr>
<tr>
<td>Thickness of gold electrode</td>
<td>0.270 µm</td>
</tr>
</tbody>
</table>

4.5.2 Electrochemical testing

The solution used to plate copper onto the gold substrates was 0.05 M H₂SO₄ + 0.005 M CuSO₄. A potentiodynamic scan was performed on a 3-cm² piece of gold foil to determine the electrochemical behavior of the system and to use as a boundary condition for the model. The scan rate was 1 mV/sec, and the range was 100 mV above the open circuit potential of the foil (+240 V vs. SCE) down to −600 mV.

Potentiostatic holds were performed on the microfabricated crevices. The crevice gap and the duration of the test were varied. A summary of the tests performed is shown in Table 4.
Table 4: A summary of the potentiostatic hold tests performed on the gold electrodes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Crevice Gap</th>
<th>Hold Potential</th>
<th>Hold Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-S-1 B</td>
<td>No crevice</td>
<td>-0.4 V vs. SCE</td>
<td>10 min</td>
</tr>
<tr>
<td>2-S-1 C</td>
<td>67 µm</td>
<td>-0.4 V vs. SCE</td>
<td>10 min</td>
</tr>
<tr>
<td>2-S-1 D</td>
<td>67 µm</td>
<td>-0.4 V vs. SCE</td>
<td>30 min</td>
</tr>
<tr>
<td>2-S-2 A</td>
<td>67 µm</td>
<td>-0.4 V vs. SCE</td>
<td>30 min</td>
</tr>
<tr>
<td>2-S-2 B</td>
<td>12 µm</td>
<td>-0.4 V vs. SCE</td>
<td>30 min</td>
</tr>
<tr>
<td>2-S-2 C</td>
<td>12 µm</td>
<td>-0.4 V vs. SCE</td>
<td>60 min</td>
</tr>
<tr>
<td>2-S-2 D</td>
<td>12 µm</td>
<td>-0.4 V vs. SCE</td>
<td>60 min</td>
</tr>
<tr>
<td>2-S-3 A</td>
<td>12 µm</td>
<td>-0.4 V vs. SCE</td>
<td>60 min</td>
</tr>
</tbody>
</table>

4.5.3 Modeling

CREVICER Version 1 was used to model the copper plating experiments. A curve was fitted to the data from the potentiodynamic scan performed on the gold foil by summing equations for the dominant anodic and cathodic reactions and varying the constants in the equations. It was assumed that oxygen reduction and copper reduction were the dominant cathodic reactions. The anodic portions of the reactions were expressed using one equation to represent their sum. The complete equation used to fit the potentiodynamic data was:

\[
i_{\text{total}} = i_{0,\text{an}} \frac{(E-E_{0,\text{an}})}{\beta_{\text{an}}} - i_{0,\text{O}_{2}^{\text{RR}}} \frac{(E-E_{0,\text{O}_{2}^{\text{RR}}})}{\beta_{\text{O}_{2}^{\text{RR}}}} \frac{10^{i_{0,\text{an}} \frac{(E-E_{0,\text{an}})}{\beta_{\text{an}}}}}{1+10^{i_{0,\text{an}} \frac{(E-E_{0,\text{an}})}{\beta_{\text{an}}}}} - \frac{i_{0,\text{Cu}}}{\beta_{\text{Cu}}} 10^{\left(\frac{(E-E_{0,\text{Cu}})}{\beta_{\text{Cu}}}\right)} \frac{10^{i_{0,\text{Cu}} \frac{(E-E_{0,\text{Cu}})}{\beta_{\text{Cu}}}}}{1+10^{i_{0,\text{Cu}} \frac{(E-E_{0,\text{Cu}})}{\beta_{\text{Cu}}}}} \tag{7}
\]

Where

\[
E_{0,\text{O}_{2}^{\text{RR}}} = 1.23 + 0.015 \log[O_{2}] + 0.06 \log[H^{+}] \text{ V (NHE)}
\]

\[
E_{0,\text{Cu}} = 0.342 + 0.03 \log[Cu^{2+}] \text{ V (NHE)}
\]

\[
i_{\lim,\text{O}_{2}^{\text{RR}}} = a \ast [O_{2}]
\]

\[
i_{\lim,\text{Cu}} = b \ast [Cu^{2+}]
\]

and \(E_{0,\text{an}}, i_{0,\text{an}}, i_{0,\text{O}_{2}^{\text{RR}}}, i_{0,\text{Cu}}, \beta_{\text{an}}, \beta_{\text{O}_{2}^{\text{RR}}}, \beta_{\text{Cu}}\), a, and b were the constants that were varied to attain a good fit. The concentrations of \(O_{2}\), \(H^{+}\), and \(Cu^{2+}\), were set to their bulk values.
(Table 4) during the curve fitting process because the potentiodynamic scan was performed in bulk solution, but during the model they varied in accordance with the concentration distributions in the crevice. The gold substrate was defined as a new material in CREVICER and the fitted curve was used as the boundary condition describing the electrochemical behavior of the substrate.

The other parameters entered into CREVICER match the conditions of the potentiostatic holds. A summary of the parameters can be found in Table 5.

Table 5: Parameters for proof-of-principle model run on CREVICER.

<table>
<thead>
<tr>
<th>INITIAL CONDITIONS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical species</td>
<td>Initial concentrations (mM)</td>
</tr>
<tr>
<td>Cu^{2+}</td>
<td>5</td>
</tr>
<tr>
<td>SO_{4}^{2-}</td>
<td>55</td>
</tr>
<tr>
<td>H^{+}</td>
<td>100</td>
</tr>
<tr>
<td>O_{2}</td>
<td>0.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>BOUNDARY CONDITIONS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Species concentrations fixed at mouth of crevice</td>
<td>Value: initial concentrations</td>
</tr>
<tr>
<td>Potential fixed at mouth of crevice</td>
<td>Value: -0.16 V (NHE)</td>
</tr>
<tr>
<td>Flux through crevice tip and sides</td>
<td>0</td>
</tr>
<tr>
<td>Flux through substrate of crevice</td>
<td>Defined by Eq. 7</td>
</tr>
<tr>
<td>Crevice gap</td>
<td>70 μm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TIME STEPPING PARAMETERS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of time step</td>
<td>0.5 sec</td>
</tr>
<tr>
<td>Number of time steps</td>
<td>600</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>OUTPUT AT EACH TIME STEP</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential distribution</td>
<td></td>
</tr>
<tr>
<td>Total flux of copper through each element</td>
<td></td>
</tr>
<tr>
<td>Copper concentration distribution in crevice</td>
<td></td>
</tr>
</tbody>
</table>

4.5.4 Analysis

Due to limitations of computational speed, the copper plating system was only modeled for five real-time minutes. The new solver routine for CREVICER had not been implemented when these tests were performed, so five real-time minutes required approximately 100 hrs of computational time. In order to compare the modeling results to the experimental data, the copper fluxes through each element in the model were
extrapolated out to thirty minutes, the actual test time. This extrapolation was performed by fitting a line through the copper flux data from the 2\textsuperscript{nd} through 5\textsuperscript{th} minutes (14 data points) and then finding the value of the line at thirty minutes. This process is described in more detail in 5.4.3. The value for the copper flux at a particular distance into the crevice was converted to a deposition thickness using Equation 8:

\[ T(x) = -\frac{f_{Cu}(x) \cdot N_A \cdot l_{Cu}}{\rho_{Cu}} \]  

Where:

- \( T(x) \) = copper deposition thickness at distance \( x \) (m)
- \( f_{Cu}(x) \) = flux of copper at position \( x \) (mol/m\(^2\))
- \( N_A \) = Avogadro’s number = \( 6.022 \times 10^{23} \) (atoms/mol)
- \( l_{Cu} \) = Cu lattice constant (3.615 \times 10^{-10} m)
- \( \rho_{Cu} \) = number of atoms per layer of a Cu lattice (1.5 \times 10^{19} atoms/m\(^2\))

This equation assumes perfect density of the deposited layer. The values for the deposition thickness at different distances into the crevice were used to create a copper deposition profile.

An experimental copper deposition profile was created through the use of profilometry. The Tencor Alpha-Step 200 contact profilometer used during the microfabrication process was also used to determine the deposition profile. Because the platinum wires used to make electrical connections to the gold electrodes were attached to the back of the substrates with silver paste, the crevice substrates were not level. This unevenness made it impossible to determine a deposition profile using a profilometry scan from the mouth to the tip of the crevice because changes in elevation caused by differences in the thickness of copper were far outweighed by changes in elevation due to
the bump from the silver paste on the back of the sample. Instead, the silicon dioxide defining the sides of the crevice substrates was utilized as a reference point for measurements. The difference in height between the oxide and the metal electrode (gold + deposited copper) was measured at several points along the length of the crevice. A schematic of this technique is shown in Figure 5. The original difference in height between the oxide and the gold electrode was known from measurements taken during fabrication, so the thickness of the deposited copper layer could be calculated.

![Figure 5: Schematic of a profilometry measurement of the height differential between the oxide and the metal electrode.](attachment:image)

### 4.6 Scaling Law Investigations

A series of experiments on microfabricated crevices and models run on CREVICER Version 2 were used to investigate the scaling laws of crevice corrosion. In this section, the fabrication of crevices for use in scaling law experiments is detailed. The potentiodynamic scans and potentiostatic holds performed on the microfabricated crevices are described as well as the techniques used to analyze the samples. The parameters of the models run on CREVICER are also described. The models were designed to enable direct comparisons between the modeling results and experimental results from the literature and from the scaling law experiments. A set of models used to
investigate the influence of the shape of the electrochemical boundary condition on the governing scaling law is also described.

4.6.1 Microfabrication processing specifics

Four separate sets of samples were microfabricated for the scaling law experiments: one set of unpatterned, undiced wafers used for a series of potentiodynamic scans, one set of crevice formers, and two sets of crevice substrates. The processing of the wafers used for potentiodynamic scans involved an initial RCA clean and then metal evaporation. The type of metal used and the thickness of each metal layer is given for the wafers in the second column of Table 9.

The processing specifics for the microfabricated formers and substrates are shown in Tables 6, 7, and 8.

Table 6: Processing specifics for the crevice formers used in the scaling law experiments.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Former</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of wafers processed</td>
<td>4</td>
</tr>
<tr>
<td>Number of samples per wafer</td>
<td>6</td>
</tr>
<tr>
<td>Oxidation furnace time</td>
<td>6 hours</td>
</tr>
<tr>
<td>Total oxide thickness</td>
<td>1.41 µm</td>
</tr>
<tr>
<td>Oxide etch time in 10:1 BOE</td>
<td>30 min</td>
</tr>
<tr>
<td>Final heights after bulk silicon etch (average of twelve measurements across wafer)</td>
<td>Wafer 3-F-1: ruined etching</td>
</tr>
<tr>
<td></td>
<td>Wafer 3-F-2: 10.94 µm</td>
</tr>
<tr>
<td></td>
<td>Wafer 3-F-3: 45.85 µm</td>
</tr>
<tr>
<td></td>
<td>Wafer 3-F-4: 95.79 µm</td>
</tr>
</tbody>
</table>

Table 7: Processing specifics for the first set of crevice substrates used in the scaling law experiments.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of wafers processed</td>
<td>9</td>
</tr>
<tr>
<td>Number of samples per wafer</td>
<td>3</td>
</tr>
<tr>
<td>Oxidation furnace time</td>
<td>23 hours</td>
</tr>
<tr>
<td>Total oxide thickness</td>
<td>2.95 µm</td>
</tr>
<tr>
<td>Photoresist thickness (two layers)</td>
<td>2.75 µm</td>
</tr>
<tr>
<td>Oxide etch time in 10:1 BOE</td>
<td>60 min</td>
</tr>
<tr>
<td>Thickness of chrome adhesion layer</td>
<td>500 Å</td>
</tr>
<tr>
<td>Thickness of nickel electrode</td>
<td>0.6 µm (seven wafers), 0.3 µm (two wafers)</td>
</tr>
</tbody>
</table>
Table 8: Processing specifics for the second set of crevice substrates used in the scaling law experiments.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of wafers processed</td>
<td>12</td>
</tr>
<tr>
<td>Number of samples per wafer</td>
<td>3</td>
</tr>
<tr>
<td>Oxidation furnace time</td>
<td>20 min</td>
</tr>
<tr>
<td>Total oxide thickness</td>
<td>0.37 µm</td>
</tr>
<tr>
<td>Photoresist thickness (two layers – both AZ4210)</td>
<td>4.2 µm</td>
</tr>
<tr>
<td>Oxide etch time in 10:1 BOE</td>
<td>15 min</td>
</tr>
<tr>
<td>Thickness of chrome adhesion layer</td>
<td>500 Å</td>
</tr>
<tr>
<td>Thickness of nickel electrode</td>
<td>0.3 µm</td>
</tr>
</tbody>
</table>

4.6.2 Electrochemical testing

All of the scaling law experiments were performed in 0.5 M H₂SO₄ with the exception of two potentiodynamic scans in 0.5 M H₂SO₄ + 1 M NiSO₄ and two potentiodynamic scans in 0.5 M H₂SO₄ + Saturated NiSO₄. The conductivity of each solution was measured. The standard three-electrode cell and crevice assembly described in Section 4.4 were used for all tests. In addition to the microfabricated samples detailed above, two additional samples were fabricated for use in executing potentiodynamic scans at slow scan rates. These were made from the nickel pellets used to stock the crucible in the evaporator. The pellets were sliced in half with an ISOMET diamond wafering saw. An eight-inch length of nickel ribbon was attached to the round side of each half with silver paint and the pellets were mounted in an epoxy mold such that the flat side was exposed on one side and the nickel ribbon on the other. The flat side was polished to 1200 grit. The epoxy-mounted nickel pellets were re-polished to 1200 grit before each potentiodynamic scan.

Prior to each experiment, the open circuit potential of the sample was monitored until it changed less than 1 mV/min. For the microfabricated samples, this required approximately 75 min. The epoxy-mounted nickel pellets took about 10 hours to stabilize.
Potentiodynamic scans were performed on all but two of the unpatterned, undiced microfabricated samples and the two epoxy-mounted nickel pellets. No crevice formers were used during the scans; the entire wafers were fully exposed to the environment. The key parameters of the scans are summarized in Table 9.

Table 9: Parameters for the potentiodynamic scans.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material (µm)</th>
<th>Solution</th>
<th>Open Circuit Potential (V vs. SCE)</th>
<th>Scan Rate (mV/sec)</th>
<th>Scan Range (V vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDS 1</td>
<td>0.05 Cr + 0.6 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>No run</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PDS 2</td>
<td>0.05 Cr + 0.6 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>No run</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PDS 3</td>
<td>0.05 Cr + 0.6 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>No run</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PDS 4</td>
<td>Si only</td>
<td>0.5 M H₂SO₄</td>
<td>-0.091</td>
<td>0.1</td>
<td>-0.091 – +1.6</td>
</tr>
<tr>
<td>PDS 5</td>
<td>0.3 Cr</td>
<td>0.5 M H₂SO₄</td>
<td>+0.067</td>
<td>2</td>
<td>+0.067 – +1.5</td>
</tr>
<tr>
<td>PDS 6</td>
<td>0.3 Cr</td>
<td>0.5 M H₂SO₄</td>
<td>+0.086</td>
<td>5</td>
<td>+0.086 – +2.0</td>
</tr>
<tr>
<td>PDS 7</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>-0.307</td>
<td>2</td>
<td>-0.366 – +1.03</td>
</tr>
<tr>
<td>PDS 8</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>-0.310</td>
<td>5</td>
<td>-0.372 – +0.70</td>
</tr>
<tr>
<td>PDS 9</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>-0.291</td>
<td>2</td>
<td>-0.340 – +0.710</td>
</tr>
<tr>
<td>PDS 10</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>-0.289</td>
<td>3</td>
<td>-0.341 – +0.709</td>
</tr>
<tr>
<td>PDS 11</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>-0.288</td>
<td>2</td>
<td>-0.340 – +0.490</td>
</tr>
<tr>
<td>PDS 12</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>-0.334</td>
<td>2</td>
<td>-0.382 – +0.690</td>
</tr>
<tr>
<td>PDS 13</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄ + 1 M NiSO₄</td>
<td>-0.304</td>
<td>2</td>
<td>-0.355 – +0.235</td>
</tr>
<tr>
<td>PDS 14</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄ + 1 M NiSO₄</td>
<td>-0.324</td>
<td>3</td>
<td>-0.374 – +0.208</td>
</tr>
<tr>
<td>PDS 15</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄ + Sat. NiSO₄</td>
<td>-0.331</td>
<td>2.5</td>
<td>-0.381 – +0.314</td>
</tr>
<tr>
<td>NiBall 1</td>
<td>Ni only</td>
<td>0.5 M H₂SO₄</td>
<td>-0.215</td>
<td>0.1</td>
<td>-0.270 – +0.7</td>
</tr>
<tr>
<td>NiBall 2</td>
<td>Ni only</td>
<td>0.5 M H₂SO₄</td>
<td>-0.178</td>
<td>5</td>
<td>-0.225 – +0.7</td>
</tr>
<tr>
<td>NiBall 1</td>
<td>Ni only</td>
<td>0.5 M H₂SO₄</td>
<td>-0.117</td>
<td>0.1</td>
<td>-0.167 – +0.790</td>
</tr>
<tr>
<td>NiBall 2</td>
<td>Ni only</td>
<td>0.5 M H₂SO₄ + Sat. NiSO₄</td>
<td>-0.240</td>
<td>0.1</td>
<td>-0.290 – +0.760</td>
</tr>
</tbody>
</table>

Potentiostatic holds were performed on the other two unpatterned, undiced wafers and one epoxy-mounted nickel pellet. The parameters for those tests are shown in Table 10.
Table 10: Parameters for the potentiostatic holds performed on the unpatterned, undiced wafers.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material (µm)</th>
<th>Solution</th>
<th>Open Circuit Potential (V vs. SCE)</th>
<th>Potentiostatic hold potential (V vs. SCE)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDH 1</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>-0.292</td>
<td>+0.3</td>
<td>4</td>
</tr>
<tr>
<td>PDH 2</td>
<td>0.05 Cr + 0.3 Ni</td>
<td>0.5 M H₂SO₄</td>
<td>-0.304</td>
<td>+0.3</td>
<td>10</td>
</tr>
<tr>
<td>NiBall 1</td>
<td>Ni only</td>
<td>0.5 M H₂SO₄</td>
<td>-0.096</td>
<td>+0.3</td>
<td>10</td>
</tr>
</tbody>
</table>

The microfabricated formers were flipped on top of the substrates to form complete crevices. Potentiostatic holds were performed on the crevices and the current was recorded throughout each test. The potentials were held at +0.25 V (SCE), +0.3 V (SCE), and +0.4 V (SCE) for 1, 2, 3, or 4 minutes. The crevices had gaps of 10.94 µm, 45.85 µm, and 95.79 µm and the crevice mouths were oriented either upward or downward. By orienting the samples downward, natural convection assisted in maintaining a constant occluded region chemistry[^37].

4.6.3 Modeling

CREVICER Version 2 was used in conjunction with the experimental work outlined above to investigate the scaling laws of crevice corrosion. Results from CREVICER were compared to the literature and to the results from the scaling law experiments performed on the microfabricated crevices. Models were also run with electrochemical boundary conditions generated using mathematical functions to investigate the influence of various characteristics of the boundary conditions on the scaling factor relevant to the system.

4.6.3.1 Common Parameters

The same crevice environment was used for all of the models relevant to the scaling law investigations. The chemical species and their initial concentrations (which
were held constant at the mouth of the crevice to simulate mixing with the bulk environment) are shown in Table 11.

**Table 11: Initial solution chemistry set in CREVICER to simulate the conditions inside the crevices during the scaling law experiments.**

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Initial concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^{2-}$</td>
<td>214</td>
</tr>
<tr>
<td>H$^+$</td>
<td>428</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.25</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0</td>
</tr>
</tbody>
</table>

Note that the concentrations of H$^+$ and SO$_4^{2-}$ do not correspond exactly to 0.5 M, the concentration used in the experimental work. Because conductivity plays a vital role in IR*-controlled crevice corrosion, primary importance was placed on matching experimental values for conductivity. Matching pH and sulfate ion concentration with their experimental values was given second priority. The solution conductivity, measured experimentally, was 0.184 $1/(\Omega\cdot\text{cm}^2)$, which correlates with the literature$^{[33]}$. For CREVICER, the SO$_4^{2-}$ and H$^+$ concentrations were adjusted to achieve that value for the conductivity.

In the scaling law models, the potential was held constant at the mouth of the crevice to simulate a potentiostatic hold. The values of the potentials ranged from +0.25 V (SCE) to +0.4 V (SCE), according to the experimental case the model was simulating. The geometries of crevices in the models varied in accordance with the experimental situation, but in all cases the crevices were closed on three sides, so in all models no flux was permitted through the crevice tip and sides.

The number of chemical time steps was set according to the experimental conditions; in some cases only an initial potential distribution was relevant, so no
chemical time steps were performed. The lengths of the chemical time steps were either 0.25 sec or 0.5 sec.

The electrochemical boundary conditions used for the scaling law models, which represent the E vs. log(i) behavior for the substrate material, were determined by one of two methods. In models used for comparison to experimental results, experimentally-determined potentiodynamic scans were fitted with a series of three higher-order polynomials using the program CurveExpert\textsuperscript{TM} v. 1.34 (Daniel Hyams), and these polynomials were used as the boundary conditions in the models. In models used to investigate the influence of various characteristics of the boundary condition on the relevant scaling factor, the boundary conditions were mathematical functions (Gaussian, piecewise, etc.) so they were expressed as equations.

4.6.3.2 Comparisons to the literature

The first set of models used to investigate scaling laws were designed so that direct comparisons could be made between modeling results and experimental work done by Pickering\textsuperscript{[33]}. The electrochemical boundary condition used for these models was taken from the literature, digitized, and fitted with a series of three higher-order polynomials. The geometry of interest was a crevice 1-cm long with a 300-\textmu m gap. The potential at the mouth of the crevice was fixed at +0.25 V (SCE), +0.3 V (SCE), and +0.4 V (SCE). For each case, the initial potential distribution in the crevice was found using CREVICER and compared to experimentally determined potential profiles from the literature. A summary of the modeling parameters can be found in Table 13.
4.6.3.3 Investigations of the effects of boundary condition shape

Extensive modeling work was done to investigate the influence of the shape of the electrochemical boundary condition on the scaling factor relevant to the system. In all of these models, the potential at the mouth of the crevice was fixed at +0.3 V (SCE) and the length of the crevice was 0.7 cm. The crevice gap varied from 1.5 µm to 150 µm. Two minutes of real time were modeled in 0.1-sec steps and the potential, nickel ion concentration, and nickel flux distributions within the crevice were monitored. The electrochemical boundary conditions used for these models were mathematical functions that simulated various characteristics of a potentiodynamic scan result (e.g., increased passive current density).

The six different boundary conditions that were used in this modeling study are shown graphically in Figure 6. All of the curves represent the electrochemical behavior of a material that exhibits an active/passive transition. The Normal curve was used as the reference boundary condition and the other curves were constructed relative to it. In each case a specific characteristic of the curve was varied while all other parameters remained constant. For example, Ipass↑ is identical to Normal except for increased passive current density. Shifted and Skewed have different primary passivation potentials than Normal, and Skinny and Double Bump have narrower and wider active noses, respectively.

Three of the curves, Normal, Shifted, and Skinny, were expressed using variations on the same equation for a normal distribution:

\[
\text{Log} (i) = K_1 \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(E-\mu)^2}{2\sigma^2}} + K_2
\]

The values for the constants used to express the three different are shown in Table 12.
Table 12: The constants used in the normal distribution equation to express the Normal, Shifted, and Skinny electrochemical boundary conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Normal</th>
<th>Shifted</th>
<th>Skinny</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$</td>
<td>0</td>
<td>-0.05</td>
<td>0</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.1</td>
<td>0.1</td>
<td>0.04</td>
</tr>
<tr>
<td>$K_1$</td>
<td>0.75</td>
<td>0.75</td>
<td>0.3</td>
</tr>
<tr>
<td>$K_2$</td>
<td>-5</td>
<td>-5</td>
<td>-5</td>
</tr>
</tbody>
</table>

The Pass↑ curve was constructed piecewise. For $E < 0.066$ V, the Normal distribution was used. For $E \geq 0.066$ V, Log $I$ was fixed at $-2.5$.

The Double Bump curve was constructed using a summation of two normal distributions:

$$Log (i) = K_1 \frac{1}{\sigma\sqrt{2\pi}} \left( e^{-\frac{(E-\mu_1)^2}{2\sigma^2}} + e^{-\frac{(E-\mu_2)^2}{2\sigma^2}} \right) + K_2$$

[10]

Where:

- $\mu_1 = 0.075$
- $\mu_2 = -0.075$
- $\sigma = 0.06$
- $K_1 = 0.425$
- $K_2 = -5$

The Skewed curve was constructed using a Gamma distribution:

$$Log (i) = K_1 \frac{1}{\beta^\alpha} \cdot \gamma (x_0 - E)^{\alpha-1} e^{\left(\frac{E-x_0}{\beta}\right)} + K_2$$

[11]

Where:

- $\beta = 0.1$
- $\alpha = 2$
- $\gamma = 1$
- $K_1 = 0.815$
- $K_2 = -5$
A summary of the modeling parameters used for these cases is given in Table 13.

4.6.3.4 Comparisons to experiments on microfabricated crevices

Two sets of models were run for the purpose of making comparisons to the results from the scaling law experiments performed on the microfabricated crevices. In the first
set, Pickering’s potentiodynamic data\textsuperscript{[33]} was used as the electrochemical boundary condition. In the second set, the results from a potentiodynamic scan on a microfabricated substrate were fitted with a series of higher-order polynomials and used as the electrochemical boundary condition. In both cases the geometric parameters matched the experimental work; the crevice was 0.7 cm in length and the crevice gap varied from 10 µm to 100 µm. The potential at the mouth was fixed at +0.3 V (SCE). The output of interest was the initial potential distribution in the crevice. A summary of the parameters used in CREVICER for these two sets of models is given in Table 13.

Table 13: A summary of the models used to investigate the scaling laws of crevice corrosion.

<table>
<thead>
<tr>
<th>Model ID</th>
<th>Boundary Condition</th>
<th>Crevice Gap (µm)</th>
<th>Crevice Length (cm)</th>
<th>Potential at mouth (V SCE)</th>
<th>Output of interest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set 1: Comparison To Lit.</td>
<td>Polynomials fitted to data from lit.</td>
<td>300</td>
<td>1</td>
<td>+0.25, +0.3, +0.4</td>
<td>Initial Potential Distributions</td>
</tr>
<tr>
<td>Set 2: Math. Function BC, Exptl. Geom.</td>
<td>Math function: Normal</td>
<td>1.5, 10, 20, 60, 100, 150</td>
<td>0.7</td>
<td>+0.3</td>
<td>Potential, Ni\textsuperscript{++} Conc. and Ni\textsuperscript{++} flux (2 min)</td>
</tr>
<tr>
<td></td>
<td>Math function: Skew</td>
<td>1.5, 10, 20, 60, 100, 150</td>
<td>0.7</td>
<td>+0.3</td>
<td>Potential, Ni\textsuperscript{++} Conc. and Ni\textsuperscript{++} flux (2 min)</td>
</tr>
<tr>
<td></td>
<td>Math function: Double Bump</td>
<td>1.5, 10, 20, 60, 100, 150</td>
<td>0.7</td>
<td>+0.3</td>
<td>Potential, Ni\textsuperscript{++} Conc. and Ni\textsuperscript{++} flux (2 min)</td>
</tr>
<tr>
<td></td>
<td>Math function: Shift \textsuperscript{↑}</td>
<td>1.5, 10, 20, 60, 100, 150</td>
<td>0.7</td>
<td>+0.3</td>
<td>Potential, Ni\textsuperscript{++} Conc. and Ni\textsuperscript{++} flux (2 min)</td>
</tr>
<tr>
<td></td>
<td>Math function: Skinny</td>
<td>1.5, 10, 20, 60, 100, 150</td>
<td>0.7</td>
<td>+0.3</td>
<td>Potential, Ni\textsuperscript{++} Conc. and Ni\textsuperscript{++} flux (2 min)</td>
</tr>
<tr>
<td></td>
<td>Math function: Shift</td>
<td>1.5, 10, 20, 60, 100, 150</td>
<td>0.7</td>
<td>+0.3</td>
<td>Potential, Ni\textsuperscript{++} Conc. and Ni\textsuperscript{++} flux (2 min)</td>
</tr>
<tr>
<td>Set 3: BC from Lit., Exptl. Geometry</td>
<td>Polynomials fitted to exptl. data</td>
<td>20, 40, 60, 80, 100</td>
<td>0.7</td>
<td>+0.3</td>
<td>Initial Potential Distributions</td>
</tr>
<tr>
<td>Set 4: Exptl. BC, Exptl. Geometry</td>
<td>Polynomial fitted to exptl. data</td>
<td>10, 20, 40, 50, 60, 80, 100</td>
<td>0.7</td>
<td>+0.3</td>
<td>Initial Potential Distributions</td>
</tr>
</tbody>
</table>
4.6.4 Analysis

After a potentiostatic hold was performed on a microfabricated crevice, it was removed from solution, disassembled, rinsed in deionized water, and blown dry with air. An optical microscope was used to measure the distance from the mouth of the crevice to the corrosion initiation site and the width of the severely corroded region. The Tencor Alpha-Step 200 contact profilometer was used to determine a depth profile of the corrosion attack in the crevices. The experimental limitations that were described for the proof-of-principle experiments were also relevant in these experiments, so the same method for determining a dissolution profile (measuring the height differential between the oxide and metal electrode at several points along the crevice) was used.

A dissolution profile was calculated from the modeling results using the Ni\(^{2+}\) flux distribution output by CREVICER at each time step. Faraday’s law was used to convert the total flux through each element to a penetration depth at each point along the crevice.
Chapter 5: Results

5.1 Improvements to the CREVICER model

The results of the revisions and additions included in Version 2 and Version 2-GUI of CREVICER are detailed in this section. The results include the impact of the new solver routine on the speed of the model and the accuracy of the iterative method for calculating aluminum hydrolysis products relative to analytical results from the literature. Numerous screen shots demonstrating the capabilities of the GUI are shown and a description of the specific changes made to CREVICER to enable communication with the GUI are given.

5.1.1 Implementation of a new solver routine

A new \textit{Solve} algorithm for CREVICER Version 2 was written, debugged and tested. The \textit{Solve} algorithm is the routine in which the matrix used in the finite element method is solved numerically. The complete code for the new procedure can be found in Appendix C. Several important characteristics of the new algorithm that distinguish it from the \textit{Solve} algorithm in Version 1 of CREVICER should be noted. Instead of a large, static \(N \times N\) array (where \(N\) = the number of nodes in the finite element mesh), the new \textit{Solve} algorithm utilizes a 1-D array of \(N\) pointers to dynamically allocate linked lists to represent the finite element matrix. A sparse matrix representation is utilized, meaning that the linked lists contain only the nonzero elements in the matrix. The implementation of a sparse matrix representation significantly increased the length and complexity of the \textit{Solve} algorithm. A new data type was defined to represent an element in the linked lists, utilization of pointers required careful allocation and deallocation of memory, and the
manipulation of the abbreviated representation of the matrix required an intricate series of if-then-else cases.

The new *Solve* algorithm was tested against the old routine for accuracy and speed. The tests were performed by modeling the first ten pseudo-timesteps for calculating the initial potential distribution inside a crevice under the conditions described in Section 4.1.1 (gold crevice held potentiostatically in a copper plating solution). Models were run under identical environments; the only difference was the *Solve* routine. The speed of the model was tested by using a stopwatch to measure the amount of time required to complete the first ten pseudo-timesteps. The test was run three times using each *Solve* routine. The results of the time trials are shown in Table 14. After the runs were completed, the output files from each of the ten time steps were compared using the UNIX command, `diff (file1) (file 2)`, which performs a character by character comparison of the files. There were no differences.

<table>
<thead>
<tr>
<th>Model</th>
<th>Time to complete 10 pseudo-timesteps (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CREVICER V.1 (old Solve algorithm)</td>
<td>Trial 1</td>
</tr>
<tr>
<td>CREVICER V.2 (new Solve algorithm)</td>
<td>2:22</td>
</tr>
</tbody>
</table>

### 5.1.2 Addition of Aluminum hydrolysis reactions

One of the improvements in Version 2 of CREVICER was the addition of a routine to account for the hydrolysis reactions for aluminum. As was described in Section 4.1.2, the new routine was written in the same format as the algorithm for chromium hydrolysis in Version 1 of CREVICER. Estimates for the concentrations of the hydrolysis products were made based on their input concentrations and their reaction distribution constants, and these estimates were recursively revised and recalculated until
the total amount of aluminum distributed among the hydrolysis products matched the amount of aluminum available in solution. The code for the aluminum hydrolysis procedure can be found in Appendix D.

The accuracy of the new routine was evaluated by varying the pH of the crevice solution from 3.26 to 10 and comparing the resulting proportions of hydrolysis products to those reported by Bucheit, Moran, and Stoner[35]. Figure 7 shows the results of these comparisons. For pH values less than 6 and greater than 9 the output of CREVICER is within a few percent of the values reported in the literature. However, for pH values between 6 and 9, the correlation is not as close. In this range, the output from CREVICER differs by as much as 25-30%.
Figure 7: Comparison of aluminum hydrolysis products calculated by CREVICER (a) with those from Bucheit, Moran, and Stoner \cite{35} (b).

### 5.1.3 Implementation of a Graphical User Interface

A graphical user interface (GUI) was designed and developed for CREVICER Version 2-GUI. The goal of the GUI was to eliminate the need for the user to reprogram CREVICER each time a new model was run. The intent was that the GUI provide a visual, point-and-click style interface for entering the parameters for a new model, simplifying and clarifying the process for the user. The complete specifications for the
GUI can be found in Appendix A and a hard copy of the code is located in Jonathan Howse’s senior thesis[^36].

The first step in the modeling process is the definition of the substrate geometry and the parameters (number and density of nodes, etc.) for the finite element mesh. The user does this using a commercial meshing program (e.g., ANSYS [Ansys, Inc., Canonsburg, PA]). The GUI can load files containing the mesh information and display a visual representation of the mesh on the screen. Figure 8 shows a screen shot of the GUI after a mesh has been loaded. This particular mesh represents a 1.125-cm x 0.085-cm rectangular crevice with one node every 500 µm. Each triangle in the mesh corresponds to one finite element, with nodes at each of the vertexes of the triangles. Physically, the finite elements represent triangular prisms of space in the crevice. The heights of the prisms are determined by the crevice gap. Each prism contains a small volume of solution. Chemical flux enters the crevice either through the triangular elements (the crevice substrate) or across the edges of the mesh (the crevice tip, mouth, and sides).
Figure 8: A screen shot from the GUI showing a finite element mesh.

The second step in setting up a model is the definition of any chemical species, materials or reactions not already contained in the GUI libraries. A screen shot of the input window for a new reaction is shown in Figure 9. Note that the user has the option of selecting three different types of reaction boundary conditions: constant (which would be used to simulate constant flux through a crevice wall), Tafel, and polynomial. The polynomial option allows the user to fit a series of three 12$^{th}$ order polynomials to potentiodynamic data for a material. This option makes it possible to model materials with nonlinear boundary conditions (e.g., materials that display an active-passive transition).
Figure 9: A screen shot from the GUI showing the input window for a user-defined heterogeneous reaction.

After the geometry and new species, etc. are defined, the GUI user sets the global parameters for the system utilizing the ‘all nodes’, ‘all elements’ and ‘all edges’ buttons. A screen shot of the ‘all nodes’ input box is shown in Figure 10. This box allows the user to define the species present in the crevice solution and their initial concentrations, the initial potential distribution in the crevice, and the temperature and pressure relevant to the system. The user also decides at this point whether or not to account for aluminum or chromium hydrolysis reactions, and which chemical species to use to maintain charge neutrality in the crevice. The ‘all elements’ and ‘all edges’ input boxes allow the user to set global substrate materials and reactions and the crevice gap.
Figure 10: A screen shot from the GUI showing the ‘all nodes’ input box.

After the global environment has been defined, the user defines localized conditions utilizing a zoom box and the ‘some nodes’, ‘some elements’ and ‘some edges’ buttons. A screen shot showing the zoom box with a few elements selected and the ‘some elements’ input box is shown in Figure 11. This input box can be utilized to change the crevice gap in one region of the crevice (simulating a subcrevice) or to change the substrate material in a small area of the crevice (simulating an inclusion). The most frequent uses of the ‘some nodes’ and ‘some edges’ options would be to fix the
concentrations of chemical species to their bulk values at the mouth of the crevice and to define the flux across the tip or sides of the crevice.

Figure 11: A screen shot from the GUI demonstrating the utilization of the zoom box to select elements. The ‘some elements’ input box is visible. This function is used to change the crevice height or substrate material in a small region of the crevice.

After any local conditions have been specified, the user advances to the final input box of the GUI, shown in Figure 12. In this box the global time stepping parameters, such as the length and number of the pseudo (potential) and real (chemical) time steps, are defined and the desired output files are selected.
Figure 12: A screen shot from the GUI showing the final input box where the time stepping parameters and the desired output files are selected.

When the ‘Launch CREVICER’ button is selected, the GUI saves the modeling parameters to a ‘setup.stp’ file and the user is instructed to exit the GUI and execute CREVICER Version 2-GUI, which reads in the parameters from the file and models accordingly.

5.1.4 Implementation of changes to CREVICER to interact with the GUI

Significant changes were made to CREVICER to enable communication between the modeling code and the GUI. The version of the code with the complete set of these changes is CREVICER Version 2-GUI. A listing of the altered or added code in that version can be found in Appendix E. The changes included the addition of generic subclasses of the TASpecies, TMaterial, and TReaction classes to allow for the incorporation of objects of these types defined by the user in the GUI. The setup routine
was completely rewritten in order to input the model parameters from the output file of the GUI. Dynamic list types were defined to contain the species, material, and reaction objects defined by the user in the GUI.

5.2 Investigating the capabilities of CREVICER

Two aspects of the numerical capabilities of CREVICER were investigated. Tests were performed to investigate the effects of mesh density and user-defined initial potential distribution on the potential distribution determined by CREVICER and the results are given. Observations were made about the convergence limits of CREVICER utilizing the results from the set of models used to investigate the effect of electrochemical boundary condition shape on the governing scaling law. Boundary condition shape and crevice gap are correlated to the stability of the potential and nickel ion concentration distributions for given mesh and time step parameters.

5.2.1 Assessing the variability of the results

Figure 13 shows the potential distributions in a 0.7-cm nickel crevice filled with 0.5-M sulfuric acid as calculated by CREVICER using two different density meshes. The crevice gap is 50 µm and the crevice mouth was held potentiostatically at +0.3 V (SCE). One mesh had a node every 70 µm, while the other mesh had a node every 17.5 µm. These meshes were chosen because of the significant difference in their node densities. As Figure 13 indicates, there is negligible difference between the potential distributions.
Figure 13: The initial potential distributions calculated by CREVICER for two meshes with different node densities.

Figure 14 shows the results of the initial potential distribution tests. Overlaid in Figure 14 are the user-defined potential distributions, ‘upper’ and ‘lower’. In one case (‘lower’) the potential was set to –0.29 V (SCE) everywhere in the crevice except at the mouth, where it was fixed at +0.3 V (SCE). In the other case (‘upper’) the potential was also fixed at +0.3 V (SCE) at the crevice mouth, but was set to –0.1 V (SCE) at all other points in the crevice. These user-defined potential distributions were chosen for their dissimilarity. Also included in Figure 14 are the initial potential distributions (before any chemical, or real-time time steps, but after one set of pseudo-timesteps) as calculated by CREVICER for ‘upper’ and ‘lower’. Even though the user-defined initial potential distributions were different, the potential distributions calculated by CREVICER are the same.
Figure 14: User-defined initial potential distributions ‘upper’ and ‘lower’ and initial potential distributions calculated by CREVICER for ‘upper’ and ‘lower’.

5.2.2 Determining the convergence limits

The models used to investigate the effects of boundary condition shape on the governing scaling laws (Section 4.6.3.3) were also utilized to investigate the convergence limits of CREVICER. Although the tests were not designed explicitly for the purpose of quantifying the convergence limits of the model, the systematic nature of the tests made them useful for observing the relationships between modeling parameters and convergence. All of the models were run under identical conditions except for the crevice gap, which varied from 1.5 μm to 150 μm, and the shape of the electrochemical boundary condition, which varied in the shape, size, and location of the active nose, as seen in Figure 6. Because only these two parameters were varied, changes in the crevice
Two types of mathematical instabilities were observed during the modeling tests. The first is related to the potential distribution inside the crevice. Under some conditions, a solution for the initial potential distribution inside the crevice that satisfied the convergence criteria (residual < 0.002) could not be found in the allotted 150 pseudo-timesteps. In these cases the model could be run no further; a stable initial potential distribution is a requirement for subsequent calculations of concentration distributions. Table 15 shows potential distribution convergence results for the Normal and Skinny boundary conditions with varying crevice gaps. The relevant mesh and time stepping parameters are also included in the table.

Table 15: The conditions under which CREVICER converged to a stable initial potential distribution for the Normal and Skinny boundary conditions with varying crevice gaps.

<table>
<thead>
<tr>
<th>Constant model parameters</th>
<th>Length of potential (pseudo) time step</th>
<th>$10^{-8}$ sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesh density</td>
<td></td>
<td>1 node/1 $\mu$m at crevice mouth, 1 node/100 $\mu$m at crevice tip</td>
</tr>
<tr>
<td>Convergence criteria</td>
<td></td>
<td>Residual &lt; 0.002</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Variable model parameters</th>
<th>Potential distribution converged?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundary condition</td>
<td>Gap ($\mu$m)</td>
</tr>
<tr>
<td>Normal</td>
<td>60</td>
</tr>
<tr>
<td>Normal</td>
<td>20</td>
</tr>
<tr>
<td>Normal</td>
<td>10</td>
</tr>
<tr>
<td>Normal</td>
<td>1.5</td>
</tr>
<tr>
<td>Skinny</td>
<td>60</td>
</tr>
<tr>
<td>Skinny</td>
<td>20</td>
</tr>
<tr>
<td>Skinny</td>
<td>10</td>
</tr>
<tr>
<td>Skinny</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The second type of mathematical instability that was observed was related to the concentration distribution of nickel ions in the crevice. Under certain conditions, the values for the nickel ion concentration at a particular distance into the crevice began to
oscillate. This phenomena is shown in Figure 15. The oscillation occurs at approximately 0.4 mm into the crevice and is visible after 87 sec. Note that after oscillating for a few seconds, the model converges to a mathematically stable, but physically unfeasible concentration distribution (89 sec). Table 16 lists the times at which the chemical instabilities appeared for the Normal, Skinny, and Double Bump boundary conditions under varying crevice gaps. The relevant mesh and time stepping parameters are also included in the table.

Figure 15: A chemical instability. At 87 sec, CREVICER does not converge to a stable solution for the concentration of nickel ions in the crevice. The mathematical oscillations are visible 0.4 mm into the crevice.
Table 16: Time elapsed before the occurrence of a chemical instability for Normal, Skinny, and Double Bump boundary conditions with crevice gaps of 20 µm, 60 µm, and 100 µm.

<table>
<thead>
<tr>
<th>Constant model parameters</th>
<th>Variable model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of chemical (real-time) time step</td>
<td>Time to chemical instability (sec)</td>
</tr>
<tr>
<td>0.1 sec</td>
<td>Boundary condition</td>
</tr>
<tr>
<td>Mesh density</td>
<td>Double Bump</td>
</tr>
<tr>
<td></td>
<td>Double Bump</td>
</tr>
<tr>
<td></td>
<td>Double Bump</td>
</tr>
<tr>
<td></td>
<td>Normal</td>
</tr>
<tr>
<td></td>
<td>Normal</td>
</tr>
<tr>
<td></td>
<td>Normal</td>
</tr>
<tr>
<td></td>
<td>Skinny</td>
</tr>
<tr>
<td></td>
<td>Skinny</td>
</tr>
<tr>
<td></td>
<td>Skinny</td>
</tr>
</tbody>
</table>

5.3 Proof of principle modeling and experiments

Proof of principle experiments were performed to demonstrate the applicability of semiconductor device manufacturing techniques to the fabrication of crevices with rigorously defined dimensions for crevice corrosion experiments. Crevices with rigorously defined dimensions are necessary for comparisons to the results from crevice corrosion models because models assume that crevices have ideal dimensions; that is, no surface irregularities or roughness. The geometry of the crevice plays a critical role in the location of attack and incubation time for crevice corrosion, so it is essential to match the geometry of the experiment with the geometry assumed by the model. In this section, the results of the first attempt at adapting microfabrication techniques to make well-defined crevices are presented. The results of the electrochemical testing performed on the microfabricated crevices are given, as well as the results from simulations of the experiments. Comparisons between the experimental and modeling results are made.
5.3.1 Microfabrication processing results

Eight wafers were processed utilizing the microfabrication techniques detailed in Section 3.3, Section 3.5.1 and Appendix B to make samples for the proof of principle experiments. Half of the wafers were used for each type of sample and four samples were processed simultaneously on each wafer, so the final yield was sixteen each of crevice formers and substrates. There were no losses due to processing difficulties; all of the samples were usable for experiments.

The mask design used to pattern the crevice former wafers is shown in Figure 16. The figure is not to scale; the actual mask pattern fits within a one-inch diameter wafer. The dark regions on the mask define the unetched regions, or ‘legs’ of the crevice formers. Note that there are four separate crevice former patterns in the mask. Four formers were fabricated together and the wafers were diced to separate the samples in the last step of processing. A photo of one of the completed formers is shown in Figure 17. A sample profilometry measurement showing the etch depth of a crevice former is shown in Figure 18. Table 17 gives the depths for each of the formers. These depths determined the crevice gaps of the assembled crevices.
Figure 16: The mask used to pattern the crevice formers. The dark regions on the mask define the oxide ‘legs’ of the formers.

Figure 17: A photo of a completed crevice former.
Figure 18: Sample profilometry scan showing the etch depth for one of the crevice formers. The etch depth determines the gap of the assembled crevice.

Table 17: Etch depths for each of the microfabricated crevice formers.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Etch depth (µm)</th>
<th>Sample ID</th>
<th>Etch depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-S-1 A</td>
<td>0.96</td>
<td>2-S-3 A</td>
<td>11.85</td>
</tr>
<tr>
<td>2-S-1 B</td>
<td>1.04</td>
<td>2-S-3 B</td>
<td>11.70</td>
</tr>
<tr>
<td>2-S-1 C</td>
<td>1.00</td>
<td>2-S-3 C</td>
<td>12.78</td>
</tr>
<tr>
<td>2-S-1 D</td>
<td>1.03</td>
<td>2-S-3 D</td>
<td>12.04</td>
</tr>
<tr>
<td>2-S-2 A</td>
<td>5.28</td>
<td>2-S-4 A</td>
<td>66.24</td>
</tr>
<tr>
<td>2-S-2 B</td>
<td>5.06</td>
<td>2-S-4 B</td>
<td>66.16</td>
</tr>
<tr>
<td>2-S-2 C</td>
<td>4.88</td>
<td>2-S-4 C</td>
<td>68.63</td>
</tr>
<tr>
<td>2-S-2 D</td>
<td>4.93</td>
<td>2-S-4 D</td>
<td>67.38</td>
</tr>
</tbody>
</table>

The same mask design that was used for the crevice formers (Figure 16) was used to pattern the crevice substrate wafers. In this case, however, the dark regions on the mask define the oxide portions of the crevice substrates, while the light areas are where gold was deposited. The oxide on the crevice substrates is the region where the ‘legs’ on the crevice former rested during testing to form a complete crevice. The actual dimensions of gold substrate electrodes were 0.5 cm x 0.8 cm. A photo of one of the completed substrates is shown in Figure 19.
The microfabricated crevice formers were flipped over and pressed against the substrates to form complete crevices. A photo of a cross-section of a complete crevice is shown in Figure 20.

Figure 19: A photo of a microfabricated crevice substrate.

Figure 20: A photo of a cross-section of a completed crevice. Note that the red microscope stage is visible through the 67 µm crevice gap.

5.3.2 Electrochemical Testing

The results of the potentiodynamic scan performed on a 3-cm² gold foil in 0.5 M H₂SO₄ + 0.05 M NiSO₄ are shown in Figure 21. Note that the cathodic reactions are mass transport limited at potentials below –0.1 V (SCE).
After microfabrication of the samples was completed, platinum wires were attached to the substrates and the substrates were mounted on Plexiglas. The crevice formers were flipped over and pressed on top of the substrates to form complete crevices with varying crevice gaps. Potentiostatic holds were performed at –0.4 V (SCE) for varying amounts of time, as detailed in Section 3.5.2. The potentiodynamic results in Figure 21 show that –0.4 V (SCE) is in the diffusion-limited regime for copper deposition. A sample result from one of the potentiostatic holds is shown in Figure 22. For this experiment the crevice gap was 67 µm and the crevice was held potentiostatically at –0.4 V (SCE) for 30 min. Figure 22a shows the current transient for sample, Figure 22b shows photographs of the mouth of the crevice at two different magnifications, and Figure 22c shows a cross-section of the crevice substrate morphology.
as determined by contact profilometry measurements at several points near the mouth of the crevice. The copper deposition profile can be correlated to the darker regions in the photographs.

(a)

(b) edge of wafer

300 μm

thick layer of copper

120 μm

thin layer of copper on gold
Figure 22: a. Current transient for a gold crevice in 0.5 M H$_2$SO$_4$ + 0.05 M NiSO$_4$ held potentiostatically at −0.4 V (SCE) for 30 min. The crevice gap is 67 µm. b. Photos of the crevice mouth. c. Profilometry measurements showing the deposition profile for copper on the gold electrode.

The results of the other potentiostatic holds on crevices with 67 µm gaps were similar to those shown in Figure 22. In the experiments on crevices with 12 µm gaps, however, the region of significant copper deposition was so close to the crevice mouth that it was impossible to attain reliable profilometry measurements because the edges of the crevice mouth tended to be rough and jagged as a result dicing process. Because of this limitation, no experiments were performed on crevices with tighter crevice gaps (using the 5 µm and 1 µm crevice formers).

5.3.3 Modeling

The constants in Equation 7 (Section 4.5.3 and repeated below) were varied to fit a curve to the results of the potentiodynamic scan (Figure 21). The fitted curve was used as the electrochemical boundary condition when the proof-of-principle experiments were
modeled using CREVICER. As Figure 21 indicates, the potentiodynamic data was represented as total current through the sample, not current density. The curve was fitted to this data. Corrections were made for the area of the sample (3 cm²) in CREVICER so current densities were utilized in the model. The values for the constants in the fitted curve were:

\[
i_{\text{total}} = i_{0,\text{an}} 10^{(E - E_{0,\text{an}})/\beta_{\text{an}}} - i_{0,\text{O}_{2}} 10^{(E - E_{0,\text{O}_{2}})/\beta_{\text{O}_{2}}} - i_{0,\text{Cu}} 10^{(E - E_{0,\text{Cu}})/\beta_{\text{Cu}}}
\]

\[E_{0,\text{an}} = 0.461 \text{ V (NHE)}\]
\[E_{0,\text{O}_{2}} = 1.23 + 0.015 \log[O_{2}] + 0.06 \log[H^{+}] \text{ V (NHE)}\]
\[E_{0,\text{Cu}} = 0.342 + 0.03 \log[Cu^{2+}] \text{ V (NHE)}\]
\[i_{\text{lim, O}_{2}} = a [O_{2}]\]
\[i_{\text{lim, Cu}} = b [Cu^{2+}]\]
\[i_{0,\text{an}} = 10^{-8} \text{ A}\]
\[i_{0,\text{O}_{2}} = 6.347 \times 10^{11} \text{ A}\]
\[i_{0,\text{Cu}} = 2.632 \times 10^{-12} \text{ A}\]
\[\beta_{\text{an}} = 0.02\]
\[\beta_{\text{O}_{2}} = 0.046905\]
\[\beta_{\text{Cu}} = 0.034359\]
\[a = 3.6 \times 10^{-4}\]
\[b = 1.2 \times 10^{-4}\]
The concentrations of $O_2$, $H^+$, and $Cu^{2+}$, were set to their bulk values (Table 4) during the curve fitting process because the potentiodynamic scan was performed in bulk solution, but during the model they varied in accordance with the concentration distributions in the crevice. The fitted curve overlaid on the experimental data is shown in Figure 23. Note that a stringent curve fit was not attained at potentials lower than $-0.6$ V (SCE) and higher than $+0.1$ V (SCE). Because the potentiostatic holds were performed at $-0.4$ V (SCE) and the potential drop within the crevice only caused the metal to depolarize as far as $-0.24$ V (SCE) (Figure 25a) the electrochemical behavior of the gold substrate at higher potentials was not needed for the model.

Figure 23: Fitted curve overlaid on the experimental potentiodynamic data for a gold electrode in 0.5 M $H_2SO_4 + 0.05$ M NiSO$_4$. At all times the potential in the crevice was $<-0.24$, so a stringent curve fit at more cathodic potentials was not needed.
Reliable profilometry measurements of the copper deposition profile were only achieved for crevices with 67-µm gaps, so only that system was modeled using CREVICER. Only the first five real-time minutes of the potentiostatic hold were modeled because of limitations in computational speed. These tests were performed prior to the implementation of the new solver routine for CREVICER, so modeling five real-time minutes required approximately 100 computational hours. The experiments were run for thirty minutes, however, so the modeling results had to be extrapolated out to thirty minutes to determine a copper deposition profile that could be compared to the experimental results. Figure 24 shows the linear extrapolation of the copper flux for several points along the crevice length. In general, for the first two minutes of the potentiostatic hold, the thickness of the copper increased rapidly. After about two minutes the deposition rate leveled off and remained constant for the duration of the test. The region where the deposition rate was constant was extrapolated out to thirty minutes, as shown in the zoom box in Figure 24.
Figure 24: The linear extrapolation of the copper flux to 30 min for several points along the crevice length. The zoom box shows the transition to a constant deposition rate.

The potential and copper concentration transients are shown in Figure 25. The potential transient (Figure 25a) shows that the potential increases with distance into the crevice. The copper concentration transient (Figure 25b) indicates that initially the copper is at its bulk concentration (5 mM) everywhere inside the crevice. After the potentiostatic hold begins, copper is depleted inside the crevice as it deposits on the gold substrate. Note that the crevice can be broken up into three regions with distinct copper depletion behaviors: <0.8 mm, 0.8-4 mm, and 4-8 mm. At distances less than 0.8 mm into the crevice a steep gradient in copper concentration develops. During the first 30 seconds, the copper concentration depletes more rapidly in the 0.8-4 mm region than in the 4-8 mm region. From 30-120 seconds, these roles are reversed: copper concentration depletes more rapidly in the 4-8 mm region than in the 0.8-4 mm region. After 120
seconds, the copper at distances greater than 0.8 mm into the crevice is nearly completely depleted. This depletion can be correlated with the beginning of the linear regions in the copper flux transients shown for various points along the crevice length in Figure 24.

Figure 25: a. The potential transient inside the crevice. b. The copper concentration transient inside the crevice.
The values of the linear extrapolations of the copper flux transients at thirty minutes were used to develop a copper deposition profile that could be directly compared to the experimental results. This profile and the experimentally obtained profiles (from profilometry measurements) for two 67-µm crevices are shown in Figure 26. All three curves follow the same trend: the copper layer is thickest at the mouth of the crevice and drops off rapidly with distance into the crevice. The shapes of all three curves are similar, but the modeling profile is roughly a factor of two greater than the experimental profiles at each point along the crevice length.

Figure 26: Comparison of modeling results to experimentally-obtained copper deposition profiles.
5.4 Scaling law investigations

The small size scale of the microfabricated crevices was utilized to investigate the scaling laws governing IR*-controlled crevice corrosion. Crevices with varying gaps were fabricated, electrochemical tests were performed on the crevices, and their corrosion morphologies were compared. Modeling work augmented the electrochemical tests, filling in gaps between data points and providing insight into which characteristics of the electrochemical behavior of the substrate material determine the controlling scaling law. In this section, the results of the processing of the microfabricated samples are presented followed by data from potentiodynamic scans used to determine the electrochemical behavior of the substrates. The results from the potentiostatic holds performed on the crevices are given, as well as examples of experimental difficulties that were experienced. Modeling results from CREVICER are compared to data from the literature and data from the experiments on the microfabricated samples. Results from models investigating the influence of the shape of the electrochemical boundary condition on the governing scaling law are also presented.

5.4.1 Microfabrication processing results

The processing of the wafers used in the potentiodynamic scans involved cleaning the wafers and evaporating one or more metal layers onto the surface. All wafers prepared in this manner were processed successfully. However, when the first three wafers, each of which had a 0.6 µm layer of nickel on top of a 500 Å layer of chrome, were placed in 0.5 M H₂SO₄, the evaporated nickel layer peeled up and broke away from the silicon substrate, floating off into the solution in several pieces. This problem did not occur with the wafers that had 0.3-µm layers of nickel. Subsequent depositions were
therefore limited to 0.3 μm of nickel. This placed severe limitations on the scan rates of the potentiodynamic scans. If a scan rate slower than approximately 2 mV/sec was used the nickel completely dissolved before the experiment was complete.

Four wafers were processed to make crevice formers for the scaling law experiments. The mask design used for the crevice formers is shown in Figure 27. Six formers were fabricated simultaneously on each wafer, three open on both ends and three open on only one end. The formers open on both ends were used to make crevices that could be oriented in solution with the mouth of the crevice downward, allowing corrosion products to flow out of the crevice by natural convection. The formers with one end closed were used to make crevices that could be oriented in solution with the mouth upward, so corrosion products would be trapped in the crevice, changing the chemistry. The first wafer was accidentally left in the KOH silicon etch bath too long and the entire wafer was dissolved. The other three wafers were processed and diced successfully. Profilometry measurements were taken at both ends of the crevice formers. The results are given in Table 18. The average etch depths, which define the gap of the completed crevice, were 10.94 μm, 45.85 μm, and 95.79 μm. The etch depth varied by a maximum of 5.66% across a former. A photo of a completed crevice former is shown in Figure 28. In this case the former is open on one end and has an etch depth of approximately 46 μm.
Figure 27: The mask design used to fabricate the crevice formers for the scaling law investigations.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Etch depth –front (µm)</th>
<th>Etch depth – back (µm)</th>
<th>Percent variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-S-2 Ao</td>
<td>97.30</td>
<td>96.97</td>
<td>0.34</td>
</tr>
<tr>
<td>3-S-2 Ac</td>
<td>97.87</td>
<td>96.18</td>
<td>1.73</td>
</tr>
<tr>
<td>3-S-2 Bo</td>
<td>96.37</td>
<td>96.52</td>
<td>0.16</td>
</tr>
<tr>
<td>3-S-2 Bc</td>
<td>94.27</td>
<td>96.79</td>
<td>2.67</td>
</tr>
<tr>
<td>3-S-2 Co</td>
<td>95.67</td>
<td>93.14</td>
<td>2.64</td>
</tr>
<tr>
<td>3-S-2 Cc</td>
<td>92.03</td>
<td>96.40</td>
<td>4.75</td>
</tr>
<tr>
<td>3-S-3 Ao</td>
<td>44.80</td>
<td>44.77</td>
<td>0.07</td>
</tr>
<tr>
<td>3-S-3 Ac</td>
<td>45.80</td>
<td>44.77</td>
<td>2.25</td>
</tr>
<tr>
<td>3-S-3 Bo</td>
<td>45.82</td>
<td>46.73</td>
<td>1.99</td>
</tr>
<tr>
<td>3-S-3 Bc</td>
<td>46.64</td>
<td>45.21</td>
<td>3.07</td>
</tr>
<tr>
<td>3-S-3 Co</td>
<td>46.53</td>
<td>46.88</td>
<td>0.75</td>
</tr>
<tr>
<td>3-S-3 Cc</td>
<td>46.89</td>
<td>45.01</td>
<td>4.01</td>
</tr>
<tr>
<td>3-S-4 Ao</td>
<td>11.08</td>
<td>10.85</td>
<td>2.08</td>
</tr>
<tr>
<td>3-S-4 Ac</td>
<td>10.43</td>
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<td>10.55</td>
<td>10.50</td>
<td>0.47</td>
</tr>
<tr>
<td>3-S-4 Bc</td>
<td>10.93</td>
<td>11.17</td>
<td>2.20</td>
</tr>
<tr>
<td>3-S-4 Co</td>
<td>11.39</td>
<td>10.96</td>
<td>3.78</td>
</tr>
<tr>
<td>3-S-4 Cc</td>
<td>11.00</td>
<td>11.35</td>
<td>3.18</td>
</tr>
</tbody>
</table>

Table 18: Etch depths at the front and back of the crevice formers fabricated for scaling law investigations.
The mask design used for the first set of crevice substrates for the scaling law experiments is shown in Figure 29. Four samples were fabricated on each wafer and nine wafers were processed. Well-defined 4 mm x 7 mm rectangular slots with nickel as the substrate material were achieved. During the substrate fabrication it was observed that when more than 0.6 \( \mu \)m of nickel was evaporated onto the substrate, the photoresist defining the crevice geometry began to peel, allowing nickel to reach the underlying oxide, ruining the nickel lift-off process. For this reason the thickness of the nickel layer on the substrates was limited to 0.6 \( \mu \)m, restricting the duration of the electrochemical experiments. During the dicing process, the nickel sometimes tore and peeled off at the mouth of the crevice, resulting in a jagged line of nickel just inside the mouth. Except where noted, substrates that were damaged in this way were not used.
Figure 29: The mask design used to define the geometry of the first set of substrates used in the scaling law experiments.

The sample design was altered in the second set of crevice substrates in an attempt to minimize the effects of nickel peel-up along the diced edges. The mask design for this set is shown in Figure 30. Three samples were fabricated on each wafer and twelve wafers were processed. When diced, the samples were cut close to the oxide on the three closed sides of the substrate, but well away from the crevice mouth. A photo of a completed substrate is shown in Figure 31. Well-defined 4 mm x 7 mm rectangular nickel slots with a region of boldly exposed nickel outside of the crevice were achieved.

Figure 30: Mask design used to define the geometry of the second set of crevice substrates used in the scaling law experiments.
The microfabricated crevice formers were flipped over and pressed against the substrates to form complete crevices with gaps of 11 µm, 46 µm, and 96 µm for the scaling law tests. Cross sections of the three different crevice geometries are shown in Figure 32.
Figure 32: Cross-sections of crevices with gaps of 11 µm, 46 µm, and 96 µm for use in the scaling law experiments. Note that the red microscope stage can be seen through the crevice gaps.

5.4.2 Electrochemical testing

5.4.2.1 Potentiodynamic scan results

The potentiodynamic scans performed on the microfabricated wafers and the epoxy-mounted nickel balls had two primary purposes: to determine the electrochemical behavior of the crevice substrates for use as a boundary condition in CREVICER, and to determine the influence of nickel accumulation in the crevice on this electrochemical behavior. To achieve the first goal, scans were run at varying scan rates on bare silicon wafers, silicon with only the chrome adhesion layer, and silicon with chrome and nickel layers. This series of scans was utilized to be sure it would be evident if the nickel
substrate was depleted during a crevice experiment. The results of these scans are overlaid in Figure 33. Scans were also performed on the epoxy-mounted nickel balls to achieve slower scan rates and for comparison to the literature. The results of these scans are shown in Figure 34.

![Graph](image)

**Figure 33:** The results of potentiodynamic scans performed on Si, Si+0.5μm of Cr, and Si+0.05μm Cr + 0.3μm Ni at varying scan rates. Environment is 0.5 M H_2SO_4.
Microfabricated substrate wafers and epoxy-mounted nickel balls were used in the second set of potentiodynamic scans. The environments were sulfuric acid solutions with varying concentrations of nickel sulfate. The measured conductivity of each solution is shown in Table 19. The purpose of the scans was to investigate the influence of nickel ion concentration on the electrochemical behavior of the nickel substrate. The results of these scans (Figure 35) were used to determine whether or not it was legitimate to use the same electrochemical boundary condition throughout a time-transient model. The data indicates that the nickel in solution causes only a small (<50 mV) shift in the position of the active nose, even when the solution is saturated. Modeling results (Figure 48) show that the nickel concentration inside the crevice does not exceed 0.35 M during a 2 min potentiostatic hold, a concentration well below the saturation point. Therefore, for this
study, the electrochemical behavior of the nickel was assumed to be constant through
time, and only one electrochemical boundary condition was used throughout each model.

Table 19: Measured conductivities of the solutions used for potentiodynamic scans on
microfabricated nickel substrate and epoxy-mounted nickel pellets.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Conductivity, $\kappa$ (1/Ω-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M H$_2$SO$_4$</td>
<td>190.3</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$ + 1 M NiSO$_4$</td>
<td>136.0</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$ + Saturated NiSO$_4$</td>
<td>85.7</td>
</tr>
</tbody>
</table>
5.4.2.2 Potentiostatic hold results

A typical result of a potentiostatic hold is shown in Figure 36. In this case, a crevice with a 46-µm gap was held at +0.3 V vs. SCE for 2 min. A photo showing the appearance of the crevice substrate after the test is shown in Figure 36a. The substrate current as a function of time is shown in Figure 36b. A plot of the profilometry measurements taken on the sample is seen in Figure 36c, showing the cross-sectional profile of the crevice substrate morphology. The profile can be correlated to the regions of visible attack on the photo.
A summary of the results of the potentiostatic holds is given in Table 20. The orientation indicates whether the mouth of the crevice was oriented upward or downward. The potential listed is that at which the crevice was potentiostatically held during the test. The distance from the mouth of the crevice to the front of the corrosion band ($x_{\text{pass}}$) and the width of the region of severe attack ($w_a$) were measured using an optical microscope. $x_{\text{crit}}$ is the distance from the mouth of the crevice to the center of the region of severe attack ($x_{\text{pass}} + w_a/2$). $x_{\text{crit}}$ and $w_a$ are indicated on the photo in Figure 36a. $I_m$ is the mean substrate current. The crevices not included in Table 20 did not have clean corrosion bands as a result of one of a variety of experimental difficulties, which will be discussed further in Section 5.4.2.3.
Several features of the data shown in Table 20 should be noted. Samples 2-S-6A, 2-S-6B, 2-S-6C, and 2-S-5D show that the results for a 50 µm crevice oriented downward were fairly reproducible. Samples 2-S-6A, 2-S-6B, and 2-S-7A suggest that $x_{\text{crit}}$ moves further from the crevice mouth with increasing applied potential. Samples 2-S-7B, 2-S-6B, and 3-S-11B show that $x_{\text{crit}}$ moves farther from the crevice mouth with increasing gap. This progression is shown in Figure 37. Sample 2-S-5B (Figure 38) shows that orienting the crevice with the mouth open upward causes corrosion to occur over a more extended region of the crevice than in cases where natural convection can prevent occluded chemistry changes.

Table 20: Summary of crevice corrosion tests for Ni in 0.5 M H$_2$SO$_4$. $w_a$ = width of the region of severe attack, $x_{\text{crit}}$ = distance from the mouth of the crevice to the center of the region of severe attack, $I_m$ = mean substrate current.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Orientation</th>
<th>Gap (µm)</th>
<th>Potential ($V_{\text{SCE}}$)</th>
<th>Test Duration (min)</th>
<th>$x_{\text{crit}}$ (mm)</th>
<th>$w_a$ (mm)</th>
<th>$I_m$ (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-S-6A</td>
<td>Down</td>
<td>50</td>
<td>0.300</td>
<td>2</td>
<td>0.92</td>
<td>0.52</td>
<td>0.302</td>
</tr>
<tr>
<td>2-S-6B</td>
<td>Down</td>
<td>50</td>
<td>0.300</td>
<td>2</td>
<td>0.99</td>
<td>0.35</td>
<td>0.250</td>
</tr>
<tr>
<td>2-S-6C</td>
<td>Down</td>
<td>50</td>
<td>0.250</td>
<td>2</td>
<td>1.25</td>
<td>0.55</td>
<td>0.597</td>
</tr>
<tr>
<td>2-S-7A</td>
<td>Down</td>
<td>50</td>
<td>0.400</td>
<td>2</td>
<td>1.88</td>
<td>0.58</td>
<td>0.315</td>
</tr>
<tr>
<td>2-S-7B</td>
<td>Down</td>
<td>10</td>
<td>0.300</td>
<td>1</td>
<td>0.92</td>
<td>0.33</td>
<td>0.250</td>
</tr>
<tr>
<td>2-S-9D</td>
<td>Down</td>
<td>100</td>
<td>0.250</td>
<td>2</td>
<td>2.13</td>
<td>0.39</td>
<td>0.372</td>
</tr>
<tr>
<td>2-S-5B</td>
<td>Up</td>
<td>100</td>
<td>0.300</td>
<td>2</td>
<td>n/a</td>
<td>n/a</td>
<td>1.56</td>
</tr>
<tr>
<td>2-S-5D</td>
<td>Down</td>
<td>50</td>
<td>0.300</td>
<td>2</td>
<td>0.95</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>3-S-7B</td>
<td>Down</td>
<td>50</td>
<td>0.300</td>
<td>4</td>
<td>3.44</td>
<td>2.56</td>
<td>0.65</td>
</tr>
<tr>
<td>3-S-8B</td>
<td>Down</td>
<td>50</td>
<td>0.300</td>
<td>3</td>
<td>2.61</td>
<td>0.45</td>
<td>1.55</td>
</tr>
<tr>
<td>3-S-10B</td>
<td>Down</td>
<td>100</td>
<td>0.300</td>
<td>3</td>
<td>1.22</td>
<td>0.25</td>
<td>0.68</td>
</tr>
<tr>
<td>3-S-11A</td>
<td>Down</td>
<td>100</td>
<td>0.300</td>
<td>3</td>
<td>1.01</td>
<td>0.53</td>
<td>0.89</td>
</tr>
<tr>
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<td>0.300</td>
<td>3</td>
<td>2.10</td>
<td>0.42</td>
<td>0.68</td>
</tr>
<tr>
<td>3-S-11C</td>
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<td>50</td>
<td>0.300</td>
<td>3</td>
<td>2.64</td>
<td>0.48</td>
<td>1.05</td>
</tr>
<tr>
<td>3-S-12C</td>
<td>Down</td>
<td>10</td>
<td>0.300</td>
<td>3</td>
<td>1.69</td>
<td>1.34</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Figure 37: Photos showing the movement of \( x_{\text{crit}} \) with crevice gap.
5.4.2.3 Experimental difficulties

Two types of anomalies appeared repeatedly in the potentiostatic hold experiments on the first set of crevice substrates. One type was the jagged nickel edges at the mouth of the crevice that resulted from the nickel layer being torn during the dicing process. The result of a potentiostatic hold performed on one of these samples is shown in Figure 39. Although the edge of the nickel is very jagged, the corrosion band is straight. The other type of anomaly was not immediately evident after fabrication, but appeared after potentiostatic holds were performed on the samples. Rather than having a clean corrosion band, these samples had light attack everywhere, broken up by small circular shapes, shown in Figure 40. The current for these crevices was approximately half that of the crevices in Table 20 and more noisy than those with clear regions of severe attack.
Figure 39: Photo showing the results of a potentiostatic hold performed on a crevice substrate with a nickel layer that was torn during dicing. Although the edge of the nickel is very jagged, the corrosion band is straight.

Figure 40: Photo of the small circular shapes that appeared on substrates that did not have clean corrosion bands.

When the second set of crevice substrates were fabricated, the wafers were placed in the evaporator for metal deposition in two batches of six. The metal liftoff and dicing processes after the evaporation were successful, and all of the samples appeared to be usable. However, when the samples from the first batch were placed in solution and
allowed to drop to open circuit, rings appeared on the metal substrates. These rings at
two different magnifications are shown in Figure 41.

![SEM micrographs of the rings that appeared on some of the substrates after they were placed in 0.5 M H\textsubscript{2}SO\textsubscript{4} and their open-circuit potentials stabilized. Magnifications are 140x and 2500x. All of the samples that exhibited the rings were in the same batch of wafers in the metal evaporator.]

5.4.3 Modeling

CREVICER was used for further investigation of the scaling laws of crevice corrosion. Results of initial models were compared to experimental results from the literature to assess the accuracy of CREVICER. The scaling law experiments described in the previous sections were modeled using two different electrochemical boundary conditions: one from the literature and one from a potentiodynamic scan on a
microfabricated sample. The influence of the shape of the boundary condition on the governing scaling law was examined in greater depth using CREVICER.

5.4.3.1 Comparisons to the literature

In the first set of scaling law models, the geometry, initial conditions, and boundary conditions of experimental work by Pickering[33] were simulated using CREVICER and the results were compared. The mouth of the crevice was held potentiostatically at +0.4 V (SCE), +0.3 V (SCE), and +0.25 V (SCE) and the initial potential distribution in the crevice was found. The modeling results are compared to experimental measurements of the potential distributions in Figure 42. The values for $x_{\text{pass}}$, the distance into the crevice at which the potential is equal to $E_{\text{pass}}$, the passivation potential, are shown for each of the applied potentials. $x_{\text{pass}}$ corresponds to the front edge of the corrosion band in the crevice. In both the experimental (Figure 42a) and modeling (Figure 42b) cases the values for $x_{\text{pass}}$ increase with increased applied potential. In both cases, at $E_{\text{hold}} = +0.25$ V (SCE), $x_{\text{pass}}$ is approximately 2.5 mm, and at $E_{\text{hold}} = +0.3$ V (SCE), $x_{\text{pass}}$ is approximately 3.5 mm. At $E_{\text{hold}} = +0.4$ V, the experimental values for the potential are higher than the values from CREVICER at most points along the crevice length, and as a result the experimental value for $x_{\text{pass}}$ is larger than the modeling value (6.7 mm vs. 5.3 mm).
Figure 42: Potential distribution inside a nickel crevice with a 300 μm gap held potentiostatically at +0.4 V (SCE), +0.3 V (SCE), and +0.25 V (SCE). a) Experimental measurements by Pickering\textsuperscript{[33]}. b) Modeling results from CREVICER.

5.4.3.2 Investigating the effects of the shape of the boundary condition

Extensive modeling work was used to investigate the influence of the shape of the electrochemical boundary condition on the governing scaling law. This work was
motivated by early modeling results that suggested that two different scaling factors were applicable in two systems that were identical except for the shape of their boundary conditions. Before those results are presented, however, it should be explained how information on the applicable scaling factor is derived from the output of CREVICER.

5.4.3.2.1 Determination of \( x_{\text{crit}} \) from CREVICER output

As was described in Section 2.3, the two scaling factors pertaining to IR*-controlled crevice corrosion discussed in the literature are \( L^2_p/G \) and \( L_p/G \), where \( L_p \) is the distance from the mouth of the crevice to the corrosion band and \( G \) is the crevice gap. Therefore, in order to determine the appropriate scaling factor, a value for \( L_p \) must be derived from the output of CREVICER (\( G \) is an input parameter). As was discussed briefly in Section 5.4.3.1, Pickering\[^{33}\] uses the parameter \( x_{\text{pass}} \) to define the location of the corrosion band. \( x_{\text{pass}} \) is the distance into the crevice at which the potential is equal to \( E_{\text{pass}} \), the passivation potential for the substrate material. \( x_{\text{pass}} \) corresponds to the edge of the corrosion band closest to the mouth of the crevice. In this study, however, the parameter \( x_{\text{crit}} \) was used to define the location of the corrosion band. \( x_{\text{crit}} \) is the distance into the crevice at which the potential is equal to \( E_{\text{peak}} \), the potential corresponding to the peak current density. \( x_{\text{crit}} \) corresponds to the point along the crevice length where the attack is most severe. \( x_{\text{crit}} \) was chosen for experimental reasons; in the potentiostatic hold experiments it was found that the width of the corrosion band varied significantly (Table 20) and that the front edge of the attack band was often not clearly delineated. The point of severest attack was visually observed to occur approximately in the center of the corrosion band, so the distance from the mouth of the crevice to the center of the corrosion band was used as a measurement of \( x_{\text{crit}} \).
The method used to calculate $x_{\text{crit}}$ from the modeling results is shown in Figure 43. Highlighted by the red dashed line on the electrochemical boundary condition is $E_{\text{peak}}$, the potential at the peak current density. Once $E_{\text{peak}}$ is determined from the boundary condition, the potential distribution in the crevice (output by CREVICER at each time step) is used to find the point along the crevice length where $E_{\text{peak}}$ is reached. The distance from the mouth of the crevice to this point is $x_{\text{crit}}$.

![Figure 43: Technique used to derive $x_{\text{crit}}$ from the output of CREVICER. $E_{\text{peak}}$ is determined from the electrochemical boundary condition and the potential distribution in the crevice is used to find the distance into the crevice where the potential is equal to $E_{\text{peak}}$.](image)

5.4.3.2.2 Motivation for boundary condition shape investigations

Figure 44 shows the preliminary modeling results that motivated the investigations of the influence of the shape of the boundary condition on the governing scaling law factor. Figure 44a and Figure 44b show two boundary conditions with similar open circuit potentials and passive current densities but differently shaped active noses. The boundary conditions are from Pickering’s work$^{[33]}$ (Figure 44a) and from preliminary results on microfabricated crevice substrates (Figure 44b). Models were run using these boundary conditions and values for $x_{\text{crit}}$ were determined for a sequence of
crevice gaps. \( x_{\text{crit}} \) vs. Gap for the two boundary conditions is shown in Figure 44c and \( x_{\text{crit}}^2 \) vs. Gap is shown in Figure 44d. In these plots, a linear relationship indicates the applicability of a particular scaling factor. Although the differences are small, Figure 44d indicates that \( x_{\text{crit}}^2 / G \) is the applicable scaling factor for the boundary condition in Figure 44b (the one obtained on a microfabricated sample), whereas Figure 44c indicates that \( x_{\text{crit}} / G \) is the applicable scaling factor for the boundary condition in Figure 44a (from the literature). Because the shape of the boundary condition was the only parameter that differed between the two cases, these results suggest that the shape of the boundary condition influences the applicability of a particular scaling factor.

![Graphs showing results from two boundary conditions](image)

**Figure 44:** Motivation for investigating the role of the shape of the boundary condition in determining the applicable scaling factor. a) Boundary condition from Pickering\(^{[33]}\) b) Boundary condition from a microfabricated sample c) \( x_{\text{crit}} \) vs. Gap for the two boundary conditions. Note the linearity of the relationship for Pickering's boundary condition. d) \( x_{\text{crit}}^2 \) vs. Gap for the two boundary conditions. Note the linearity of the relationship for the boundary condition from a microfabricated sample.
5.4.3.2.3 Scaling law results

The influence of the shape of the electrochemical boundary condition on the governing scaling factor was investigated using six different mathematical functions to represent boundary conditions with different characteristics (e.g., size and shape of active nose). The equations and graphical representations of the functions were given in Section 4.6.3.3. Values for $x_{\text{crit}}$ were determined for each of the boundary conditions for a range of crevice gaps. Figure 45 shows $x_{\text{crit}}$ vs. Gap and $x_{\text{crit}}^2$ vs. Gap for the six boundary conditions. In all cases, the $x_{\text{crit}}^2$ vs Gap relationship is more linear than the $x_{\text{crit}}$ vs. Gap relationship. The $x_{\text{crit}}^2$ vs. Gap relationship for the Skinny and Shifted curves are slightly nonlinear at large crevice gaps. It should be noted that $x_{\text{crit}}$ is nearing the length of the crevice (7 mm) at these points.
Figure 45: $x_{\text{crit}}$ vs. Gap and $x_{\text{crit}}^2$ vs. Gap for the six boundary conditions generated from mathematical functions.
The boundary condition from the literature that served as motivation for this study (Figure 44a) was used again to model a larger range of crevice gaps, from 10 µm to 150 µm. The $x_{\text{crit}}$ vs. Gap relationship for this boundary condition over the extended range of gaps is shown in Figure 46b. Also shown in Figure 46b are the $x_{\text{crit}}$ vs. Gap relationships over the broad range of gaps for the Skewed and Double Bump boundary conditions. The three boundary conditions are overlaid in Figure 46a.

**Boundary Conditions**

![Boundary Conditions Graph](image-url)
Figure 46: Comparison of boundary conditions (a) and \( x_{\text{crit}} \) vs. Gap relationships (b) for two mathematically-generated boundary conditions and one boundary condition from the literature.

5.4.3.2.4 Time transient results

An example of time transient result from the boundary condition shape modeling study is shown in Figure 47. In this case, the Normal boundary condition was used and the crevice gap was 100 \( \mu \text{m} \). Figure 47a shows the movement of the potential distribution in the crevice through time. Figure 47b show the morphology of the corrosion attack inside the crevice through time. This dissolution profile was calculated using Faraday’s law from the values for the nickel flux output by CREVICER at each time step. Three points of interest are highlighted on this profile: the edge of the corrosion attack nearest the mouth of the crevice (\( x_{\text{pass}} \)), the point of maximum nickel dissolution after 120 sec (\( x_{\text{crit \ max \ dissolution}} \)), and the point corresponding to \( x_{\text{crit}} \) as calculated using the initial potential distribution output by CREVICER (\( x_{\text{crit modeling}} \)).
Figure 47: The time transient result for the Normal boundary condition with a crevice gap of 100 µm. a) The movement of potential distribution in the crevice through time. b) The morphology of the corrosion attack through time.

The time transient results for two different boundary conditions are compared in Figure 48. The boundary conditions are Normal and Double Bump. In both cases the crevice gap is 100 µm. The development of the nickel concentration distributions and the corrosion morphologies through time are shown for the two boundary conditions.
5.4.3.3 Comparisons to experiments on microfabricated crevices

Two sets of models were run using the geometries and environmental conditions from the scaling law experiments detailed in Section 5.4.2. In each set the crevice gap was
varied from 10 to 100 µm while the other parameters were held constant. In one set the potentiodynamic scan data from Pickering’s work\textsuperscript{[33]} was fitted with higher order polynomials and used as the electrochemical boundary condition. The scan rate was 0.08 mV/s and the substrate material was commercially pure (99.53 wt%) nickel. In the other set, the results of a potentiodynamic scan on one of the microfabricated wafers was used. The data is from this scan is shown in red in Figure 49a. The sudden decrease in the current at $E = +0.14$ V (SCE) indicates that the nickel layer was depleted before the scan was completed. Unfortunately, samples with thicker layers of nickel could not be fabricated because of limitations imposed by the metal lift-off process. When 0.6 µm of nickel was deposited, the photoresist began to peel up, allowing metal to reach the underlying silicon, ruining the lift-off. To circumvent the nickel depletion problem and obtain a usable electrochemical boundary condition, potentiostatic holds were performed at potentials of $+0.3$ V (SCE) (Table 10) to verify the value of the passive current density. The result of one of these holds is shown in Figure 49b. The current approaches $1.6 \times 10^{-4}$ A as the wafer passivates, a value which corresponds to the value of the current immediately preceding the depletion of the nickel during the potentiodynamic scan (Figure 49a). Therefore, for use in CREVICER, polynomials were fitted to the potentiodynamic scan data below $E = +0.14$ V (SCE), and the current was set to a constant $1.6 \times 10^{-4}$ A above that potential. The fitted curve is shown in green in Figure 49a.
Figure 49: a. Results from potentiodynamic scan on microfabricated nickel sample overlaid with fitted curve used as electrochemical boundary condition in models. b. Current transient from nickel sample held potentiostatically at +0.3 V (SCE). Used to determine passive current density for fitted curve in a.

$x_{\text{crit}}$ as a function of crevice gap for the models using the two different boundary conditions are shown in Figure 50. Included in the plots are some of the data points from the scaling law experiments performed on the microfabricated crevices (Table 20).
Figure 50: $x_{crit}$ vs. $G$ for the boundary condition from the literature and the boundary condition obtained on the microfabricated samples. Overlaid are data points from the scaling law experiments performed on the microfabricated crevices.
Chapter 6: Discussion

6.1 Improvements to the CREVICER model

The advantages of the additions and improvements included in Version 2 and Version 2-GUI of CREVICER are discussed in this section. These benefits include the increased speed and decreased static memory requirements that resulted from the implementation of the new solver routine as well as the expanded applicability of CREVICER that resulted from the addition of a routine to account for aluminum hydrolysis reactions. The numerous advantages of the GUI, all of which are related to increased usability of the model, are also discussed.

6.1.1 Implementation of a new solver routine

There are several advantages to the new Solve algorithm implemented for Version 2 of CREVICER. In the old Solve procedure, a static NxN array (where N = the number of nodes in the finite element mesh) was used to represent the matrix utilized in the finite element technique. Because this matrix was static, or fixed in size, the memory for it was allocated at compile-time. However, most C++ compilers (e.g., Microsoft Visual C++™) put a stringent limit on the amount of memory that can be statically allocated. This rule limits the size of the array that can be utilized by CREVICER, which in turn means that the number of nodes in the mesh is limited. Exploring more complex crevice environments, particularly ones that have two-dimensional features like subcrevices or inclusions, requires an increasingly fine, dense mesh, with a larger number of finite elements and nodes. Therefore, because the array in the Solve routine was statically allocated, the capabilities of CREVICER Version 1 were limited. In the new Solve
algorithm, the large majority of the array is dynamically allocated. A one-dimensional array of size N of pointers is statically allocated (one to identify each row in the matrix) but all of the elements in the rows are created and destroyed as needed during the execution of the program. This approach enables the use of much denser meshes with many more nodes, increasing the capabilities of the model. For example, a model running in Microsoft Visual C++™ is limited to approximately 3000 nodes when the old solver routine is used because an array with 9,000,000 elements (NxN) has to be statically allocated. With the new solver routine, however, up to 9,000,000 nodes can be used because only a 1-D array of size N is statically allocated.

Another notable feature of the new Solve algorithm is that the rows of the matrix are represented using a sparse matrix notation, meaning that only the nonzero elements of each row are stored. As was explained in Section 4.1.1, the vast majority of the elements in the matrix are zero, so representing the matrix using a sparse notation is beneficial. This representation decreases the amount of memory that is dynamically allocated and deallocated and speeds up the model significantly. More than 95% of the execution time of CREVICER Version 1 is spent in the Solve routine, performing row reduction and back substitution operations to solve the matrix. The sparse matrix notation eliminates unnecessary comparisons and operations on zero elements. As can be seen from the time trial data in Table 13, the implementation of the new Solve routine in Version 2 of CREVICER increased the speed of the model by more than an order of magnitude.

The only significant disadvantage of the new Solve routine is that it is more complicated and less intuitive than the old routine. This increased complexity made
debugging of the code during development laborious and time-consuming and would make future changes or additions to the Solve routine more difficult.

6.1.2 Addition of aluminum hydrolysis reactions

Another improvement in Version 2 of CREVICER is the addition of a procedure to correct the concentrations of aluminum and aluminum hydrolysis product ions to account for the occurrence of the aluminum hydrolysis reactions in the solution inside the occluded region. Tests performed to assess the accuracy of the new routine showed fair correlation to the literature (Figure 7). For pH values < 6, where Al\(^{3+}\), AlOH\(^{2+}\), and AlOH\(^{2+}\) are the predominant ions, the percentages of the hydrolysis products match the values from the literature very closely. At pH values between 6 and 9, however, where AlOH\(_3\) and AlOH\(_4\)^{-} are the predominant ions, the percentage of AlOH\(_3\) is significantly lower (up to 30\%) than the reported value and the percentage of AlOH\(_4\)^{-} is correspondingly higher. The reason for this discrepancy is unclear. One possibility is that the limits of the precision of the numerical values of the variables play a role at near neutral pH, where the concentration of hydrogen ions is a very small number. If so, the procedure could be rewritten using logarithmic values. It should be noted that this procedure was never used in this study, so the discrepancy between the CREVICER output and the literature had no impact the results presented in Chapter 5. The aluminum hydrolysis procedure was implemented only as a useful addition to CREVICER; extensive testing of its accuracy was not part of this study.
6.1.3 Implementation of a graphical user interface

The graphical user interface was one of the most significant improvements to CREVICER. To set the environmental parameters for a model using the previous version of CREVICER, the user had to alter the source code and recompile the program before running the model. In most cases, it was necessary to make changes in several different procedures and even to define new C++ classes. These alterations required detailed knowledge of the structure of CREVICER, so running a model required the assistance of one of a handful of CREVICER experts. The GUI provides an interface that distances the user from the source code, so intimate knowledge of it is no longer required. The GUI utilizes standard Windows™ conventions including text boxes, function buttons, and input fields, and has a step-by-step user’s guide that remains on the screen at all times. These features enable any person familiar with Windows 95™-style applications to use the model, widening the pool of potential users dramatically.

The other primary improvement the GUI provides for CREVICER is a visual representation of the crevice geometry and the finite element mesh. The user can simply point and click on nodes and elements and set boundary or localized conditions at those points. Previously, the user could only access particular nodes or elements using their x- and y-coordinates. For example, setting a constant potential at the mouth of the crevice required searching through all of the nodes and finding those with y-coordinates equal to zero (corresponding to the mouth of the crevice) and fixing the value of the potential for those nodes. With the GUI, the user can see the nodes on the screen, click on the ones at the mouth, and set the boundary conditions. Setting localized conditions, such as a different material for a small region in the crevice (simulating an inclusion) was even
more difficult without the GUI because the user had to know the coordinates where the
inclusion was to be located and search through all of the elements to find ones that had
nodes with coordinates within that range. The GUI simplifies this process dramatically;
the picture of the mesh on the screen and the zoom box allow the user to easily identify
the elements of interest and alter their properties.

6.1.4 Implementation of changes to CREVICER to interact with the GUI

The changes implemented to allow CREVICER to interact with the GUI provided
several advantages in themselves, in addition to enabling communication between the
model and the GUI. The new C++ classes that were defined to allow the generic
definition of species, reactions, and materials by the GUI user generalized these
definitions in the model. As a result, even if the GUI is not used, it is no longer necessary
to have intimate knowledge of the structure of CREVICER to run models with it. The
definitions of the environmental parameters for the model can all be made in the main
procedure. In addition, the revisions in CREVICER Version 2-GUI make it possible to
compile and run the model on a PC platform using a Borland C++™ V.5 or Microsoft
Visual C++™ compiler. The availability of these compilers in addition to the UNIX-
based gnu compiler that the previous version of CREVICER ran on makes CREVICER
Version 2-GUI more versatile.

6.2 Testing the capabilities of CREVICER

The results of the tests performed to assess the influence of mesh density and user-
deefined initial potential distribution on the potential distributions calculated by
CREVICER are discussed in this section. Observations are made about the convergence
limits of CREVICER using the results of the models from the scaling law investigations. Emphasis is placed on the dependence of convergence on the crevice gap and the shape of the electrochemical boundary condition. The practical utility of the convergence observations for providing guidelines for mesh and time step parameter selection is discussed.

6.2.1 Assessing the variability of the results

The results of both of the tests run on CREVICER to investigate the variability of the numerical solutions of the model were reassuring. In the first test, all of the parameters of the model were held constant except for mesh density and the initial potential distribution in the crevice was calculated. As can be seen in Figure 13, there is no significant difference between the two solutions. This result indicates that a coarser mesh can be used in place of a finer mesh without sacrificing accuracy of the model. This is a useful result because it is often desirable to utilize a coarser mesh in the interest of computational speed (fewer nodes = fewer calculations = less time required to run the model). There is a limit to the level of coarseness that can be utilized, however. At some point CREVICER can no longer converge to a numerically stable solution. These convergence limits are discussed in greater detail in Section 6.2.2.

In the second test, the steady-state potential distribution in the crevice was calculated for two cases that were identical except for their user-defined initial potential distributions. Figure 14 shows that there is no significant difference between the steady-state potential distributions found for the two cases. This result indicates that the user does not need to worry that what he selects as an initial potential distribution will have an effect on the outcome of the model, provided that CREVICER can still converge to a
stable solution. The more the initial potential distribution differs from the steady-state solution the longer the convergence process takes, however, so in the interest of time the user is still better off selecting an initial potential distribution that is a reasonable approximation of the steady-state solution. For a situation where the substrate material has an active/passive transition and the mouth of the crevice is held at a constant potential in the passive region, so that the potential decreases with distance into the crevice due to IR drop, the open circuit potential for the substrate material is a reasonable initial condition for the crevice. An alternative is to have the potential drop linearly from the value at the mouth to the open circuit potential at the tip of the crevice. If a material is held at a potential more anodic than the open circuit potential (e.g., cathodic protection or electroplating), the material inside the crevice will tend to depolarize, meaning that the potential will increase with distance into the crevice until it reaches the open circuit potential. In this case, the open circuit potential is again a good choice for an initial condition. An alternative is a linear potential increase from the value at the mouth to the open circuit potential at the tip of the crevice.

6.2.2 Examining the convergence limits

The motivation for the observations made about the convergence limits of CREVICER was the necessity of providing novice CREVICER users with guidelines for the selection of mesh and time step parameters appropriate for their system. In the interest of computational speed it is desirable the use the coarsest mesh and longest time step lengths possible while still maintaining the needed spatial and temporal resolution. However, at some level of coarseness CREVICER can no longer converge to a stable numerical solution. These observations were aimed at providing an outline of the
combinations of parameter values that will or will not achieve convergence. An exhaustive, quantitative evaluation of the convergence limits of CREVICER was not the goal.

The set of models used to investigate the influence of the shape of the electrochemical boundary condition on the governing scaling law proved to be useful for making observations about the convergence limits of CREVICER because all other parameters in the models were held constant while the crevice gap and the shape of the electrochemical boundary condition were varied. Therefore, convergence of the model could be correlated to changes in these parameters. This correlation is particularly useful for practical applications because the crevice gap and the shape of the boundary condition are two parameters that often vary experimentally.

Table 15 shows that under the given mesh and potential time step parameters (mesh density varying from 1 node/1 µm at mouth to 1 node/100 µm at tip, potential time step length = $10^{-8}$), the Normal and Skinny boundary conditions converged to a stable initial potential distribution for all crevice gaps except Skinny at a 1.5 µm gap. In general, this means that CREVICER has more difficulty converging at tighter crevice gaps and for electrochemical boundary conditions with thinner, sharper active noses. This observation makes intuitive sense because both of these parameters correspond to steeper potential gradients. A tighter crevice gap causes more IR drop, so the potential drops off more steeply just inside the crevice mouth. A steeper gradient in potential increases the potential difference between adjacent nodes in the mesh, making convergence across the nodes more difficult. Decreasing the distance between nodes
(increasing the mesh density) would decrease the potential difference between them, which would help alleviate a convergence problem.

These data provide practical guidelines for utilizing CREVICER. A user could compare his experimental conditions (boundary condition and crevice gap) to the parameters in Table 15 and then adjust the mesh and time step parameters to find a convergent combination. For example, if his boundary condition is similar to Skinny and his crevice gap is 1 µm, then he should use a higher density mesh or shorter potential time steps than those outline in Table 15. However, it should be noted that these tables only provide guidelines, not strict rules. Other parameters (e.g., solution conductivity) also influence the ability of CREVICER to converge to a stable solution.

Two trends are evident from the chemical convergence data in Table 16. CREVICER becomes unstable earlier for tighter crevice gaps and for electrochemical boundary conditions with wider active noses. If the crevice gap is tighter, the concentration of nickel ions in solution will increase more rapidly because there is less volume of solution for it to disperse into. This rapid increase in nickel ion concentration gives rise to a steep concentration gradient at the mouth of the crevice, where the nickel concentration is fixed at zero (the bulk value). This steep gradient causes the instability.

A wider active nose on the electrochemical boundary condition has a similar effect. Because the peak current densities of the active noses of the boundary conditions were kept constant, a wider active nose means that a larger amount of current is passed. A larger current corresponds to a larger quantity of nickel ions entering the solution, so again a steep concentration gradient is developed quickly, causing the instability.
The data in Table 16 also provides practical guidelines for utilizing CREVICER. A user could compare his experimental conditions to the boundary conditions and crevice gaps in the table, decide how many seconds he wishes to model, and shorten the length of the chemical time steps or increase the density of the mesh accordingly.

6.3 Proof of principle modeling and experiments

This set of experiments demonstrates that microfabrication techniques can be utilized to fabricate crevices with rigorously defined dimensions. The scientific implications of this result are discussed in this section. The functionality of the crevice assembly is also evaluated. The results of the copper deposition experiments are discussed, with emphasis on the limitations of the experimentally determined deposition profiles. The output of the CREVICER model is used to correlate a constant copper deposition rate to the period of time when the crevice is under mass transport control. The copper deposition profile determined by CREVICER is compared to the experimentally determined profiles and possible reasons for discrepancies are discussed.

6.3.1 Microfabrication processing results

The results of the fabrication of the first set of microfabricated samples met or exceeded all expectations. The quality of the samples was consistent and the yield was 100%; no samples were lost due to processing problems. The fact that four samples could be fabricated simultaneously on the same wafer made processing the formers and substrates efficient. The semiconductor processing techniques adapted easily to this application. For example, no problems were encountered with the significant increase in time the wafers spent in the wet oxidation furnace when the oxide thickness was
increased from 0.5 µm, which is standard for semiconductor applications, to 1.26 µm for the crevice formers. The size of the crevice features (except for the crevice gap, which depends on the silicon etch process) was limited only by the resolution of the Mylar masks. The Mylar masks were chosen because they can be made quickly, easily, and inexpensively (<$10). If, in the future, crevices with smaller features (< 50 µm) are desired, chrome-plated glass masks are available, although they are much more expensive ($1000-$5000) and delivery takes several weeks.

The microfabrication of crevice formers yielded four sets of formers with etch depths varying from 1 µm to 70 µm. As the profilometry measurements indicate (Figure 18), these formers defined crevices with consistently vertical sidewalls and precise crevice gaps. These results demonstrate that microfabrication techniques can be used to fabricate crevices with rigorously defined dimensions. The demonstration of this ability has serious practical and scientific implications. An understanding of the mechanisms and controlling factors of crevice corrosion is needed to accurately specify design parameters to minimize crevice corrosion problems in practical situations. In order to better understand the mechanisms and controlling factors of crevice corrosion, models must be developed that can accurately predict the onset of crevice corrosion. An essential feature of a model is that it reproduces crevice corrosion phenomena that are seen experimentally. The development of crevice corrosion models has been hindered in this capacity because of discrepancies in crevice geometry. Models, in the interest of reducing coding complexity and increasing computational speed, assume that crevices have ideal dimensions. Most experimental crevices, however, have many surface irregularities. Crevice geometry plays a vital role in the onset and location of attack, so
these discrepancies in geometry have made comparisons between experimental and modeling results difficult. The demonstration that microfabrication techniques can be used to make crevices with ideal dimensions means that this difficulty has been overcome. Microfabricated crevices can be used in conjunction with computational models to further the understanding of crevice corrosion.

The microfabrication of the crevice substrates yielded sixteen well-defined rectangular slots with gold as the substrate material. The success of this batch of samples demonstrated that the metal lift-off process described in detail in Section 2.2.1 can be applied to the fabrication of crevices, which involve much larger features (> 50 µm) and thicker layers of metal (> 0.3 µm) than standard semiconductor devices (< 10 µm and < 0.05 µm, respectively).

These results indicate that semiconductor device manufacturing techniques are a valuable tool for the fabrication of crevices. They can be used to make crevices on the size scale relevant to practical crevices, so no assumptions must be made about how the mechanisms of crevice corrosion scale with geometry. The crevices have rigorously controlled dimensions so models can accurately simulate their geometries.

6.3.2 Electrochemical Testing

The electrical contact made to the gold substrates through the platinum wires attached to the back of the wafers proved to be low resistance (< 5 Ω) and a viable method for applying a potential to the crevice. The maximum potential drop due to the contact resistance was approximately 50 mV. The crevice samples consistently reached similar (within 10 mV) open circuit potentials in the same amount of time (approx. 75 min.). This indicates that the vacuum grease between the crevice substrate and the
Plexiglas support effectively sealed the silver paste on the back of the wafer from the solution. The vacuum grease also eased the alignment of the crevice substrate and former when the former was flipped on top of the substrate to form a complete crevice.

The results of the potentiostatic holds were as anticipated. The thickness of the deposited copper was greatest at the mouth of the crevice and dropped off with distance into the crevice, as would be expected for a system under mass transport control.

There were serious limitations to the accuracy of the experimentally determined copper deposition profiles. As was described in Section 4.5.4, a deposition profile was constructed using a series of height differential measurements between the oxide along the sides of the crevice substrate and the metal electrode. Measurements at the mouth of the crevice were difficult because of the roughness of the silicon and gold introduced during the dicing process. As can be seen in Figure 22c, the first point in the deposition profile is not until almost 50 µm into the crevice. The steepest gradient in the thickness of the deposited copper layer occurred within the first 100 µm of the crevice mouth, so an important portion of the profile could not be measured.

A source of error in the deposition profiles was the measurement of the distance into the crevice where each profilometry scan took place. The profilometer used can only measure distance in the direction of the scan. Because of this limitation, distinguishing features, or “landmarks” on the sample near where each height measurement was taken were noted and then the distance from the mouth of the crevice to these landmarks was found later using an optical microscope. As a result, the x-coordinates in Figure 22c are only accurate within approximately 10-50 µm.
Another source of error in the deposition profile measurements was the variability in the thickness of the oxide and its effect on the determination of the thickness of the “background” copper layer. The “background” layer is the copper that was deposited uniformly onto the gold substrate at the very beginning of the experiment from the solution already present inside the crevice. A measurement of the thickness of this layer was attempted by measuring the oxide/electrode height differential at several places deep into the crevice (where little additional copper was deposited during the remainder of the test). This differential was compared to the oxide/gold height differential measured before the experiment. However, differences in the two differentials caused by the “background” copper layer, which is < 500 Å, were indistinguishable from differences caused by variations in the oxide thickness (possibly up to 0.1 µm). The oxide thickness varied depending on the orientation of the sample in the wet oxidation furnace.

Considering these limitations, the experimental deposition profiles are at best indicators of relative trends, rather than absolute copper thickness values.

6.3.3 Modeling

The fitted curve (Figure 23) used as the electrochemical boundary condition in the models showed good agreement to the experimental potentiodynamic scan results for values of potential less than +0.1 V (SCE). This potential range includes the mass transport limited regime (< -0.13 V SCE) which is the region of interest for these experiments.

The results of the CREVICER model of the copper deposition experiments were as expected. At distances less than 0.8 mm into the crevice a steep gradient in copper
concentration developed (Figure 25b). This distance corresponds fairly well to the theoretical value for the diffusion distance of copper:

\[ x_{\text{diff}} = \sqrt{Dt} = \sqrt{7.13 \times 10^{-6} \text{ cm}^2/\text{sec} \times 300 \text{ sec}} = 0.05 \text{ cm} = 0.5 \text{ mm} \]

Two competing effects cause the 0.8-4-mm and 4-8-mm regions in the crevice to have different copper depletion behaviors (Figure 25b). The potential transient (Figure 25a) shows that the potential increases with distance into the crevice. This depolarization means that initially there is slightly less driving force for copper deposition deeper into the crevice (In Figure 23 the fitted curve has a slight negative slope for E < -0.1 V (SCE)). Correspondingly, at times less than 30 seconds, the copper in solution depletes slower at the tip of the crevice, as seen in Figure 25b. However, the limiting current density is also dependent on copper ion concentration (Equation 7). As the copper in solution is depleted, the current density decreases, so for times between 30 and 120 seconds, the copper in solution depletes slower in the 1-4 mm region.

Figure 24b shows that within the first 90 seconds of the potentiostatic hold the concentration of copper inside the crevice fell to less than 10% of its initial value of 5 mM. During this initial 90 seconds, the rate of copper deposition is not constant, as can be seen by the nonlinearity of the lines in the zoom box in Figure 24. This graph also shows that for regions deeper into the crevice, the duration of the nonlinear period is slightly shorter. These results suggest that the nonlinear region corresponds to the period of time when the deposition of copper is not under diffusion control. Copper from the bulk solution would diffuse more quickly to regions of the crevice closer to the mouth, so a longer period of time would be required before these regions would be completely mass transport controlled. This idea justifies the use of only the linear region to extrapolate the
data out to 30 minutes. Once the system reaches a mass transport limited state, the deposition rate should remain constant if the nickel in the bulk solution is not depleted at the mouth. This assumption could be tested by setting the initial concentration of copper to zero everywhere within the crevice. Under these conditions, the deposition of copper in the crevice should be under diffusion control at all times and the deposition rate should always be constant. This prediction could be verified experimentally by filling the crevice with pure sulfuric acid (no cupric sulfate) prior to the potentiostatic hold.

The deposition profile that was calculated using the linear extrapolation of the modeling data (Figure 26) followed the expected trends. The copper layer was thickest at the mouth of the crevice, where the diffusion path for the copper was shortest, and the thickness dropped off rapidly as the diffusion path lengthened. At distances greater than one millimeter into the crevice the thickness reached a nearly constant level, which probably corresponds to the “background” layer of copper that was deposited during the initial 90 seconds of the potentiostatic hold (before the copper was depleted inside the crevice).

Comparison of the modeling and experimental deposition profiles (Figure 26) shows that all three curves follow the same downward trend and are similar in shape. The two experimentally determined deposition profiles correlate to each other, indicating that the results of the copper deposition experiments using the microfabricated crevices are reproducible. The values of the thickness of the copper layer from CREVICER are roughly a factor of two greater than the experimental values. This discrepancy may be due to the combination of several experimental problems or possibly inaccurate boundary conditions in the model.
The difficulties involved with using profilometry to determine the experimental deposition profile were discussed in the previous section and probably contributed to the discrepancy. Additionally, the roughness from the dicing process may have decreased the crevice gap below 67 µm at the mouth of the crevice. This increased gap at the mouth would cause the experimental deposition profile to be shifted left relative to the modeling profile, as is seen in Figure 26.

Another source of the discrepancy between model and experiment may have been the electrochemical boundary condition used in the model. The potentiodynamic scan was performed on a gold foil, which may have varied slightly in electrochemical behavior from the gold on the crevice substrates. It is also possible that the polarization curve depends on the concentration of copper in solution, meaning that a time-dependent boundary condition should have been used for the model. In the modeling work for these experiments it was assumed that the electrochemical boundary condition was steady state.

6.4 Scaling law investigations

The fabrication portion of the scaling law investigations demonstrates that electrodes of a material of interest to crevice corrosion studies (i.e., nickel) can be made utilizing microfabrication techniques. The precision and reproducibility of the dimensions of these crevices are discussed in this section. The results of the scaling law experiments performed on the crevices are also discussed, with emphasis on the impact of experimental difficulties. The utility of the results of the potentiodynamic scans in justifying the use of a single electrochemical boundary condition throughout a time transient model is described. The implications of the modeling work on the influence of the shape of the electrochemical boundary condition on the governing scaling law are
also discussed. In particular, the effects of the width of the active nose on the governing scaling law, which caused the apparent discrepancy in applicable scaling factor that motivated this study, are described. The practical danger of the utilization of the incorrect scaling factor is also discussed.

### 6.4.1 Microfabrication processing results

The fabrication work for the scaling law investigations, like that for the proof-of-principle experiments, demonstrated the viability of utilizing semiconductor device manufacturing techniques to make crevices with rigorously controlled dimensions on a size scale relevant to practical crevices. Additionally, this work showed that a material of interest to crevice corrosion experiments \( i.e. \), nickel) can be deposited on crevice substrates in layers thick enough that corrosion tests of a reasonable length that produce useable results can be performed. Patterned deposition of nickel was achieved and produced a material with very similar electrochemical behavior to bulk nickel. Like the samples fabricated for the copper deposition experiments, these substrates and formers had high dimensional accuracy and reproducibility. The yield was not 100%, however; some samples in the first batch of crevice substrates could not be used because the nickel at the mouth of the crevice tore and peeled up during the dicing processes, resulting in a jagged line of nickel just inside the crevice mouth. The most likely cause of the peeling was dullness or misorientation of the blade on the dicing saw. A new blade was used to dice the wafers in the second set of substrates and very little peeling occurred.

The feature size and definition of the samples was limited only by the type of mask used for the patterning. If smaller features are necessary in future experiments, the more expensive chrome-plated glass masks described in Section 6.3.1 can be utilized.
The batch processing nature of the fabrication allowed mass production of highly reproducible geometries.

As was mentioned briefly in Section 6.3.1, alterations were required in the wafer processing to accommodate the large sizes of the crevice features (relative to modern semiconductor devices). Substantially extended deposition and etch times for the wafers were needed to form the substrates and crevice formers. Thicker oxides ( > 2 \( \mu \text{m} \) for the crevice samples versus < 0.5 \( \mu \text{m} \) for a typical semiconductor device) were achieved without difficulty, as were bulk silicon etch depths up to 96 \( \mu \text{m} \), which defined the crevice gaps. However, the thickness of the evaporated nickel layer was limited to < 0.6 \( \mu \text{m} \) to achieve clear definition of the crevice features. The metal lift-off process was the source of this limitation. When 0.6-\( \mu \text{m} \) nickel layers were evaporated, the photoresist began to peel up around the edges, exposing the underlying silicon. Nickel deposited in the exposed region, blurring the definition of the crevice substrate features. To avoid these problems, only 0.3 \( \mu \text{m} \) of nickel was deposited on the majority of the crevice substrates. As a result, the duration of the crevice corrosion experiments was limited to four minutes.

6.4.2 Electrochemical Testing

6.4.2.1 Potentiodynamic scan results

The first set of potentiodynamic scans were performed to determine an electrochemical boundary condition for use in modeling the scaling law experiments. The determination of this boundary condition was complicated by the processing limitations that restricted the thickness of the deposited nickel layer to < 0.6 \( \mu \text{m} \). This limitation precluded the use of slow scan rates and introduced the possibility of nickel
depletion during a scan. If the nickel layer was depleted during a scan, the chrome and silicon layers underneath the nickel thin film might affect the potentiodynamic results, which would lead to the use of inaccurate boundary condition in the model. The results of the scans performed on the silicon substrate and the silicon wafer with a chrome thin film (Figure 33) show that for the potentials of interest in the scaling law experiments (< 0.4 V SCE) the current density on both of these metals is less than 1 μA/cm². This means that if the nickel is depleted on a wafer the current density should drop to these values. This can be seen in Figure 42a, which shows potentiodynamic data for a 0.3 μm nickel thin film in sulfuric acid. At E = +0.140 V the current drops abruptly, indicating the depletion of the nickel layer.

Figures 33 and 34 compare the electrochemical behaviors of evaporated and bulk nickel and show the effects of scan rate on the shape of the boundary condition. The figures show that although the open circuit potentials and passive current densities of the two types of nickel are similar, the active nose of the evaporated nickel curve is narrower and has a higher peak current density than its bulk nickel counterpart. This difference and its implications on the scaling laws for crevice corrosion are addressed in detail in Section 6.4.3.2. These figures also show that the scan rate primarily affects the passive current density of the potentiodynamic result. For the evaporated and the bulk nickel, the shape of the active nose is comparable for the two scan rates. However, at the faster scan rate (5 mV/sec), the passive current density is considerably higher. Because of this result, the electrochemical boundary condition used in CREVICER was constructed by splicing together two curves. For potentials less than the passivation potential the results of a potentiodynamic scan were used. For potentials greater than the passivation potential
a constant passive current density determined by a potentiostatic hold in the passive region was used. This process was described in Section 5.4.3.2.

The second set of potentiodynamic scans was used to assess the influence of nickel ion concentration on the electrochemical behavior of the substrate. Figure 35a shows that the size and shape of the active nose is virtually identical for evaporated nickel in all concentrations of nickel ions. The sudden drop in current density that occurred in all of the scans at potentials between -0.1 V SCE and +0.05 V SCE is due to depletion of the nickel thin film. Integration of the curve for the microfabricated wafer in 0.5 M H$_2$SO$_4$ + Sat. NiSO$_4$ indicates that the total charge passed was 4.39 C. Using Faraday’s Law, this corresponds to a penetration depth of 0.298 µm, which is extremely close to the amount of nickel that was evaporated. Because the nickel was depleted, comparisons of the passive current densities are not easily gleaned from this data. However, the slight leveling of the current around 100 µA at approximately 0.0 V SCE for the 3 mV/sec scan in 1 M NiSO$_4$ and the 2.5 mV/sec scan in saturated NiSO$_4$ may correspond to the beginning of the passive region. Additionally, Figure 35b shows that for slow scans on bulk nickel samples in solutions with different concentrations of nickel ions the same passive current density and similar passivation potentials are achieved, which suggests that same is true for the evaporated nickel samples. These results contradict data obtained by Wang, Pickering, and Xu$^{[37]}$ which show an order of magnitude decrease in peak current density in a saturated nickel sulfate solution. The reasons for this discrepancy are unclear. One possibility is effects of sample composition; the data from the literature was obtained on 99.6% pure nickel specimens whereas 99.9% pure nickel was used in this study.
The similarities in the electrochemical behavior of nickel in solutions with a wide variety of concentrations of nickel ions that are seen in these results legitimize the use of a constant electrochemical boundary condition in time transient models of nickel dissolution in a crevice. As the model steps through time and the nickel substrate corrodes, nickel ions accumulate in the crevice. However, because the electrochemical behavior of the substrate changes negligibly with these changes in nickel ion concentration, it is sufficient to use the same boundary condition at all times. This result is utilized in the time transient models discussed in Section 6.4.3.2.

6.4.2.2 Potentiostatic hold results

The qualitative results from the potentiostatic tests are encouraging. The basic results of a typical experiment were as expected. The crevice substrate surface could be separated into three regions (Figure 36). The region nearest the mouth underwent passive dissolution. The region farthest from the mouth was only lightly attacked as the potential of the metal presumably fell well below the primary passivation potential and therefore dissolution rates diminished. These two regions were separated by a region of severe attack. Visual observation of the attack showed that the deepest attack was in the middle of the severely attacked region, as also observed in this system by Wang et al.\cite{37} at short times with larger samples.

As expected from all proposed scaling laws\cite{3,29-33}, $x_{crit}$ increased with increasing gap. The limited amount of data and experimental difficulties prevented a quantitative assessment of the dependence. Future studies will have that determination as part of their focus for the Ni/H$_2$SO$_4$ system as well as other crevice corrosion systems.
The observation of an increase in $x_{\text{crit}}$ with increasing potential allows a differentiation between the different models for crevice corrosion, providing support for the IR* model of Pickering for the Ni/H$_2$SO$_4$ system under conditions of sufficient natural convection. Models that are based upon occluded chemistry changes leading to activation of the surface if the passive current density is considered to be independent of potential would not predict this potential dependence. Under such conditions, the location of the point of attack would be independent of potential because the flux causing the chemistry change would not be changed. The IR* model does predict a dependence of $x_{\text{crit}}$ on potential due to the change in the amount of ohmic drop required to lead to activation. Figure 38 shows the corrosion band for sample 2-S-5D that extends straight across the width of the wafer despite the jaggedness of the edge of the nickel that resulted from processing. This observation suggests that for this material system, the position of the edge of the occluded region defines $x_{\text{crit}}$, not the edge of the substrate material, further strengthening the idea that it is not the passive current that leads to the ohmic drop, but the presence of the current from the active region. Thus, it would be expected that the approximation of Xu and Pickering$^{[3]}$, which indicates that the applicable scaling factor for this system should be $x_{\text{crit}}/G$, would apply.

It can also be seen in Table 20 that, with the exception of sample 3-S-8B, the mean current is fairly constant independent of crevice gap or applied potential. It should be noted that the larger current in sample 3-S-8B was consistent with the observed cross-sectional profile and visual inspection of the sample, which showed more attack than the other samples. The origins of this increased attack are not clear.
A final observation involves the morphology of the attack for the sample with the mouth facing upward (sample 2-S-5B, Figure 38). As the base of the crevice was closed in this sample, the natural convection caused by density gradients in the occluded solution would not lead to the maintenance of a constant occluded electrolyte as in the case of the other samples. Instead, the natural convection forces would tend to increase the concentration of the nickel dissolution products at the base.

6.4.2.3 Experimental difficulties

The experiments using the first set of crevice substrates that did not produce a clear corrosion band were apparently affected by a rough edge developed at the mouth of the crevice during dicing. The rough edge reduced the gap irregularly along the mouth of the crevice. This reduction in the gap increased the potential drop dramatically, causing the entire crevice to be in the active region (i.e., at potentials below the primary passivation potential). The active corrosion led to the formation of hydrogen gas bubbles, which produced the pattern shown in Figure 40. Adjustments were made to the design of the crevices in the second set of substrates to avoid this problem as well as the tearing of the nickel at the mouth of the crevice during the dicing process that made many samples from the first set unusable. These design adjustments were described in Section 5.4.1. They were successful; the jagged nickel edges were no longer a factor and the bubble pattern did not reappear in the results from the second set.

The origin of the rings that appeared on the first batch of wafers in the second set of substrates is unknown. It can be speculated that they may have been a result of contamination in the evaporator or residual stresses in the deposited layer that resulted from anomalous processing conditions.
The considerable scatter in the experimentally determined values for $x_{\text{crit}}$ that prohibited the quantitative assessment of the scaling factor operating in this case was most likely due to inconsistencies in the crevice gap and misalignment of the crevice former and substrate. The bump created by the electrical connection on the back of the substrates made it difficult to align the crevice former and clamp it onto the substrate evenly and reproducibly. Additionally, the sealant (vacuum grease or Microstop lacquer) used to isolate the silver paste from the solution may have partially blocked the crevice in some cases. Improvements should be made to the experimental setup and crevice assembly to minimize these factors.

6.4.3 Modeling

6.4.3.1 Comparisons to the literature

There is a fair correlation between the potential profiles generated by CREVICER and Pickering and coworkers\(^{[33]}\) experimentally determined potential profiles for a nickel crevice in sulfuric acid held potentiostatically at three different potentials (Figure 41). The shapes of the curves are similar, but Pickering, et al.’s curves are generally shifted to lower potentials relative to the curves generated by CREVICER. This may be because the reference electrode is a finite distance from the crevice mouth in the experimental work. As a result, the potentials at the crevice mouth ($y = 0$) are actually slightly lower than the applied potentials. The discrepancies between the potential distributions also may be an indication that the electrochemical behavior of the nickel substrate is not constant through time. The model determines the initial potential distributions inside the crevice, whereas the profiles in the experimental work take several minutes to obtain. Another possibility is that the probe used to measure the
potential in the experimental work affects the system. A probe would partially block the crevice, increasing the IR drop, and shifting the potentials to lower values. That type of shift corresponds to the discrepancy between the experimental and modeling results.

The fair correlation between experimental and modeling results demonstrated in this test provides some experimental verification of CREVICER.

6.4.3.2 Investigating the effects of the shape of the boundary condition

6.4.3.2.1 Influence on applicable scaling factor

The linear character of the curves in the plot of $x_{\text{crit}}^2$ vs. Gap (Figure 45b) indicates that $x_{\text{crit}}^2/G$ is the appropriate scaling factor for all of the boundary condition shapes investigated. The slight nonlinearity at large gaps for the Shifted and Skinny curves may be related to the fact that $x_{\text{crit}}$ is approaching the length of the crevice at these points, meaning that the crevices are nearing the critical geometry where the potential never decreases enough to activate the crevice. If there is not sufficient crevice length for the potential to drop to the open circuit potential, less total current will be passed. A smaller amount of current will alter the location of $x_{\text{crit}}$, possibly resulting in the nonlinearity seen at large gaps for Shifted and Skinny. This possible reason for the nonlinearity could be tested by increasing the length of the crevice.

The boundary condition in which the passive current density is only three times smaller than the peak current density ($I_{\text{pass}}\uparrow$) is similar to a boundary condition in which the crevice substrate is entirely active. Turnbull utilized that type of boundary condition in his theoretical determination of the $L^2/G$ scaling factor$^{[29]}$. The results from CREVICER support this theoretical work; they indicate that $x_{\text{crit}}^2/G$ is the appropriate scaling factor for the $I_{\text{pass}}\uparrow$ boundary condition (Figure 45b).
Several trends should be noted in the plot of \( x_{\text{crit}} \) vs. Gap (Figure 45a). First, the curvature of all curves increases at tighter crevice gaps, indicating that the scaling factor has an increasingly \( x_{\text{crit}}^2/G \) character. This has practical significance because it exposes the danger of assuming that results obtained on larger crevice gaps are relevant at smaller gaps. If experiments are performed on larger scale crevices (gap > 50 \( \mu \)m), \( x_{\text{crit}}/G \) may appear to be the appropriate scaling factor because the curves are generally linear in this region. If a line is fitted to a portion of the \( x_{\text{crit}}/G \) curve at large gaps and extrapolated back to small gaps (< 10 \( \mu \)m - the sized relevant to most practical crevices), the values for \( x_{\text{crit}} \) will be overestimated. For example, a line fitted to the 80-120 \( \mu \)m region of the Shifted curve in Figure 45a and extrapolated back to 10 \( \mu \)m yields a value for \( x_{\text{crit}} \) of about 1.8 mm. However, the actual value is 1 mm. If the linear extrapolation values are used as design parameters, they will overestimate the maximum allowable crevice length to maintain crevice passivity, possibly causing premature failures of equipment.

Other trends evident in the \( x_{\text{crit}} \) vs. Gap plot are that the \( x_{\text{crit}}^2/G \) character (i.e., the curvature) decreases as the width of the active nose of the boundary condition increases and as the total charge (area underneath the boundary condition curve) increases. These trends explain the apparent discrepancy in the scaling factors applicable to systems using different boundary conditions (Figure 44). It was this apparent discrepancy that motivated this investigation. The active nose of the boundary condition from the literature\(^{[33]}\) was much wider than the active nose of the boundary condition determined from a potentiodynamic scan on a microfabricated sample. Thus, over the limited range of crevice gaps considered, the scaling factor for the system from the literature appeared to be \( x_{\text{crit}}/G \) while the scaling factor for the microfabricated system appeared to be \( x_{\text{crit}}^2/G \).
When these tests were extended to tighter crevice gaps, the nonlinearity of the $x_{\text{crit}}$ vs. $G$ curve became evident (Figure 46), indicating the applicability of the $x_{\text{crit}}^2/G$ scaling factor.

### 6.4.3.2.2 Time transient effects

There are several important aspects of the time transient results of the boundary condition modeling work that should be highlighted. First, the shift of the potential distribution in the crevice through time (Figure 47a) reveals a possible source of discrepancy between modeling and experimental values for $x_{\text{crit}}$. The potential distribution shifts toward the mouth of the crevice as the nickel ion concentration in the crevice increases, decreasing the conductivity of the solution (Table 19) and causing a larger IR drop per unit distance into the crevice. The result is that the location of the maximum dissolution of nickel shifts toward the mouth of the crevice through time (Figure 47b). This has been seen experimentally for an IR-drop controlled crevice corrosion system by Pickering\textsuperscript{[33]}\,\cite{Pickering1998}. In experiments, usually either the distance into the crevice where maximum dissolution occurred (as determined by profilometry) or the leading edge of the severely corroded region ($x_{\text{pass}}$) is used to define the location of the corrosion band. In modeling work, however, $x_{\text{crit}}$ is generally determined from the initial potential distribution in the crevice. These results show that all three of these values may vary significantly.

The time transient nickel concentration distributions and dissolution profiles for the normal and double bump boundary conditions (Figure 48) demonstrate the significant effect the shape of the electrochemical boundary condition has on the modeling results.
This indicates the importance of matching the boundary condition in the model as closely as possible to the true electrochemical behavior of the crevice substrate material. Simplifications (e.g., square waves to represent the behavior of an active/passive metal\textsuperscript{13}) are often used in models to reduce coding complexity and increase computational speed. These simplifications are a likely source of discrepancy between modeling and experimental results.

The occurrence of mathematical instabilities in the nickel ion concentration distributions (Figure 15) were discussed in detail in Section 6.2.2 in relation to the limits of the computational model. These instabilities also raise questions about the appropriateness of the boundary conditions at the mouth of the crevice. The nickel ion concentration was fixed at zero at the mouth of the crevice. As dissolution occurred and nickel accumulated in the crevice, an unnaturally steep concentration gradient developed at the mouth of the crevice, creating the instabilities. This result suggests that this boundary condition is inappropriate; the nickel concentration at the mouth should be able to change through time. This idea is supported by the literature; Harb and Alkire\textsuperscript{38} found that concentration gradients actually extend well beyond the mouth of the crevice (Figure 51).
Figure 51: Figure from Harb and Alkire\cite{38} indicating that concentration gradients extend well beyond the mouth of the crevice \((z/r_0 = 0)\).

### 6.4.3.3 Comparisons to experimental results

The \(x_{\text{crit}}\) vs. gap relationships for the two experimental boundary conditions (one from the literature and one from the microfabricated crevices) overlaid on the \(x_{\text{crit}}\) values for various crevice gaps from the potentiostatic hold experiments (Figure 50) show that the modeling and experimental results are within fairly close proximity of each other. This results is promising considering the host of experimental difficulties that contributed to inaccuracies in the experimental determinations of \(x_{\text{crit}}\). Improvements must be made in the reproducibility of the experimental results before serious assessments of the accuracy of the model and experimental quantification of the governing scaling laws can be made. Specific refinements of the experimental techniques that should increase the reproducibility of results are described in Chapter 8.
Chapter 7: Conclusions

The objectives for this study, which were outlined in Chapter 3, have been accomplished. CREVICER has been developed into a comprehensive, user-friendly tool for modeling crevice corrosion. Semiconductor device manufacturing techniques have been shown to be a viable method for fabricating crevices with rigorously defined dimensions on the size scale relevant to practical crevices. These characteristics of the microfabricated crevices have helped overcome two of the major hurdles to the development of an accurate, comprehensive model of the mechanisms and controlling factors of crevice corrosion. The rigorously defined dimensions of the microfabricated crevices enable comparisons of experimental results to results from models, which assume ideal crevice dimensions. The size scale of the microfabricated crevices is similar to that of practical crevices, so experimental findings can be directly applied to practical crevice corrosion situations. The size scale also enables experimental investigations of the scaling laws governing crevice corrosion, a feature utilized in this study.

Modeling results indicated that the appropriate scaling factor for IR*-controlled crevice corrosion is $x_{crit}^2/G$, where $x_{crit}$ is the distance into the crevice where corrosion initiates and $G$ is the crevice gap. The trends of experimental results were consistent with this scaling factor, but experimental difficulties prohibited verification of the scaling law.

The specific achievements of this study are:

**CREVICER**: A new routine for solving the matrix of equations used in the finite element was implemented that increased the speed of the model by a factor of eight. The capability to account for aluminum hydrolysis reactions inside the crevice was added to
CREVICER, expanding the applicability of the model to crevice corrosion situations involving aluminum alloys. A graphical user interface (GUI) was added to CREVICER. It provides a visual representation of the crevice geometry and the finite element mesh and simplifies the process for defining the initial and boundary conditions for a model. It also eliminates the need for the user to reprogram CREVICER each time a new system is modeled. Appropriate changes were made to CREVICER to enable interactions with the GUI. CREVICER and the GUI can now run in a Windows™ environment, which has increased the pool of potential users.

**Microfabrication:** Semiconductor device manufacturing techniques were utilized to microfabricate crevice formers and substrates with rigorously defined dimensions on a size scale relevant to practical crevices. The etch depths of the crevice formers, which defined the crevice gaps, varied by a maximum of 5.7% across a sample, with 0.5-2% more typical. The roughness of the ‘ceilings’ of the crevices (the bottoms of the etched wells in the crevice formers) was 2% of the total crevice gap (etch depth). The dimensions were reproducible; crevice gaps varied by only 6.2% among the samples. Crevice substrates with gold and nickel as the electrode materials were fabricated. The metal lift-off process limited the thickness of the nickel electrodes to 0.6 µm. This limited the length of the potentiostatic hold experiments to a maximum of four minutes.

**Experimental Verification of CREVICER:** Copper deposition experiments on microfabricated crevices with gold substrates were used to verify the accuracy of CREVICER. Difficulties in determining the experimental deposition profiles made stringent comparisons to modeling results unachievable, but the curves followed the same trends. Initial potential distributions determined by CREVICER for nickel crevices held
potentiostatically at three different potentials in 0.5 M H₂SO₄ compared fairly well to experimentally determined potential profiles from the literature.

**Scaling Law Investigations:** Modeling results indicated that the appropriate scaling factor for IR*-controlled crevice corrosion is \( x_{\text{crit}}^2 / G \), where \( x_{\text{crit}} \) is the distance into the crevice where corrosion initiates and \( G \) is the crevice gap. The results showed that the \( x_{\text{crit}}^2 / G \) character of the scaling factor is more pronounced at tighter crevice gaps, and increases with increasing sharpness of the active nose on the electrochemical boundary condition. Experimental investigations of the scaling laws using microfabricated crevices were hindered by experimental difficulties. These included peeling of the nickel substrates during dicing and inconsistent alignment of the crevice formers and substrates. The trends of the data are consistent with the modeling results, however.
Chapter 8: Future Work

This study has laid the groundwork for future investigations of the mechanisms of crevice corrosion. CREVICER, now faster and more user friendly, is more of a tool than a project under development, so a wider range of corrosion scientists can use it to model their crevice corrosion systems. Semiconductor device manufacturing techniques have proved to be a viable technique for fabricating crevice samples with rigorously-defined dimensions on a size scale relevant to practical crevices. These well-defined dimensions have been shown to be a valid representation of the ideal dimensions assumed by CREVICER, so results from experiments on microfabricated samples can be correlated to modeling results. Modeling results have indicated that $x_{crf}^{2}/G$ is the correct scaling law for IR*-controlled crevice corrosion and have shown that this dependence is particularly dominant for crevices with dimensions on the size scale of practical crevices. Preliminary experimental results have trends consistent with this scaling factor, but experimental difficulties have prohibited conclusive verification of the scaling law.

The tools and techniques utilized in this study, although useful in their present state, would benefit from refinements and additions. Some specific examples of these are:

C. **CREVICER**

1. **Additional modeling capabilities:** There are some crevice corrosion phenomena that CREVICER does not consider. These include the precipitation of a salt film inside the crevice, changes in the morphology of the crevice through time, and homogeneous reactions other than chromium and aluminum hydrolysis. This study has shown that fixing the concentrations of chemical species to their bulk values at
the mouth of the crevice is not always an accurate representation of true crevice chemistry. This limitation would be removed if concentration gradients were allowed to extend outside the crevice mouth. The addition of these capabilities would make CREVICER a more comprehensive model of crevice corrosion, and would broaden its applicability.

2. Continued development of graphical user interfaces (GUIs): Portions of the input GUI still require minor debugging efforts. An output GUI that provides a visual representation of the time transient potential and concentration distributions in the crevice would be a useful addition because it would eliminate the chore of importing the raw data from CREVICER into commercial graphing software for analysis. Conversion of the GUI into an internet-accessible format would make CREVICER available to off-site corrosion scientists.

MICROFABRICATION TECHNIQUES

1. Improvements to the crevice substrates: Currently, the primary limiting factor in substrate fabrication is the thickness of the metal electrode. Thicker electrodes are needed to increase the duration of electrochemical experiments. The capabilities of deposition techniques such as electroplating and sputtering should be investigated. Another desirable improvement is the fabrication of individually addressable segmented electrodes on the crevice substrates (Figure 52). An array of electrodes would provide spatial resolution of the current distribution in the crevice.

2. Improvements to the crevice formers: The fabrication of two-dimensional features on the crevice formers would be useful for investigating the role of subcrevices in crevice corrosion. An additional patterning and etching step would be necessary to
differentiate the subcrevices from the ‘legs’ of the crevice former. Another useful addition to the crevice formers would be arrays of microsensors fabricated into the ‘ceiling’ of the crevice. pH and chloride ion concentration sensors would provide valuable spatially resolved in-situ information about the crevice chemistry.

![Figure 52: Schematic of a microfabricated crevice with an array of individually addressable electrodes.](image)

In this study, microfabrication techniques and the CREVICER model were applied to investigations of the scaling laws governing \( \text{IR}^* \)-controlled crevice corrosion. Although the results of this study were informative, much work is needed for conclusive quantification of the scaling laws. Specific improvements related to this work are:

**SCALING LAW INVESTIGATIONS**

1. **Alleviation of experimental difficulties:** The scaling law investigations in this study were plagued by experimental difficulties that made reproducible results difficult to obtain. The development of a standard method for pressing the crevice former
against the substrate would alleviate some of these problems. An improved method for aligning the substrate and former would also be useful. The bump created by the platinum wire and silver paste on the back of the substrates contributed to the alignment problems. A method for making electrical connection to the crevice electrode on the front of the sample would help alleviate these difficulties.

2. **Use of smaller crevice gaps**: Although crevices were microfabricated on the size scale of practical crevices (1-10 µm crevice gaps), most experiments were performed on crevices with gaps in the 50-100 µm range. The modeling results also indicated that the scaling factors are easiest to differentiate at crevice gaps in the 1-10 µm range. In order to quantify the scaling laws, experiments must be performed on crevices with this range.
References


Appendix A: GUI specifications

Formal specifications and a code print out can be found in Howse[36].

Specifications for a GUI for CREVICER

The GUI is designed to provide an interactive input interface to CREVICER, thereby eliminating the need to modify class files, header files, and the main program. This allows the user easier access to CREVICER by hiding the details of CREVICER.

On the left side of the control panel there is a column of buttons in the following order: “SETUP FILE,” “NEW CREVICE”, “NODE PROPERTIES”, “ELEMENT PROPERTIES”, “RUN THE SIMULATOR”, “SAVE SETUP”, and “EXIT”. The function of each button is outlined below.

1. When the application is launched and the control panel opens, the “SETUP FILE” button automatically activates and a “SETUP FILE” box immediately opens that contains:
   - A “New / Default” button that loads the setup file for a generic square crevice with simple boundary conditions (the user may alter it to suit his purposes) and closes the “SETUP FILE” box.
   - A “Predefined by User” button that opens a file browser which allows a previously defined setup file to be loaded. An “ok” button in the browser loads the setup file and closes the “SETUP FILE” box, an error message is generated if the file is in the wrong format and cannot be loaded properly, and a “cancel” button returns the user to the “SETUP FILE” box.
   - An “Exit” button that closes the control panel, exiting the application.

In the instance that a crevice is already loaded on the screen, “SETUP FILE” will cause all other open windows to close and the zoom box to clear, but the 3D CREVICE TEXTURE and the CREVICE MESH will remain on screen until new ones are selected to replace these. This allows for the user to cancel the “SETUP FILE” mode.

2. When the “NEW CREVICE” button is pushed, a “CREVICE TYPE” box opens which has six features:
   - A click-down list of crevice types available in the library – the one currently loaded should already be highlighted
   - When one of the crevice types is highlighted, a small 3-D sketch (if possible, otherwise several 2-D views) of the crevice appears in a small window in the “CREVICE TYPE” box. The sketch should indicate the location of the 2-D meshed region of the crevice and contain x, y, and z axes.
   - Also when one of the crevice types is highlighted, a click-down list of the available meshes for that crevice type should appear.
   - A “select from file” button which activates a file browser that allows the user to select and load his own node and element files. An “ok” button in the browser should load the files (creating a 2-D mesh picture in the large window of the control panel) and close the browser and the “CREVICE TYPE” box, an error message should appear if the files are in the wrong format and cannot be loaded properly, and a “cancel” button should close the file browser and return the user to the “CREVICE TYPE” box.
• An “OK” button that loads the element and node files (from the library) corresponding to the highlighted crevice and mesh types and close the “CREVICE TYPE” box. When the box closes, the 3-D sketch should appear in a small window on the left of the control panel below the buttons and a 2-D picture of the mesh should appear in the large window covering the majority of the control panel. If the files are loaded via the “select from file” button, the large 2-D mesh picture should appear but the window for the 3-D sketch should contain the words “User defined – no picture available”.

• A “CANCEL” button that closes the “CREVICE TYPE” box, leaving whatever crevice was previously loaded on the screen of the control panel.

In the instance that a crevice is already loaded on the screen, “NEW CREVICE” will cause all other open windows to close and the zoom box to clear, but the 3D CREVICE TEXTURE and the CREVICE MESH will remain on screen until new ones are selected to replace these. This allows for the user to cancel the “NEW CREVICE” mode.

3. When the “NODE PROPERTIES” button is pushed, a “NODE SELECT” box opens with three buttons: “ALL NODES”, “SELECTED NODES”, and “DONE”.

When the “ALL NODES” button is pushed, all of the nodes in the mesh change color and an “ALL NODES” box opens containing:

• A fill-in-the-blank Temperature (K)
• A fill-in-the-blank Pressure (Pa)
• A fill-in-the-blank Potential (V)
• A fill-in-the-blank list of species names and concentrations (mol/m$^3$) – note that all species that will be in the solution must be listed even if their initial concentrations are zero (e.g. corrosion products)
• An “OK” button that initializes and sets the initial chemistry at each of the nodes in the mesh. The CRC is checked for each of the species entered and if it is not found the user is prompted to enter the species’ charge number (z), ionic mobility (u), and standard chemical potential ($u_0$). The “ALL NODES” box closes, returning the user to the “NODE SELECT” box. Changes are retained.

• A “CANCEL” button that closes the “ALL NODES” box, returning the user to the “NODE SELECT” box. Changes are not retained.

When the “SELECTED NODES” button is pushed, a moveable zoom box appears on the mesh and a magnified view of the elements and nodes in the zoom box appears elsewhere on the control panel. The nodes in the zoom box are clickable, and change color when selected. A “SELECTED NODES” box opens containing:

• A fill-in-the-blank Temperature (K)
• A fill-in-the-blank Potential (V) with selectable fixed/not fixed
• A list of species (from ALL NODES) with changeable concentrations and selectable fixed/not fixed
• An “OK” button that sets the chemistry at the selected nodes, closes the “SELECTED NODES” box and returns the user to the “NODE SELECT” box.

• A “CANCEL” button that closes the “SELECTED NODES” box, returning the user to the “NODE SELECT” box. All changes are retained.

When the “DONE” button is pushed, the “NODE SELECT” box closes, returning the user to the control panel.

4. When the “ELEMENT PROPERTIES” button is pushed, and “ELEMENT SELECT” box opens with three buttons: “ALL ELEMENTS”, “SELECTED ELEMENTS”, and “DONE”.

When the “ALL ELEMENTS” button is pushed, all of the elements in the mesh change color and an “ALL ELEMENTS” box opens containing:

- A fill-in-the-blank height function where the user specifies the coefficients and exponents of x and y and a constant.
- A fill-in-the-blank material name
- A fill-in-the-blank 12 item list of reaction names, each with a corresponding “reaction properties” button that, when pushed, opens a “REACTION PROPERTIES” box that prompts the user for the names of the reactants and products and their stoichiometric coefficients (note that the products should have been listed in “NODE PROPERTIES → ALL NODES”), the number of electrons transferred in the reaction, and the ten polynomial coefficients for the polarization curve (the exact implementation of this will be ironed out at a later date).
- An “OK” button that initializes the material and reactions for all of the nodes, closes the “ALL ELEMENTS” box, and returns the user to the “ELEMENT SELECT” box.
- A “CANCEL” button that closes the “ALL ELEMENTS” box, returning the user to the “ELEMENT SELECT” box. No changes in element properties are retained.

When the “SELECTED ELEMENTS” button is pushed, a box opens with three buttons: “INTERIOR ELEMENTS”, “BOUNDARY EDGES”, and “CANCEL”:

- When the “INTERIOR ELEMENTS” button is pushed, a moveable zoom box appears on the mesh and a magnified view of the elements and nodes in the zoom box appears elsewhere on the control panel. The elements in the zoom box are clickable, and change color when selected. A “SELECTED INTERIOR ELEMENTS” box opens containing the same options as given above for the “ALL ELEMENTS” button, with the exception that the height is now a constant, instead of a function.
- When the “BOUNDARY EDGES” button is pushed, a moveable zoom box appears on the mesh and a magnified view of the elements and nodes in the zoom box appears elsewhere on the control panel. The edges of elements along the boundary of the mesh are clickable, and change color when selected. A “SELECTED BOUNDARY EDGES” box opens containing the same options as given above for the “ALL ELEMENTS” button, with the exception that there is neither a height function nor a constant.
- When the “CANCEL” button is pushed, the “SELECTED ELEMENTS” box closes and the user is returned to the “ELEMENT SELECT” box.

When the “DONE” button is pushed, the “ELEMENT SELECT” box closes, returning the user to the control panel. All changes in element properties are retained.

If “ELEMENT PROPERTIES” is activated before a crevice is loaded, an ERROR BOX will be displayed telling the user to load a crevice first.

5. When the “RUN THE SIMULATOR” button is pushed, an “OUTPUT” box opens which contains:

- A 12 item list of selectable output options containing potential and the concentrations of all of the species specified in “NODE PROPERTIES → ALL NODES”
- A fill-in-the-blank time step length
- A fill-in-the-blank number of time steps
- A fill-in-the-blank degree of implicitness/explicitness (must be between 0 and 1)
- An “OK” button that creates a setup file, starts CREVICER, and opens a “STATUS” box that displays the names of the output files as they are dumped out, the run time, and contains a “TERMINATE CREVICER” button that halts the program. The “STATUS” box should also alert the user when CREVICER is finished running. While CREVICER is running the user should be unable to do anything else on the
control panel – to run simultaneous programs the user should have to minimize the control panel and start another copy of the application.

- A “CANCEL” button that closes the “OUTPUT” box and returns the user to the control panel

If “RUN THE SIMULATOR” is activated before a crevice is loaded, an ERROR BOX will be displayed telling the user to load a crevice first.

6. When the “SAVE SETUP” button is pushed, a “SAVE” box opens that prompts for a filename and allows the user to save the setup file a directory of choice. If “SAVE SETUP” is activated before a crevice is loaded, an ERROR BOX will be displayed telling the user to load a crevice first.

7. When the “EXIT” button is pushed, the user is prompted to save the setup file if it has been changed and not saved, and then the control panel closes, exiting the application.

All MAIN MENU buttons are also default cancel operations for other processes except for “TERMINATE CREVICER”. When a MAIN MENU button is used to cancel operations, the command for the button is activated.
Appendix B: Microfabrication processing sheets

Process sheet: RCA clean

1. Dip wafer in TCE for 3 min.
2. Dip wafer in acetone for 3 min.
3. Dip wafer in methanol for 3 min.
4. Rinse wafer in DI water for for 1 min.
5. Dip wafer in NH$_4$OH/H$_2$O$_2$/H$_2$O (1:1:5) for 12 minutes. Maintain temperature of solution at 75-80 °C.
6. Rinse wafer in DI water for 1 min.
9. Immediately dip wafer in HCl/ H$_2$O$_2$/H$_2$O (1:1:6) for 12 minutes. Maintain temperature of solution at 75-80 °C.
10. Rinse wafer in flowing DI water for 2 min.
12. Inspect wafer under a bright light and microscope. If wafer does not appear clean, repeat steps 1-12.
Process sheet: Wet oxidation

1. Turn on the wet oxidation furnace and the current source and set the temperature to 2120 °F (1160 °C).
2. Turn the valve by the bubbler so that the bubbler is bypassed.
3. Flow nitrogen (open left and lower valves by O₂ tank) at 1.5 L/min. The black ball on the flow meter should be set at 50.
4. Fill the bubbler with DI water.
5. Start the bubbler by turning on the Variac and setting it to 95 °C.
6. Once the furnace has reached the set point, turn the valve by the bubbler so that gas flows only through the bubbler.
7. Open the valve to the oxygen tank and close the lower valve, shutting off the nitrogen flow.
8. Adjust the oxygen flow using the flow meter until the black ball is at 20.
9. Let oxygen flow for 10 min.
10. Insert wafers into the boat and slowly push the boat into the furnace.
11. Heat the wafers for the desired time, refilling the bubbler when necessary. If the wafers are going to be left overnight, put a note on break #11 in the circuit box by the dicing saw to be sure that it is not shut off in the evening.
12. When the wafers have been oxidized for the desired time, switch the gas flow back to nitrogen.
13. Turn off the Variac.
14. Rotate the valve by the bubbler so that the bubbler is bypassed.
15. Turn off the furnace and wait 10 min.
16. Turn off the nitrogen flow.
17. Slowly (taking about 5 min) remove the wafer boat from the furnace.
Process sheet: One step photoresist application and exposure – for crevice formers

1. Place wafer on spinner.
2. Spray for 5 sec. with ethanol.
3. Spray for 5 sec. with TCA.
4. Spray for 5 sec. with methanol.
5. Repeat steps 2-4 two more times.
7. Place wafer on 120 °C hot plate for 5 min to dehydrate.
8. Place wafer in HMDS evaporation dish for 10 min.
9. Place wafer on photoresist spinner.
10. Test vacuum, bring spinner up to 6000 rpm.
11. Blow dry wafer with nitrogen gun for 30 sec at 6000 rpm.
12. Apply AZP4110 and spin for 30 sec at 6000 rpm.
13. Immediately place wafer on 100 °C hot plate for 45 sec to soft bake.
14. Place mylar mask on the mask holder/vacuum chuck on the exposure machine.
15. Turn on the mask vacuum.
16. Place the wafer on the tray and push it in.
17. Raise the wafer with the lever on the left and adjust the stage height so that the mask just touches the wafer when the lever is about ¾ turned.
18. Look through the microscope, focus on the mask, and adjust the wafer so that the mask pattern is centered on the wafer.
19. Turn the lever completely, slide the bar forward, and press the white button to set the vacuum.
20. Set the exposure time to 20 sec.
21. Press the green button to start the exposure.
22. After the exposure is complete, slide the bar back, turn the lever back the other way (lowering the wafer), and remove the wafer and the mask from the exposure machine.
23. Rinse the wafer in AZ Developer/DI (1:4) for 1.5 min.
24. Rinse the wafer under flowing DI water for 30 sec.
25. Look at the pattern under low light in the microscope. If the pattern is unclear, either expose the photoresist longer or rinse the wafer in acetone for several minutes until the photoresist is removed and repeat steps 1-24.
26. Place the wafer on the 120 °C hot plat for 2 min. to hard bake.
Process sheet: Two step photoresist application and exposure – for crevice substrates

1. Place wafer on spinner.
2. Spray for 5 sec. with ethanol.
3. Spray for 5 sec. with TCA.
4. Spray for 5 sec. with methanol.
5. Repeat steps 2-4 two more times.
7. Place wafer on 120 °C hot plate for 5 min to dehydrate.
8. Place wafer in HMDS evaporation dish for 10 min.
9. Place wafer on photoresist spinner.
10. Test vacuum, bring spinner up to 6000 rpm.
11. Blow dry wafer with nitrogen gun for 30 sec at 6000 rpm.
12. Apply AZP4110 and spin for 30 sec at 6000 rpm.
13. Immediately place wafer on 100 °C hot plate for 45 sec to soft bake.
14. Place the wafer on the tray on the exposure machine and push it in.
15. Raise the wafer with the lever on the left and slide the bar forward.
16. Set the exposure time to 30 sec and press the green button to start the flood exposure (no mask).
17. After the exposure is complete, slide the bar back, turn the lever back the other way (lowering the wafer), and remove the wafer from the exposure machine.
18. Place the wafer on the 120 °C hot plate for 1.5 min to hard bake.
19. Place the wafer on the photoresist spinner again.
20. Test vacuum, bring spinner up to 6000 rpm.
21. Blow dry wafer with nitrogen gun for 30 sec at 6000 rpm.
22. Apply AZP4210 and spin for 30 sec at 6000 rpm.
23. Immediately place wafer on 100 °C hot plate for 45 sec to soft bake.
24. Place mylar mask on the mask holder/vacuum chuck on the exposure machine.
25. Turn on the mask vacuum.
26. Place the wafer on the tray and push it in.
27. Raise the wafer with the lever on the left and adjust the stage height so that the mask just touches the wafer when the lever is about ¾ turned.
28. Look through the microscope, focus on the mask, and adjust the wafer so that the mask pattern is centered on the wafer.
29. Turn the lever completely, slide the bar forward, and press the white button to set the vacuum.
30. Set the exposure time to 20 sec.
31. Press the green button to start the exposure.
32. After the exposure is complete, slide the bar back, turn the lever back the other way (lowering the wafer), and remove the wafer and the mask from the exposure machine.
33. Rinse the wafer in AZ Developer/DI (1:4) for 2.5 min.
34. Rinse the wafer under flowing DI water for 30 sec.
35. Look at the pattern under low light in the microscope. If the pattern is unclear, either expose the photoresist longer or rinse the wafer in acetone for several minutes until the photoresist is removed and repeat steps 1-34.
36. Place the wafer on the 120 °C hot plat for 2 min. to hard bake.
Process sheet: Oxide etch

1. Fill a teflon beaker with 10:1 BOE.
2. Spin moderately – DO NOT HEAT.
3. Place wafer in wafer boat and place boat in beaker.
4. Stir wafer gently for approx. 25 min per micron of oxide.
5. Rinse wafer under flowing DI water for 2 min.
6. Perform a profilometry scan on the wafer.
7. Place wafer back in BOE for an additional 8 min.
8. Perform another profilometry scan on the wafer.
9. If there is a noticeable change in height, continue etching until no height change occurs.
Process sheet: Metal evaporation

1. Load wafers on sample holders, place in evaporator chamber.
2. Change the glass slide on the chamber lid.
3. Make sure the crystal health is over 80 – change if not.
4. Make sure there is enough metal in the crucible – add more if not.
5. Close the vent valve.
6. Turn the mechanical pump on.
7. Open the rough valve.
8. Wait for the pressure at TC2 (inside the chamber) to drop to 8 Pa.
9. Close the rough valve.
10. Open the hi-vac valve.
11. Pressure should drop rapidly.
12. Close the mechanical pump breaker.
13. Wait until pressure is in the 10^-6 range (several hours). (Turn filament on to check pressure)
14. Turn water on – valves behind chamber counter-clockwise.
15. On the power supply, turn the main breaker on, the keylock on, and the high voltage on.
16. Turn the turret source to the proper place (usually Cr first for adhesion layer).
17. Turn the gun filament on.
18. Record the pressure in the log book.
19. On the film deposition controller, select Film # and Set Process # (same as the turret number for the metal).
20. Scroll through and check the settings against the reference sheet located near the evaporator.
21. Set the desired deposition thickness (turn the key to unlock the program to set the thickness).
22. Make sure the shutter is set to auto.
24. Turn gun filament off.
25. Wait 5 min before switching sources to next metal.
26. Repeat 17-25 for each layer.
27. Turn gun filament, high voltage, keylock, main breaker, and water off in reverse order.
28. Wait 5 min before venting chamber.
29. Turn the pressure filament off.
30. Close the hi-vac valve.
31. Open the vent valve.
32. When vented, open the chamber and remove the wafers.
33. Repeat steps 5-12 to pump chamber back down before leaving station.
Process sheet: Photoresist removal

Quick version:
1. Rinse wafer in acetone for 3 minutes.
2. If performing a metal liftoff, continue rinsing until all unwanted metal has been removed.
3. Rinse wafer in flowing DI water for 2 min.
4. Dry wafer with nitrogen gun and inspect.

Longer version – only necessary if very careful removal of photoresist is needed:
1. Dip wafer in 300T photoresist stripper for 5 min at 50 °C.
2. Rinse wafer in flowing DI water for 1.5 min.
3. Dry with nitrogen gun.
4. Load wafer into plasma etcher.
5. Evacuate the chamber by pressing the power strip on and pressing the start button.
6. Wait until the pressure gauge reads 0.5 torr. Turn on the O₂ by turning the switch fully to the right and then letting it settle in the middle position.
7. Turn on the RF to light the plasma.
8. Plasma etch for 5 min.
9. Turn off the RF. Turn off the O₂. Stop the vacuum and turn off the main power switch.
10. Remove the water.
Process sheet: Bulk silicon etch

1. Prepare solution of 23.4 wt% KOH + 13.3 wt% isopropyl alcohol + 63 wt% H₂O. This is approximately 52 mL of 50% KOH solution, 30 mL of isopropyl alcohol, and 67 mL of DI water.
2. Heat solution to 80 °C.
3. Stir solution throughout process in order to minimize thermal gradients – etch depth is very temperature-dependent.
4. Once heated, place wafer in wafer boat and place in solution.
5. Cover beaker with glass dish.
6. Remove wafer intermittently and take profilometry measurement to monitor etch depth – etch rate should be approx. 0.6 µm/min.
7. When desired etch depth has been obtained, remove wafer from solution.
8. Rinse in flowing DI water for 2 min.
Process sheet: Dicing

1. Mount wafer on small piece of scrap silicon using black wax.
2. Mount small piece of silicon (w/ wafer on top) on large scrap silicon wafer.
3. Turn on water and compressed air using the yellow handles on the white pipes to the left of the dicing saw.
4. Turn on the main breaker, lamp, TV and camera (switches to right of saw).
5. Open lid and attach blade.
6. Place holder against blade and tighten using the tool stored on top of the saw.
7. Place the safety cover over the blade and holder and tighten screws. Make sure the nozzle points to the right.
8. Close lid.
9. Push ‘spindle on’ on display – should read 30,000 rpm.
10. Allow saw to warm up for ½ - 1 hour.
11. Open lid and place mounted wafer on stage.
12. Press ‘vacuum’ and ‘setup’ to auto-align the blade.
13. Use ‘shift’ to scroll through the settings – make necessary changes.
14. Make sure z-index is set to desired distance above the stage (approximately 0.050 is the height of two wafers)
15. Use ‘jog/scan’ to align blade in the proper location for a cut.
17. Press the button with an arrow pointed upward and to the right to begin a cut.
18. Once the cut has begun, press ‘jog/scan’ to get out of the semi-auto mode so that the blade stops after one cut.
19. Repeat steps 15-18 until all cuts have been made.
20. Press ‘spindle off’ perform steps 3-8 in reverse order to power down.
21. Unmount diced wafer and rinse in TCE to remove black wax.
22. Take diced samples into clean room and perform a spin clean (ethanol, TCE, and methanol repeated three times while wafer is on spinner).
23. Blow dry with nitrogen gun.
Appendix C: Solver routine

void Solve(TSolutionVolume * els[3000], int iNumOfElements, NodeInfo * nodes[6000],
int iNumOfNodes, double time, TSpeciesName name)
{
    TBArrElm* B[2000]; // array of linked lists, each forming a row of the matrix
    double C[2000]; // num of nodes
    int count1, count2, cur_i, cur_j, cur_k, flag, count3;
    TBArrElm *debug;
    TBArrElm *remove;
    char matrixfile[20];
    // Initialize matrices
    for(count1=0;count1<= iNumOfNodes;count1++)
    {
        B[count1] = new TBArrElm();
        C[count1] = 0;
    }
    // debugging stuff
    sprintf(matrixfile, "matrix%d.txt", 1);
    ofstream outmatrix(matrixfile, ios::out);
    // notation on matrices is \[down\][over]
    for(count1=0;count1 < iNumOfElements;count1++)
    {
        cur_i = els[count1]->i->iNodeId;
        cur_j = els[count1]->j->iNodeId;
        cur_k = els[count1]->k->iNodeId;
        // outmatrix << cur_i << " " << cur_j << " " << cur_k << endl;
        current = B[cur_i];
        if ((current->right == 0) && (current->val*current->val < 1e-300)) // empty list
        {   
            *current = current->AddElem(cur_i, els[count1]->Bii(time)*1e7,1);
        } 
        else if (cur_i < current->col) // insert at beginning
        {   
            *current = current->AddElem(cur_i, els[count1]->Bii(time)*1e7,2);
            B[cur_i] = current->left;
        } 
        else if (cur_i == current->col)
        {   
            current->val = current->val + els[count1]->Bii(time)*1e7;
        } 
        else // insert in middle or at end of list
        {   
            if (current->right == 0) // insert at beginning
            {   
                *current = current->AddElem(cur_i, els[count1]->Bii(time)*1e7,1);
            } 
            else if (cur_i < current->col) // insert at beginning
            {   
                *current = current->AddElem(cur_i, els[count1]->Bii(time)*1e7,2);
                B[cur_i] = current->left;
            } 
            else if (cur_i == current->col)
            {   
                *current = current->AddElem(cur_i, els[count1]->Bii(time)*1e7);
            } 
            else // insert in middle or at end of list
            {   
                if (current->right->col < current->right) // add at end
                {   
                    *current = current->AddElem(current->right->col, els[count1]->Bii(time)*1e7,3);
                } 
                else if (current->right->col == current->right) // add to existing elem
                {   
                    current->val = current->val + els[count1]->Bii(time)*1e7;
                } 
                else // add new elem in middle
                {   
                    *current = current->AddElem(cur_i, els[count1]->Bii(time)*1e7,3);
                } 
        }
    current = B[cur_i]; // set back to beginning of row;
    if (cur_i < current->col) // insert at beginning
    {   
        *current = current->AddElem(cur_i, els[count1]->Bij(time)*1e7,2);
        B[cur_i] = current->left;
    } 
    else if (cur_i == current->col)
    {   
        current->val = current->val + els[count1]->Bij(time)*1e7;
    } 
    else // insert in middle or at end of list
    {   
        if (current->right != 0) // add at end
        {   
            *current = current->AddElem(cur_i, els[count1]->Bij(time)*1e7,3);
        } 
        else if (current->right->col == current->right) // add to existing elem
        {   
            current->val = current->val + els[count1]->Bij(time)*1e7;
        } 
        else // add new elem in middle
        {   
            *current = current->AddElem(cur_i, els[count1]->Bij(time)*1e7,3);
        } 
    }
}
else if (current->right->col == cur_j)  // add to existing elem
    { current = current->right;
      current->val = current->val + els[count1]->Bij(time)*1e7;
    }
else                                            // add new elem in middle
    { *current = current->AddElem(cur_j, els[count1]->Bij(time)*1e7);
    }

current = B[cur_i];                    // set back to beginning of row;

if (cur_k < current->col)                  // insert at beginning
    { *current = current->AddElem(cur_k, els[count1]->Bik(time)*1e7,2);
      B[cur_i] = current->left;
    }
else if (cur_k == current->col)
    { current->val = current->val + els[count1]->Bik(time)*1e7;
    }
else // insert in middle or at end of list
    if (current->right != 0)        // add at end
        if (current->right->col < cur_k)
            { flag = 0;
              while (flag == 0)
                { current = current->right;
                  if (current->right == 0)
                      { flag = 1;
                      }
                  else if (current->right->col >= cur_k)
                      { flag = 1;
                      }
                }
        }
    }
else if (current->right == 0)        // add at end
        { *current = current->AddElem(cur_k, els[count1]->Bik(time)*1e7);
        }
else if (cur_i < current->col)        // insert at beginning
    { *current = current->AddElem(cur_i, els[count1]->Bji(time)*1e7,1);
      B[cur_j] = current->left;
    }
else if (cur_i == current->col)
    { current->val = current->val + els[count1]->Bji(time)*1e7;
    }
else // insert in middle or at end of list
    if (current->right != 0)        // add at end
        if (current->right->col < cur_i)
            { flag = 0;
              while (flag == 0)
                { current = current->right;
                  if (current->right == 0)
                      { flag = 1;
                      }
                  else if (current->right->col >= cur_i)
                      { flag = 1;
                      }
                }
        }
    }
else if (current->right == 0)        // add at end
        { *current = current->AddElem(cur_i, els[count1]->Bji(time)*1e7,3);
        }
else if (current->right->col == cur_i)        // add to existing elem
    { current = current->right;
      current->val = current->val + els[count1]->Bji(time)*1e7;
    }
else // add new elem in middle
    { *current = current->AddElem(cur_i, els[count1]->Bji(time)*1e7,3);
    }
}
current = B[cur_j];                    // set back to beginning of row;
if (cur_j < current->col) // insert at beginning
{ current = current->AddElem(cur_j, els[count1]->Bjj(time)*1e7,2);
  B[cur_j] = current->left;
}
else if (cur_j == current->col)
{ current->val = current->val + els[count1]->Bjj(time)*1e7;
}
else // insert in middle or at end of list
if (current->right != 0)
{ if (current->right->col < cur_j)
    while (flag == 0)
      { current = current->right;
        if (current->right == 0)
          flag = 1;
        else if (current->right->col >= cur_j)
          flag = 1;
      }
  if (current->right == 0)  // add at end
  else if (current->right->col == cur_j) // add to existing elem
    { current = current->right;
      current->val = current->val + els[count1]->Bjj(time)*1e7;
    }
  else // add new elem in middle
    { *current = current->AddElem(cur_j, els[count1]->Bjj(time)*1e7,3);
    }
}
current = B[cur_j]; // set back to beginning of row;
if (cur_k < current->col) // insert at beginning
{ current = current->AddElem(cur_k, els[count1]->Bjk(time)*1e7,2);
  B[cur_k] = current->left;
}
else if (cur_k == current->col)
{ current->val = current->val + els[count1]->Bjk(time)*1e7;
}
else // insert in middle or at end of list
if (current->right != 0)
{ if (current->right->col < cur_k)
    while (flag == 0)
      { current = current->right;
        if (current->right == 0)
          flag = 1;
        else if (current->right->col >= cur_k)
          flag = 1;
      }
  if (current->right == 0)  // add at end
  else if (current->right->col == cur_k) // add to existing elem
    { current = current->right;
      current->val = current->val + els[count1]->Bjk(time)*1e7;
    }
  else // add new elem in middle
    { *current = current->AddElem(cur_k, els[count1]->Bjk(time)*1e7,3);
    }
}
current = B[cur_k];
if (current->right == 0) && (current->val*current->val < 1e-300) // empty list
{ current = current->AddElem(cur_i, els[count1]->Bki(time)*1e7,1);
  B[cur_i] = current->left;
}
else if (cur_i < current->col) // insert at beginning
{ current = current->AddElem(cur_i, els[count1]->Bki(time)*1e7,2);
  B[cur_i] = current->left;
}
else if (cur_i == current->col)
{ current->val = current->val + els[count1]->Bki(time)*1e7;
}
else // insert in middle or at end of list
if (current->right != 0)
{ if (current->right->col < cur_i)
    while (flag == 0)
      { current = current->right;
        if (current->right == 0)
          flag = 1;
        else if (current->right->col >= cur_i)
          flag = 1;
      }
}
if (current->right == 0)  // add at end
  (*current = current->AddElem(cur_i, els[count1]->Bki(time)*1e7, 3));
else if (current->right->col == cur_i) // add to existing elem
  (*current = current->right;
   current->val = current->val + els[count1]->Bki(time)*1e7);
else  // add new elem in middle
  (*current = current->AddElem(cur_i, els[count1]->Bki(time)*1e7, 3));
}
current = B[cur_k];  // set back to beginning of row;
if (cur_j < current->col) // insert at beginning
  (*current = current->AddElem(cur_j, els[count1]->Bkj(time)*1e7, 2);
  B[cur_k] = current->left;
} else if (cur_j == current->col)
  current->val = current->val + els[count1]->Bkj(time)*1e7;
else  // insert in middle or at end of list
  if (current->right->col < cur_j)
    flag = 0;
    while (flag == 0)
      (current = current->right;
       if (current->right == 0)
         (flag = 1);
       else if (current->right->col >= cur_j)
         (flag = 1);
      };
  if (current->right == 0)  // add at end
    (*current = current->AddElem(cur_j, els[count1]->Bkj(time)*1e7, 3));
  else if (current->right->col == cur_j) // add to existing elem
    (*current = current->right;
     current->val = current->val + els[count1]->Bkj(time)*1e7);
  else  // add new elem in middle
    (*current = current->AddElem(cur_j, els[count1]->Bkj(time)*1e7, 3));
}
current = B[cur_k];  // set back to beginning of row;
if (cur_k < current->col) // insert at beginning
  (*current = current->AddElem(cur_k, els[count1]->Bkk(time)*1e7, 2);
  B[cur_k] = current->left;
} else if (cur_k == current->col)
  current->val = current->val + els[count1]->Bkk(time)*1e7;
else  // insert in middle or at end of list
  if (current->right->col < cur_k)
    flag = 0;
    while (flag == 0)
      (current = current->right;
       if (current->right == 0)
         (flag = 1);
       else if (current->right->col >= cur_k)
         (flag = 1);
      };
  if (current->right == 0)  // add at end
    (*current = current->AddElem(cur_k, els[count1]->Bkk(time)*1e7, 3));
  else if (current->right->col == cur_k) // add to existing elem
    (*current = current->right;
     current->val = current->val + els[count1]->Bkk(time)*1e7);
  else  // add new elem in middle
    (*current = current->AddElem(cur_k, els[count1]->Bkk(time)*1e7, 3));
}
C[cur_i] = C[cur_i] + els[count1]->Ci(time)*1e7;
C[cur_j] = C[cur_j] + els[count1]->Cj(time)*1e7;
C[cur_k] = C[cur_k] + els[count1]->Ck(time)*1e7;
/*
for(count3=0; count3<iNumOfNodes; count3++)
{ debug = B[count3];
    outmatrix << count3 << " " ;
while (debug != 0)
{ outmatrix << debug->col << " " << debug->val << " ";
    debug = debug->right;
}
    outmatrix << count3 << " " << C[count3];
outmatrix << endl;
}
*/

// Solve the matrix
// First: Pass thru back to front, removing rows and columns, and fixing C
int iThis, iLast;
iLast = iNumOFNodes-1; //row number of last spot

// Note: pass from back to front to avoid destroying numbering
for(iThis= iNumOFNodes-1;iThis >= 0;iThis--)
{ if (nodes[iThis]->iFixed == 1) // Is this a constant element that needs to be removed
    { Fix C
        for(count1=0 ; count1<iLast ; count1++)
        { current = B[count1];
            if (current->col == iThis) // first element is the right one
            { C[count1] = C[count1] - current->val * nodes[iThis]->chem->GetConcentration(name);
            }
            else if (current->col < iThis) // may be somewhere in the row
            { if (current->right != 0) // may be somewhere in the row
                { if (current->right ! = 0) // not at end
                    { if (current->right->col < iThis)
                        { flag = 0;
                            while (flag == 0)
                            { current = current->right;
                                if (current->right == 0)
                                { flag = 1;
                                }
                                else if (current->right->col >= iThis)
                                { flag = 1;
                                }
                            }
                        }
                        if (current->right != 0) // not at end
                        { if (current->right->col < iThis) // found it
                            { C[count1] = C[count1] - current->right->val * nodes[iThis]->chem->GetConcentration(name);
                            }
                        }
                    }
                }
            }
            //Remove the C entry
            for(count1=iThis ; count1<iLast ; count1++)
            { C[count1] = C[count1+1];
                temp2=C[count1];
            }
            //Remove Rows
            for(count1=iThis ; count1<iLast ; count1++)
            { B[count1] = B[count1+1];
            }
            //Remove Columns and renumber
            for(count2=0;count2<iLast;count2++)  // traverse list of rows
            { current = B[count2];
                if (current->col == iThis)
                { *current = current->DeleteElem();
                    if (current->right ! = 0)
                    { B[count2] = B[count2]->right;
                        remove = current;
                        current = current->right;
                        delete remove;
                        while (current != 0)
                        { current->col = current->col - 1;
                        current = current->right;
                        }
                    }
                }
                else if ((current->col <= -1) || (current->col < iThis))
                { // may be in row
                    if (current->right ! = 0)
                    { if (current->right->col < iThis)
                        { flag = 0;
                            while (flag == 0)
                            { current = current->right;
                                if (current->right == 0)
                                { flag = 1;
                                }
                            }
                        }
                        else if (current->right->col >= iThis)
                    } else if (current->right->col < iThis)
if (current->right != 0)
    { current = current->right;
      if (current->col == iThis)
      { *current = current->DeleteElem();
        remove = current;
        current = current->right;
        delete remove;
      }
      while (current != 0)
      { current->col = current->col - 1;
        current = current->right;
      }
    }
  }
else if (current->col > iThis)
  // no deletion, just decrement column numbers
  { while (current != 0)
    { current->col = current->col - 1;
      current = current->right;
    }
  }

  // Decrement iLast
  iLast--;

/*
for(count1=0;count1<=iLast;count1++)
{ debug = B[count1];
  outmatrix << count1 << " ";
  while (debug != 0)
  { outmatrix << debug->col << " " << debug->val << " ";
    debug = debug->right;
  }
  // outmatrix << count1 << " " << C[count1];
  outmatrix << endl;
}
*/

// Solve by Gaussian Elimination

double temp;
TBArrElem *comp_cur;

//printf("starting gauss elimination\n");
for(iThis = 0 ; iThis<iLast ; iThis++)
{ current = B[iThis];
  if (current->col < iThis)
  { flag = 0;
    while (flag == 0)
    { current = current->right;
      if (current == 0)
      { flag = 1;
      }
    }
  }
  else if (current->col == iThis)
  { flag = 1;
    if ((current->col == iThis) && (current->val*current->val > 1e-300))
    { //cout << "inner loop ";
      for(count1=iThis+1 ; count1<=iLast ; count1++)
      { //cout << " start count1 " << count1 << " " << iLast << endl;
        current = B[count1];
        if (current->col < iThis)
        { //cout << " 1";
          flag = 0;
          while (flag == 0)
          { current = current->right;
            if (current == 0)
            { flag = 1;
            }
          }
          comp_cur = B[count1];
          if (comp_cur->col < iThis) // could be in row
          { //cout << " 2";
            flag = 0;
            while (flag == 0)
            { comp_cur = comp_cur->right;
              if (comp_cur == 0)
              { flag = 1;
              }
else if (comp_cur->col >= iThis)
{ flag = 1;
}
}
}
if (comp_cur != 0)
{
if ((comp_cur->col == iThis) && (comp_cur->val*comp_cur->val > 1e-300))
  // this value also exists and is nonzero
  //cout << " a";
    *comp_cur = comp_cur->DeleteElem();
if ((comp_cur->left == 0) && (comp_cur->right != 0)) // first in list
  B[count1] = comp_cur->right;
remove = comp_cur;
comp_cur = comp_cur->right;
delete remove;
current = current->right;
}
else if ((comp_cur->left != 0) && (comp_cur->right == 0)) // middle of list
  remove = comp_cur;
comp_cur = comp_cur->right;
delete remove;
current = current->right;
}
else if ((comp_cur->col > current->col) // need to insert an elem
  //cout << " c";
    *comp_cur = comp_cur->AddElem(current->col,temp*current->val,2);
if (comp_cur->left->left == 0) // added to beginning
  B[count1] = comp_cur->left;
}
else if (comp_cur->col < current->col) // keep traversing
  //cout << " d",
  comp_cur = comp_cur->right;
}
else if ((comp_cur->col < current->col) && (comp_cur->right != 0)) // middle of list
  if (comp_cur->left != 0) && (comp_cur->right != 0)) // middle of list
  remove = comp_cur;
comp_cur = comp_cur->right;
delete remove;
current = current->right;
}
else if (comp_cur->col > current->col) // need to insert an elem
  //cout << " a";
    *comp_cur = comp_cur->AddElem(current->col,temp*current->val,2);
if (comp_cur->left->left == 0) // added to beginning
  B[count1] = comp_cur->left;
}
else if (comp_cur->col == current->col)
  //cout << " b";
if (comp_cur->right != 0)
  comp_cur = comp_cur->right;
}
else if ((comp_cur->col < current->col) && (comp_cur->right != 0)) // keep traversing
  //cout << " c";
    *comp_cur = comp_cur->AddElem(current->col,temp*current->val,2);
if (comp_cur->left->left == 0) // added to beginning
  B[count1] = comp_cur->left;
}
else if (comp_cur->col == current->col) // first in list
  B[count1] = comp_cur->right;
remove = comp_cur;
comp_cur = comp_cur->right;
delete remove;
current = current->right;
}
else
  //cout << " a";
    *comp_cur = comp_cur->right;
}
else if (comp_cur->col > current->col) // need to insert an elem
  //cout << " b";
    *comp_cur = comp_cur->right;
}
else if (comp_cur->col == current->col) // first in list
  B[count1] = comp_cur->right;
remove = comp_cur;
comp_cur = comp_cur->right;
delete remove;
current = current->right;
}
else
  //cout << " c";
    *comp_cur = comp_cur->right;
}
else
  //cout << " d";
    *comp_cur = comp_cur->right;
}
// Back Substitute
for(count1=iLast ; count1>=0 ; count1--)
{  temp =C[count1];
    current = B[count1];
    if (current->col != count1)
    { flag = 0;
      while (flag == 0)
      { current = current->right;
        if (current == 0)
        { flag = 1;
        }
        else if (current->col == count1)
        { flag = 1;
        }
      }
    }
    if (current != 0)
    { diagonal = current;
      current = current->right;
      while (current != 0)
      { temp3 = current->val;
        temp2 = C[current->col];
        temp = temp - (temp2 * temp3);
        current = current->right;
      }
      C[count1] = temp/diagonal->val; // first element in list is diagonal element
    }
  }

for (count1=0;count1==iLast;count1++)
{  outmatrix << count1 << " " << C[count1] << endl;
 } */

// Grab the nodal values
count1 = 0; //keeps track of unfixed nodes
for(iThis = 0 ; iThis < iNumOfNodes ; iThis++)
{ if(nodes[iThis]->iFixed != 1) // fixed node
{    nodes[iThis]->chem->SetConcentration(name,C[count1]);
    count1++;
 }
}

// Delete the B array (dynamically allocated so must be deleted)
for(count1=0;count1<iNumOfNodes;count1++)
{  current = B[count1];
    while (current != 0)
    { TBArrElm *temp4 = current;
      current = current->right;
      delete temp4;
    }
  }

TBArrElm.C  L. DeJong 7/21/98
TBArrElm is the class of objects that are elements in the B matrix used by the solver.C routine to solve the matrices used in the finite elements method. These elements can be added or deleted, they can be queried for their value and column location, and their values can be changed.

**********************************************************************/
#include "tbarrelm.H"
#include <iostream.h>
#include <fstream.h>
#include <math.h>

TBArrElm::TBArrElm()
//**************************************************************************
// TBArrElm(): Minimal constructor for class
***************************************************************************/
{  col = -1;
    val = 0.0;
    right = 0;
    left = 0;
    }

TBArrElm::TBArrElm(int colnum, double value)
//**************************************************************************
// TBArrElm(int colnum, double value) Constructor for class
// Defines a new element in the array
***************************************************************************/
{  col = colnum;
    val = value;
    right = 0;
    }
left = 0;
}

TBArrElm::~TBArrElm()
/***************************************************************************/
TBArrElm(): Destructor for class [Deallocates an element in the array]
***************************************************************************/
{
right = 0;
left = 0;
}

TBArrElm& TBArrElm::AddElem(int colnum, double value, int flag)
/***************************************************************************/
AddElem(...): [Constructs and adds a new element to the matrix.]
The variable flag designates whether the new element is to replace
the current one (flag=1), be inserted before it (flag=2), or be
inserted after it (flag=3).
The linked list for its row is re-linked to incorporate it.
***************************************************************************/
{
TBArrElm *newelem;
newelem = new TBArrElm(colnum,value);
if (flag == 1) // replace the current element
{
newelem->right = this->right;
newelem->left = this->left;
*this = *newelem;
}
else if (flag == 2) // insert before the current element
{
if (this->left == 0) // beginning of list
{
newelem->right = this;
newelem->left = this->left;
this->left = newelem;
}
else // middle of list
{
newelem->right = this;
newelem->left = this->left;
this->left->right = newelem;
this->left = newelem;
}
}
else if (flag == 3) // insert after the current element
{
if (this->right == 0) // end of list
{
newelem->right = this->right;
newelem->left = this;
this->right = newelem;
}
else // middle of list
{
newelem->right = this->right;
newelem->left = this;
this->right->left = newelem;
this->right = newelem;
}
return *this;
}

TBArrElm& TBArrElm::DeleteElem()
/***************************************************************************/
DeleteElem(...): [Deletes the current element from the B matrix and re-links the
linked list for its row.]
***************************************************************************/
{
if ((this->left == 0) && (this->right == 0)) // only element
{
this->val = 0.0;
}
else if ((this->left != 0) && (this->right == 0)) // last element
{
this->left->right = this->right;
}
else if ((this->left == 0) && (this->right != 0)) // first element
{
this->right->left = this->left;
}
else //middle element
{
this->left->right = this->right;
this->right->left = this->left;
}
return *this;
}
This module defines the elements of the dynamically allocated B array used in the finite element method. These functions are used by the solver.C routine.

class TBArrElm

public:
int col; // column location number in the B matrix
double val; // value of this element in the B matrix
TBArrElm * right; // pointer to the element to the right in the B matrix
TBArrElm * left; // pointer to the element to the left in the B matrix
TBArrElm(); // constructor
TBArrElm(int colnum, double value); // constructor
~TBArrElm(); // destructor
TBArrElm AddElem(int colnum, double value, int flag);
TBArrElm DeleteElem();
private:
;
#endif
Appendix D: Aluminum hydrolysis routine

TAllSpecies::AlEquilibria(TChemistry * chem)
/************************************************************************
Requirements:
Hp,OHm, Alppp,AlOHpp,AlOHppp,AlOHHPp,AlOHHPHP must be in chem
written 12/2/98 by Lisa DeJong
************************************************************************/
{double Q11, Q12, Q13, Q14, I;
  double H,OH, Al0,Al1,Al2,Al3,Al4;
  double logH, logOH, logCr0, logCr1, logCr2, logCr3, logCr4;
  double a,b,c,x; // values for determining the concentrations of H and OH
  double TotAl, TestH, DerAl, DerH;
  // double lambdaCr, lambdaH;
  int done = 0;
  TSpeciesName Alppp;
  double fit, exp, lambda;
  Alppp = "Al+++";
  // Grab the concentrations of the relevant species
  if (!chem->GetFixed(Alppp) && (chem->GetConcentration("Al++") > 0))
  {H      = chem->GetConcentration("H+");
   OH     = chem->GetConcentration("OH-");
   Al0    = chem->GetConcentration("Al+++");
   Al1    = chem->GetConcentration("AlOH++");
   Al2    = chem->GetConcentration("AlOHOH+");
   Al3    = chem->GetConcentration("AlOHOHOH");
   Al4    = chem->GetConcentration("AlOHOHOHOH-");
  // cout << "H " << H << " OH " << OH << " Al0 " << Al0 << " Al1 "
    << Al1 << " Al2 " << Al2 << " Al3 " << Al3 << " Al4 " << Al3 << endl;
  // cout << endl;
  // Calculate how much OH would be generated if all Al-species dehydrolyzed
  OH = OH + Al1 + 2*Al2 + 3*Al3 + 4*Al4;
  // cout << "dehyro OH " << OH << endl;
  // Equilibrate H and OH
  // want to find x such that (H-x) * (OH-x) = 1e-8 (mol/m^3)
  a = 1;
  b = -H - OH;
  c = H * OH - 1e-8;
  x = (-b - sqrt(b*b - 4*a*c))/2*a;
  H  = H - x;
  OH = OH - x;
  // cout << "new H " << H << " new OH " << OH << endl;
  //Set the total Al that has to be apportioned among the products
  TotAl = Al0 + Al1 + Al2 + Al3 + Al4;
  // cout << "TotAl " << TotAl << endl;
  // Set the Formation quotients
  I = 0.6; // ionic strength value used to compare to Bucheit,Moran,Stoner
  exp = -1.97 + (-2.044*sqrt(I))/(1 + sqrt(I)) + 0.52*1;
  Q11 = pow(10,exp);  //Baes + Mesmer -4.97 (+3 for /m^3)
  exp = -3.3 + (-3.066*sqrt(I))/(1 + sqrt(I)) + 0.55*1;
  Q12 = pow(10,exp);  //Baes + Mesmer -9.3  (+6 for /m^3)
  exp = -6.0 + (-3.066*sqrt(I))/(1 + sqrt(I)) + 0.45*1;
  Q13 = pow(10,exp);  //Baes + Mesmer -15.0 (+9 for /m^3)
  exp = -11.0 + (-2.044*sqrt(I))/(1 + sqrt(I)) + 0.36*1;
  Q14 = pow(10,-11.0); //Baes + Mesmer -23.0 (+12 for /m^3)
  Al0 = TotAl; //initialize the first guess for Al=-log(
  TestH = H;   //initialize the first guess for H
  exp = -4; lambda = 4;
  while (!done)
  {TestH = pow(10,exp);
\[ A_1 = Q_11 \times A_0 / (\text{TestH}); \]
\[ A_2 = Q_12 \times A_0 / (\text{TestH}\times\text{TestH}); \]
\[ A_3 = Q_13 \times A_0 / (\text{TestH}\times\text{TestH}\times\text{TestH}); \]
\[ A_4 = Q_14 \times A_0 / (\text{TestH}\times\text{TestH}\times\text{TestH}\times\text{TestH}); \]

// Find out how much TOTAL Al is produced by these conditions
\[ \text{DerAl} = A_0 + A_1 + A_2 + A_3 + A_4; \]

// Correct Al0 to get the exact amount of Al+3 required to match TotAl
\[ A_0 = A_0 \times \text{TotAl}/\text{DerAl}; \]

// Recalculate the Conc's of all hydrolysis products
// Could just multiply by TotAl/DerAl - this is clearer to read
\[ A_1 = Q_11 \times A_0 / (\text{TestH}); \]
\[ A_2 = Q_12 \times A_0 / (\text{TestH}\times\text{TestH}); \]
\[ A_3 = Q_13 \times A_0 / (\text{TestH}\times\text{TestH}\times\text{TestH}); \]
\[ A_4 = Q_14 \times A_0 / (\text{TestH}\times\text{TestH}\times\text{TestH}\times\text{TestH}); \]

// This finds the total [H] b4 it redistributes with OH
\[ \text{DerH} = H + A_1 + 2\times A_2 + 3\times A_3 + 4\times A_4; \]
//cout << "DerH " << DerH << " H " << H << endl;

// Settle the [H] and [OH] conc's for with the formation of H2O
\[ a = 1; \]
\[ b = -\text{DerH} - \text{OH}; \]
\[ c = \text{DerH}\times\text{OH} - 1e-8; \]
\[ x = (-b - \sqrt{b^2 - 4\times a\times c})/2\times a; \]
\[ \text{DerH} = \text{DerH} - x; \]
//cout << "DerH " << DerH << endl;

// If the resulting [H] (DerH) > initial [H] (TestH) the next TestH should be higher
// If less, next TestH should be lower
// If the relative position cross over need to reverse the sign and shrink lambda
if(DerH > TestH) // started too basic need lambda > 0
    {if(lambda < 0) // just crossed over
        {lambda = -0.49 * lambda;}
    }
else // started too acidic, need lambda < 0
    {if(lambda > 0)
        {lambda = -0.49 * lambda;}
    }

fit = fabs((DerAl-TotAl)/TotAl) + fabs((TestH-DerH)/TestH);
//printf("%lg  %lg  %lg  %lg  %lg  %lg  %lg \n",A0,
//TotAl, DerAl, TestH,  DerH, fit, lambda);
if(fabs(lambda) < 1e-6)
    {done = 1;}
else
    {exp = exp + lambda;}

H = DerH;
OH = OH - x;

// put the Values back into chem
chem->SetConcentration("H+","H");
chem->SetConcentration("OH-","OH");
chem->SetConcentration("Al+++","A0");
chem->SetConcentration("AlOHOH++","A12");
chem->SetConcentration("AlOHOHOH++","A3");
chem->SetConcentration("AlOHOHOHOH--","A4");
# Appendix E: CREVICER/GUI interaction code

```cpp
#include <iostream.h>
#include <fstream.h>
#include <string.h>
#include <math.h>
#include "tchem.H"
#include "taspecie.H"
#include "tallspec.H"
#include "tmateria.H"
#include "tbarrelm.H"
#include "solver.H"
#include "treaclst.H"
#include "tmatlst.H"
#include "treactio.H"

ifstream input;

// This function reads in the GUI setup file
void setup(TSolutionVolume *els[3250], int *iNumOfElements,
NodeInfo *nodes[6500], int *iNumOfNodes, TAllSpecies *crc,
double *thetap, double *thetac, int *numcts, long double *lencts,
long double *lenpts, double *convcrit, TAllSpecies *outspec, int *al_hydro,
int *cr_hydro, TSpeciesName neutname, char **all_species)
{
    // These interface with the file
    char buffer[50];
    double temp_real;
    long temp_val;
    // End interface variables

    int speciesz;        // charge number
    double speciesu;     // ionic mobility
    double speciesu0;    // chemical potential
    TReacName curvetype;
    int nume, coefr1, coefr2, coefp1, coefp2; // coefficients and num e's
    TSpeciesName reac1, reac2, prod1, prod2; // names of reacs and prods
    double c0, c1, c2, c3, c4, c5, c6, c7, c8, c9, c10; // polynomial coefficients
    //outspec->size = 0;
    int numreacs;  // number of reactions on this material
    TReacListElem *matreaclist; // list of reactions on this material

    int nodeid;             // the id number of the node
    double x, y;             // the x and y coordinates for the node
    double newtemp;         // temperature for the node
    double newpress;        // pressure for the node
    double newelec;         // potential for the node
    int isfixedp, isfixedc; // potential and chemical isFixed variables
    TSpeciesName specname;  // the name of the species being read in

    int elemid;             // the id number of the elem
    int l, j, k;             // the node numbers for the element
    double height;          // the height for the element
    TMatName matname;       // the name of the base material of the elem
    TMatListElem *current;
    TMaterial *newmat;
    int flag = 0;

    //int numofedges;         // the number of edges
    int edgewidth; // the number of that edge
    int tempint;
    //int nodeone, nodetwo;   // the two node numbers associated with it
    //TMatName edgename;      // the name of the material
    TMatListElem *current;
    TMaterial *newedge;
    TReacListElem *reactlist = new TReacListElem();
    TMaterial *newmat = new TMaterial();
    TMatListElem *matlist = new TMatListElem();
    TWhere *where = new TWhere();
    TAllSpecies *outspec = new TAllSpecies();
    //crc = new TAllSpecies();
    //outspec = new TAllSpecies();
}
```
int spec_counter = 0;
all_species = new char*[100];
for (i = 0; i < 100; i++)
    all_species[i] = new char[50];
int counter = 0; // For looping
input.open("runthis.stp");

/* Read in the charge neutrality species name and put it in neutname 
I don't know where it is in the setup file - just read it when 
you get to it - neutname is of type TSpeciesName which is char * 
*/
/* START SPECIES USED FROM STATIC LIBRARY 
index = number of species to follow (read in) 
loop through index number of times 
read in specname 
at this point you need to new an object of the proper subclass of 
TASpecies - the one associated with this species - and add it 
to the crc.  I would recommend a long list of if statements, unless 
you have a better idea.  Example:
readspecies = new TAlppp();
if (specname == readspecies->name) 
    { crc->AddSpecies(readspecies); 
      initchem->AddSpecies("Al+++",0,0); 
    }
else 
    { readspecies = new THp();
      if (specname == readspecies->name) 
          { crc->AddSpecies(readspecies);
            initchem->AddSpecies("H+",0,0);
          }
    }
else 
    { readspecies = new TOHm();
      if (specname == readspecies->name) 
          { crc->AddSpecies(readspecies);
            initchem->AddSpecies("OH-",0,0);
          }
    }
    //  And so on through all of the static subclasses (there are only about 20)
    //  You also need to add temperature, pressure, and potential 
readspecies = new TElectrical();
    crc->AddSpecies(readspecies);
initchem->AddSpecies("electrical",0,0);
readspecies = new TTemperature();
    crc->AddSpecies(readspecies);
initchem->AddSpecies("temperature",298.1);
readspecies = new TPressure();
    crc->AddSpecies(readspecies);
initchem->AddSpecies("pressure",1e5,1);
END SPECIES USED FROM STATIC LIBRARY*/
if (!input.is_open())
{ 
    cout << "Failure opening file!!!"; 
    return;
}
input >> buffer; //cout << buffer << endl;
input >> temp_val; //cout << temp_val << endl;
for (i = 0; i < temp_val; i++)
{
    input >> all_species[spec_counter];
    if (StringsEqual(all_species[spec_counter], "Al+++")
    {
        readspecies = new TAlppp();
        crc->AddSpecies(readspecies);
initchem->AddSpecies(all_species[spec_counter++],0,0);
    }
/*if (buffer == "AlOH++")
{
    readspecies = new TAOHpp();
    crc->AddSpecies(readspecies);
initchem->AddSpecies(buffer,0,0);
}
if (buffer == "AlOHOn")
{
    readspecies = new TAOHOrp();
*/
if (buffer == "AlOHOHOH")
{
    readspecies = new TAlOHOHOH();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(buffer,0,0);
}
if (buffer == "AlOHOHOHOH-")
{
    readspecies = new TAlppp();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(buffer,0,0);
} /*
else if (StringsEqual(all_species[spec_counter], "H+"))
{
    readspecies = new THp();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "Ag+"))
{
    readspecies = new TAgp();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "OH-"))
{
    readspecies = new TOHm();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "Cl-"))
{
    readspecies = new TClm();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "Cr+++"))
{
    readspecies = new TCrppp();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "CrO4--"))
{
    readspecies = new TCrO4mm();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "CrOH++"))
{
    readspecies = new TCrOHpp();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "CrOHOH+"))
{
    readspecies = new TCrOHOHp();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "CrOHOHOH"))
{
    readspecies = new TCrOHOHOH();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "CrOHOHOHOH-"))
{
    readspecies = new TCrOHOHOHm();
    crc->AddSpecies(readspecies);
    initchem->AddSpecies(all_species[spec_counter++],0,0);
else if (StringsEqual(all_species[spec_counter], "Cu++"))
{
  readspecies = new TCupp();
  crc->AddSpecies(readspecies);
  initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "Fe++"))
{
  readspecies = new TFepp();
  crc->AddSpecies(readspecies);
  initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "K+"))
{
  readspecies = new TKp();
  crc->AddSpecies(readspecies);
  initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "Li+"))
{
  readspecies = new TLip();
  crc->AddSpecies(readspecies);
  initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "Na+"))
{
  readspecies = new TNap();
  crc->AddSpecies(readspecies);
  initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "Ni++"))
{
  readspecies = new TNipp();
  crc->AddSpecies(readspecies);
  initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "NO3-"))
{
  readspecies = new TNO3m();
  crc->AddSpecies(readspecies);
  initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "O2"))
{
  readspecies = new TO2();
  crc->AddSpecies(readspecies);
  initchem->AddSpecies(all_species[spec_counter++],0,0);
}
else if (StringsEqual(all_species[spec_counter], "SO4--"))
{
  readspecies = new TSO4mm();
  crc->AddSpecies(readspecies);
  initchem->AddSpecies(all_species[spec_counter++],0,0);
}
readspecies = new TTemperature();
crc->AddSpecies(readspecies);
initchem->AddSpecies("temperature",298,1);
readspecies = new TPressure();
crc->AddSpecies(readspecies);
initchem->AddSpecies("pressure",1e5,1);
readspecies = new TElectrical();
crc->AddSpecies(readspecies);
initchem->AddSpecies("electrical",0,0);
/* START MATERIALS USED FROM STATIC LIBRARY
index = number of materials to follow (read in)
loop through index number of times
read in matname at this point you need to new an object of the proper subclass of
TMaterial and add it to the list of materials. I would follow
the same procedure you used above for species - newing readmaterial
as all of the different subclass types and comparing names with matname
The new material needs to be added to the list of materials - this
class doesn’t have any functions or information hiding

tempmat->material = readmaterial;
tempmat->next = 0;
if (matlist == 0) // list empty
{ matlist = tempmat;
}
else // matlist not empty
{ tempmat->next = matlist;
matlist = tempmat;
}

END MATERIALS USED FROM STATIC LIBRARY*/

input >> buffer;
input >> temp_val;
for (i = 0; i < temp_val; i++)
{
    input >> buffer;
    if (StringsEqual(buffer, "Ag"))
    {
        readmaterial = new TAg(crc);
        tempmat->material = readmaterial;
tempmat->next = 0;
if (matlist == 0) // list empty
{ matlist = tempmat;
}
else // matlist not empty
{ tempmat->next = matlist;
matlist = tempmat;
}
}
else if (StringsEqual(buffer, "FooMaterial"))
{
    readmaterial = new TFooMaterial(crc);
tempmat->material = readmaterial;
tempmat->next = 0;
if (matlist == 0) // list empty
{ matlist = tempmat;
}
else // matlist not empty
{ tempmat->next = matlist;
matlist = tempmat;
}
}
else if (StringsEqual(buffer, "Gold"))
{
    readmaterial = new TGold(crc);
tempmat->material = readmaterial;
tempmat->next = 0;
if (matlist == 0) // list empty
{ matlist = tempmat;
}
else // matlist not empty
{ tempmat->next = matlist;
matlist = tempmat;
}
}
else if (StringsEqual(buffer, "SAF2205"))
{
    readmaterial = new TSAF2205(crc);
tempmat->material = readmaterial;
tempmat->next = 0;
if (matlist == 0) // list empty
{ matlist = tempmat;
}
else // matlist not empty
{ tempmat->next = matlist;
matlist = tempmat;
}
}
else if (StringsEqual(buffer, "TestMaterial"))
{
    readmaterial = new TTestMaterial(crc);
}
tempmat->material = readmaterial;
tempmat->next = 0;
if (matlist == 0) // list empty
    
    matlist = tempmat;
else // matlist not empty
    
    tempmat->next = matlist;
    matlist = tempmat;

}

else if (StringsEqual(buffer, "EmptyMaterial"))
{
    readmaterial = new TMaterial(crc);   // fluxes are zero
    tempmat->material = readmaterial;
tempmat->next = 0;
if (matlist == 0) // list empty
    
    matlist = tempmat;
else // matlist not empty
    
    tempmat->next = matlist;
    matlist = tempmat;

}

} /* START REACTIONS USED FROM STATIC LIBRARY
index = number of reactions to follow (read in)
loop through index number of times
read in reacname
New an object of the proper subclass of TReaction following the same
procedure you used above
Add the new reaction to the list of reactions:
tempreac->reaction = readreaction;
tempreac->next = 0;
if (reaclist == 0) // list empty
    
    reaclist = tempreac;
else // reaclist not empty
    
    tempreac->next = reaclist;
    reaclist = tempreac;
END REACTIONS USED FROM STATIC LIBRARY*/

input >> buffer;
input >> temp_val;
for (i = 0; i < temp_val; i++)
{
    input >> buffer;
    if (StringsEqual(buffer, "304_1An"))
    
    readreaction = new T304_1An(crc);
tempreac->reaction = readreaction;
tempreac->next = 0;
if (reaclist == 0) // list empty
    
    reaclist = tempreac;
else // reaclist not empty
    
    tempreac->next = reaclist;
    reaclist = tempreac;

    }
else if (StringsEqual(buffer, "304_1Ca"))
    
    readreaction = new T304_1Ca(crc);
tempreac->reaction = readreaction;
tempreac->next = 0;
if (reaclist == 0) // list empty
    
    reaclist = tempreac;
else // reaclist not empty
    
    tempreac->next = reaclist;
    reaclist = tempreac;

}
else if (StringsEqual(buffer, "304A"))
    

readreaction = new T304A(crc);
    tempreac->reaction = readreaction;
    tempreac->next = 0;
    if (reaclist == 0) // list empty
    {
        reaclist = tempreac;
    }
    else // reaclist not empty
    {
        tempreac->next = reaclist;
        reaclist = tempreac;
    }
}
else if (StringsEqual(buffer, "AlDiss") )
{
    readreaction = new TAlDiss(crc);
    tempreac->reaction = readreaction;
    tempreac->next = 0;
    if (reaclist == 0) // list empty
    {
        reaclist = tempreac;
    }
    else // reaclist not empty
    {
        tempreac->next = reaclist;
        reaclist = tempreac;
    }
}
/*else if (buffer = "AuAnodic")
{
    readreaction = new TAuAnodic(crc);
    tempreac->reaction = readreaction;
    tempreac->next = 0;
    if (reaclist == 0) // list empty
    {
        reaclist = tempreac;
    }
    else // reaclist not empty
    {
        tempreac->next = reaclist;
        reaclist = tempreac;
    }
}*/
else if (StringsEqual(buffer, "CuRed") )
{
    readreaction = new TCuRed(crc);
    tempreac->reaction = readreaction;
    tempreac->next = 0;
    if (reaclist == 0) // list empty
    {
        reaclist = tempreac;
    }
    else // reaclist not empty
    {
        tempreac->next = reaclist;
        reaclist = tempreac;
    }
}
else if (StringsEqual(buffer, "HER") )
{
    readreaction = new THER(crc);
    tempreac->reaction = readreaction;
    tempreac->next = 0;
    if (reaclist == 0) // list empty
    {
        reaclist = tempreac;
    }
    else // reaclist not empty
    {
        tempreac->next = reaclist;
        reaclist = tempreac;
    }
}
else if (StringsEqual(buffer, "ORR") )
{
    readreaction = new TORR(crc);
    tempreac->reaction = readreaction;
    tempreac->next = 0;
    if (reaclist == 0) // list empty
    {
        reaclist = tempreac;
    }
    else // reaclist not empty
    {
        tempreac->next = reaclist;
        reaclist = tempreac;
    }
}
tempreact->next = reaclist;
  reaclist = tempreact;
}

else if (StringsEqual(buffer, "SAF2205Diss"))
{
  readreaction = new TSAF2205Diss(crc);
  tempreact->reaction = readreaction;
  tempreact->next = 0;
  if (reaclist == 0) // list empty
  {
    reaclist = tempreact;
  }
  else // reaclist not empty
  {
    tempreact->next = reaclist;
    reaclist = tempreact;
  }
}

else if (StringsEqual(buffer, "SumAnodic"))
{
  readreaction = new TSumAnodic(crc);
  tempreact->reaction = readreaction;
  tempreact->next = 0;
  if (reaclist == 0) // list empty
  {
    reaclist = tempreact;
  }
  else // reaclist not empty
  {
    tempreact->next = reaclist;
    reaclist = tempreact;
  }
}

#include "userdefinedreactions.h"

/* START USER DEFINED SPECIES 
  int speciesz; // charge number
  double speciesu; // ionic mobility
  double speciesu0; // chemical potential 
  index = number of species to follow (read in) 
  loop through index number of times 
  read in specname, speciesz, speciesu, speciesu0 
  readspecies = new TASpecies(speciesz,speciesu,speciesu0,specname); 
  crc->AddSpecies(readspecies); 
  initchem->AddSpecies(specname,0,0); 
  end loop 
END USER DEFINED SPECIES*/

input >> buffer;
input >> temp_val;
  counter = temp_val;
for (i = 0; i < counter; i++)
{
  input >> all_species[spec_counter];
  input >> temp_val;
  speciesz = temp_val;
  input >> temp_real;
  speciesu = temp_real;
  input >> temp_real;
  speciesu0 = temp_real;
  readspecies = new TASpecies(speciesz,speciesu,speciesu0,buffer);
  crc->AddSpecies(readspecies);
  initchem->AddSpecies(all_species[spec_counter++], 0, 0);
}

/*NOTE: User-defined reactions need to be read in before the user-defined 
materials so that the reaction objects already exist (they're used 
by the materials)*/

/* START USER DEFINED REACTIONS 
  TReacName curvetype; 
  int nume, coefr1, coefr2, coefp1, coefp2; // coefficients and num e's 
  TSpeciesName react1, react2, prod1, prod2; // names of reacs and prods 
  double c0,c1,c2,c3,c4,c5,c6,c7,c8,c9,c10; // polynomial coefficients 
  read in index [num of reactions to follow] 
  start loop with index iterations 
  read in reaction 
  read in curve type (constant, tafel, polynomial) 
  read in name, coefr1,coefr2,coefp1,coefp2,react1,react2,prod1,prod2, 
  c0,c1,c2,c3,c4,c5,c6,c7,c8,c9,10 */
if (curvetype == "constant")
{ readreaction = new TGenericConst(reacname, reac1, reac2, prod1, prod2,
  coefr1, coefr2, coefp1, coefp2, nume, c0); }
else if (curvetype == "tafel")
{ readreaction = new TGenericLine(reacname, reac1, reac2, prod1, prod2,
  coefr1, coefr2, coefp1, coefp2, nume, c0, c1); }
else if (curvetype == "polynomial")
{ readreaction = new TGenericPoly(reacname, reac1, reac2, prod1, prod2,
  coefr1, coefr2, coefp1, coefp2, nume, c0, c1,
  c2, c3, c4, c5, c6, c7, c8, c9, c10); }
  // c0 is the slope, cl is the intercept
  // Add the new reaction to the list of reactions:
  tempreaction->reaction = readreaction; // do I lose the subclass type?
  tempreaction->next = 0;
  if (reaclist == 0) // list empty
  { reaclist = tempreaction; }
  else // reaclist not empty
  { tempreaction->next = reaclist;
    reaclist = tempreaction; }
end loop with index interations
END USER DEFINED REACTIONS/*
input >> buffer;
input >> temp_val;
counter = temp_val;
for (i = 0; i < counter; i++)
{
  input >> buffer;
  reacname = buffer;
  input >> buffer;
  curvetype = buffer;
  input >> temp_val;
  nume = temp_val;
  input >> temp_val;
  coefr1 = temp_val;
  input >> temp_val;
  coefr2 = temp_val;
  input >> temp_val;
  coefp1 = temp_val;
  input >> temp_val;
  coefp2 = temp_val;
  input >> buffer;
  reac1 = buffer;
  input >> buffer;
  reac2 = buffer;
  input >> buffer;
  prod1 = buffer;
  input >> buffer;
  prod2 = buffer;
  input >> temp_real;
  c0 = temp_real;
  input >> temp_real;
  c1 = temp_real;
  input >> temp_real;
  c2 = temp_real;
  input >> temp_real;
  c3 = temp_real;
  input >> temp_real;
  c4 = temp_real;
  input >> temp_real;
  c5 = temp_real;
  input >> temp_real;
  c6 = temp_real;
  input >> temp_real;
  c7 = temp_real;
  input >> temp_real;
  c8 = temp_real;
  input >> temp_real;
c9 = temp_real;
input >> temp_real;
c10 = temp_real;
if (curvetype == "constant")
{
    readreaction = new TGenericConst(reacname, reac1, reac2, prod1, prod2, coefr1, coefr2, coefp1, coefp2, nume, c0);
}
else if (curvetype == "tafel")
{
    readreaction = new TGenericLine(reacname, reac1, reac2, prod1, prod2, coefr1, coefr2, coefp1, coefp2, nume, c0, c1);
} // c0 is the slope, c1 is the intercept
else if (curvetype == "polynomial")
{
    readreaction = new TGenericPoly(reacname, reac1, reac2, prod1, prod2, coefr1, coefr2, coefp1, coefp2, nume, c0, c1, c2, c3, c4, c5, c6, c7, c8, c9, c10);
}

/* START USER DEFINED MATERIALS
int numreacs;  // number of reactions on this material
TReacListElem *matreaclist; // list of reactions on this material
matreaclist = new TReacListElem();
read in index (number of materials to follow)
start loop with index iterations
read in matname
read in numreacs
start loop with numreacs iterations
read in reacname
look through list of reactions for the right one:
  tempreac = reaclist;
  while (tempreac->reaction->reacname != reacname)
    tempreac = tempreac->next; // assuming reaction is in list
if (matreaclist == 0) // list empty
  {matreaclist = tempreac;
    }
else // list not empty
  {tempreac->next = matreaclist;
    matreaclist = tempreac;
    }
end loop with numreacs iterations
readmaterial = new TGenericMaterial(matname, matreaclist);
temprect->material = readmaterial;
if (matlist == 0) // list empty
  {matlist = readmaterial;
    }
else // material list not empty
  {matlist->next = matlist;
    matlist = temprect;
    }

end loop with index iterations
END USER DEFINED MATERIALS*/
input >> buffer;
input >> temp_val;
counter = temp_val;
for (i = 0; i < counter; i++)
{
    input >> buffer;
    input >> temp_val2;
    for (int j = 0; j < temp_val2; j++)
    {
        input >> buffer;
        tempreac = reaclist;
        while (tempreac->reaction->reacname != buffer)
        {
            tempreac = tempreac->next; // assuming reaction is in list
        }
        if (matreaclist == 0) // list empty
        {
            matreaclist = tempreac;
        }
        else // list not empty
        {
            tempreac->next = matreaclist;
            matreaclist = tempreac;
        }
    }
    readmaterial = new TGenericMaterial(matname, matreaclist);
temprect->material = readmaterial;
temprect->next = 0;
if (matlist == 0) // list empty
```cpp
    { matlist->material = readmaterial;
    }
    else // material list not empty
    {
        tempmat->next = matlist;
        matlist = tempmat;
    }
}

/* START NODES
// loop through the number of nodes and read in the node information:
number of nodes -> iNumOfNodes (passed into function from main)
int nodeid;       // the id number of the node
int x,y;          // the x and y coordinates for the node
double newtemp;   // temperature for the node
double newpress;  // pressure for the node
double newelec;   // potential for the node
int isfixedp, isfixedc; // potential and chemical isFixed variables
TSpeciesName specname; // the name of the species being read in
double newconc;    // the new concentration of the species

    initchem->SetConcentration("electrical",newelec);
initchem->SetConcentration("pressure",newpress);
initchem->SetConcentration("temperature",newtemp);
initchem->SetFixed("electrical",isfixedp);
    // loop through species, setting conc and isfixed for each
    initchem->SetConcentration(specname,newconc);
initchem->SetFixed(specname,isfixedc);

    nodes[nodeid] = new NodeInfo;
    nodes[nodeid]->chem = new TChemistry(initchem);
    nodes[nodeid]->oldchem = new TChemistry(initchem);
    nodes[nodeid]->dbX = x;
    nodes[nodeid]->dbY = y;
    nodes[nodeid]->dbZ = 0;
    nodes[nodeid]->iUsed = 1;
    nodes[nodeid]->iNodeId = nodeid;
END NODES*/

input >> buffer;
input >> temp_val;
counter = temp_val;
*iNumOfNodes = temp_val;
for (i = 0; i < counter; i++)
{
    input >> temp_val;
    nodeid = temp_val;
    x = temp_real;
    input >> temp_real;
    y = temp_real;
    input >> temp_real;
    newtemp = temp_real;
    input >> temp_real;
    newpress = temp_real;
    input >> temp_real;
    newelec = temp_real;
    input >> temp_val;
    isfixedp = temp_val;
    input >> temp_val2;
    initchem->SetConcentration("electrical",newelec);
initchem->SetConcentration("pressure",newpress);
initchem->SetConcentration("temperature",newtemp + 273);
initchem->SetFixed("electrical",isfixedp);
    for (int j = 0; j < temp_val2; j++)
    {
        input >> buffer;
        specname = buffer;
        input >> temp_real;
        newconc = temp_real;
        input >> temp_val;
        isfixedc = temp_val;
        initchem->SetConcentration(specname,newconc);
initchem->SetFixed(specname,isfixedc);
    }
    nodes[nodeid] = new NodeInfo;
    nodes[nodeid]->chem = new TChemistry(initchem);
    nodes[nodeid]->oldchem = new TChemistry(initchem);
    nodes[nodeid]->dbX = x;
```

nodes[nodeid]->dBY = y;
nodes[nodeid]->dBZ = 0;
nodes[nodeid]->iUsed = 1;
nodes[nodeid]->iNodeId = nodeid;
}

/* START ELEMENTS
// loop through the number of elements and read in the element information:
number of elements -> iNumOfElements (passed into function from main)
int elemid;             // the id number of the elem
int j,k;               // the node numbers for the element
double height;          // the height for the element
TMatName matname;       // the name of the base material of the elem
TMatListElem * current;
TMaterial newmat;
int flag = 0;
current = matlist;
while ((current != 0) && (flag == 0))
{
    if (current->material->matname == elementname)
    {
        flag = 1;
    }
    else
    {
        current = current->next;
    }
}
if (flag == 1)
{
    newmat = current->material;  // set newmat equal to that material
}
// now that you've read everything in, new the TSolutionVolume for this
// element - setting the edge material to the base material for now
els[elemid] = new TSolutionVolume(nodes[i-1],nodes[j-1],nodes[k-1],
    height,newmat,newmat,newmat,newmat,crc);
END ELEMENTS*/

input >> buffer;
input >> temp_val;
counter = temp_val;
iNumOfElements = temp_val;
flag = 0;

newedge = new TMaterial; // just doing this for now until TMaterial is added to static library
for (int l = 0; l < counter; l++)
{
    input >> temp_val;
    elemid = temp_val;
    input >> temp_val;
    i = temp_val;
    input >> temp_val;
    j = temp_val;
    input >> temp_val;
    k = temp_val;
    input >> temp_real;
    height = temp_real;
    input >> temp_val2;
    for (int m = 0; m < temp_val2; m++)
    {
        input >> buffer;
        current = matlist;
        while ((current != 0) && (flag == 0))
        {
            if (StringsEqual(current->material->matname, buffer))
            {
                flag = 1;
            }
            else
            {
                current = current->next;
            }
        }
        if (flag == 1)
        {
            newmat = current->material;  // set newmat equal to that material
            flag = 0;
        }
    }
}

els[elemid] = new TSolutionVolume(nodes[i-1],nodes[j-1],nodes[k-1],
    height,newmat,newmat,newmat,newmat,crc);  // edges are set to mat material until next section

/* START EDGES
// loop through the number of edges and read in the edge information:
int numofedges; // the number of edges
int edgeid; // the number of that edge
int nodeone, nodetwo; // the two node numbers associated with it
TMatName edgename; // the name of the material

// Search the list of materials for the one of that name
TMatListElem * current;
TMaterial newedge;
int flag = 0;
current = matlist;
while ((current != 0) && (flag == 0))
{ if (current->material->matname == edgename)
{ flag = 1;
}
else
{ current = current->next;
}
}
if (flag == 1)
{ newedge = current->material;  // set newedge equal to that material
}

// In the setup file, you don't output the node numbers associated with
// an edge - do you always output them in the same order (i,j,k)?
// If so, the checks below won't be necessary
// Check els[(edgeid DIV 3)]->i and els[(edgeid DIV 3)]->j
// and els[(edgeid DIV 3)]->k to see which edge you have
// Set els[(edgeid DIV 3)]->ijmat = newedge or els[...]->ikmat
// or els[...]->jkmat accordingly

// Finish looping through all of the edges
END EDGES*/
input >> buffer;
input >> temp_val;
counter = temp_val;
flag = 0;
for (i = 0; i < counter; i++)
{
input >> temp_val;
edgeid = temp_val;
input >> temp_val;
for (int j = 0; j < temp_val2; j++)
{
input >> buffer;
current = matlist;
while ((current != 0) && (flag == 0))
{ if (current->material->matname == buffer)
{ flag = 1;
}
else
{ current = current->next;
}
}
if (flag == 1)
{ newedge = current->material;  // set newedge equal to that material
flag = 0;
}
}
tempint = floor(edgeid/3);
if (fmod(edgeid,3) == 0) // this works b/c edges are put into setup file in ij,jk,ik order
{ els[tempint]->ijmat = newedge;
}
else if (fmod(edgeid,3) == 1)
{ els[tempint]->jkmat = newedge;
}
else if (fmod(edgeid,3) == 2)
{ els[tempint]->ikmat = newedge;
}

/* START OUTPUT INFO
read in output information:
degree of implicit/explicit  -> theta
number of chem time steps   -> numcts
number of pot  time steps   -> numpts
length of chem time steps   -> lencts
*/
I need you to add a variable to the output info - another theta
One is needed for chemical and one for potential
END OUTPUT INFO*/
flag = 0;
input >> buffer;
input >> buffer;  // Charge neutrality species
neutname = buffer;
input >> temp_val;  // Al hydrolysis
*al_hydro = temp_val;
input >> temp_val;  // Cr Hydrolysis
*cr_hydro = temp_val;
input >> temp_real;  // Al theta
*thetac = temp_real;
input >> temp_real;  // Cr theta
*thetap = temp_real;
in...
int kt;
int stable;
int al_hydro;
int cr_hydro;

// local variables //
int count1, count2, count3, count4;
double residual;
int done = 0;
int outelec = 0;
char nm[20];
char name[20];
char **all_species;
crc = new TAllSpecies();
Out_spec = new TAllSpecies();
cout << "Calling setup routine" << end;
setup(els, &iNumOfElements, nodes, &iNumOfNodes, crc, &thetap, &thetac, &numcts,
&numpts, &lencts, &lenpts, &convcrit, Out_spec, &al_hydro, &cr_hydro, neutname, all_species);
cout << "To main" << endl;
for (count3=0; count3<Out_spec->size; count3++)
{ if (Out_spec->allspecies[count3]->name == "electrical")
  outelec = 1;
}
if (Out_spec->allspecies[count3]->name == neutname)
  outneut = 1;
for (count1=0; count1<numcts; count1++) // loop through chemical time steps
  // chemical time steps
  // Copy the new values to the old to prepare for the next timestep
  SetOldChem(nodes, iNumOfNodes);
cout << "Time period " << count1 << " started" << end;
done = 0; //set flag for electrical finished to false
sprintf(name, "electrical");
k0 = 1; // check for Peclet stability
//initialize elements for electrical
for (count4=0; count4<iNumOfElements; count4++)
{ stable = stable && els[count4]->SetConstants(name, kt, thetap);
}
if (!stable) cout << "Not stable" << end;
char testfile[20];
sprintf(testfile, "Altest%d.txt", 1);
ofstream outtest(testfile, ios::out);
for (count4=0; count4<iNumOfElements; count4++)
{ outtest << count4 << endl;
  outtest << els[count4]->i->iNodeId << " " << els[count4]->i->dbX << " " << els[count4]->i->dbY << " "
  << els[count4]->i->dbZ << " " << els[count4]->i->iUsed << " " << els[count4]->i->iFixed << endl;
  for (count2=0; count2<els[count4]->i->chem->size; count2++)
    { outtest << els[count4]->i->chem->names[count2] << " " << els[count4]->i->chem->concentrations[count2] << " "
      << els[count4]->i->chem->fixed[count2] << endl;
    }
  outtest << els[count4]->j->iNodeId << " " << els[count4]->j->dbX << " " << els[count4]->j->dbY << " "
  << els[count4]->j->dbZ << " " << els[count4]->j->iUsed << " " << els[count4]->j->iFixed << endl;
  for (count2=0; count2<els[count4]->j->chem->size; count2++)
    { outtest << els[count4]->j->chem->names[count2] << " " << els[count4]->j->chem->concentrations[count2] << " "
      << els[count4]->j->chem->fixed[count2] << endl;
    }
  outtest << els[count4]->k->iNodeId << " " << els[count4]->k->dbX << " " << els[count4]->k->dbY << " "
  << els[count4]->k->dbZ << " " << els[count4]->k->iUsed << " " << els[count4]->k->iFixed << endl;
  for (count2=0; count2<els[count4]->k->chem->size; count2++)
    { outtest << els[count4]->k->chem->names[count2] << " " << els[count4]->k->chem->concentrations[count2] << " "
      << els[count4]->k->chem->fixed[count2] << endl;
    }
  outtest << els[count4]->theta << " " << els[count4]->h << " " << els[count4]->mat->matname << " "
    << els[count4]->ijmat->matname << " " << els[count4]->ikmat->matname << " " << els[count4]->jkmat->matname << end;
}
outtest << endl;
}
count2 = 0; //reset to get out of loop if needed
while (done != 1) // loop until stable E-I
{ SetOldChem(nodes, iNumOfNodes);
cout << "Entering solver" << end;
Solve(els, iNumOfElements, nodes, iNumOfNodes, lenpts, name);
cout << "Back from solve" << end;
residual = AvgDifference(nodes, iNumOfNodes);
if (residual < convcrit)
  done = 1; //have converged to stable E-I
if (outelec == 1) // potential is on list of things to output
( sprintf(nm, "el%d.txt", count1);
    Print(iNumOfNodes, nodes, nm, name);
    cout << "File " << nm << " output " << endl;
 }
 else
    cout << "residual = " << residual << endl;
    sprintf(nm, "b%d.txt", count2);
    Print(iNumOfNodes, nodes, nm, name);
    cout << "Potential intermediate file " << nm << " output " << endl;
    count2++;
    if (count2>=numpts) done = 1;
    // reinitialize the variables
    for (count4=0; count4<iNumOfElements; count4++)
        els[count4]->SetConstants(name, kt, thetap);
 }
}

for (count3=0; count3<Out_spec->size; count3++)
{// loop through species to be output calculating concentrations
    sprintf(name, Out_spec->allspecies[count3]->name);
    if ((name != "electrical") && (name != neutname))
    {
        cout << "Starting " << name << endl;
        stable = 1;
        // initialize elements for this species
        for (count4=0; count4<iNumOfElements; count4++)
            { stable = stable && els[count4]->SetConstants(name, kt, theta);
            }
        if (!stable) cout << "Not stable " << name << endl;
        cout << "Entering solver" << endl;
        Solve(els, iNumOfElements, nodes, iNumOfNodes, lencts, name);
        cout << "Time period " << count1 << " " << name << " found " << endl;
        sprintf(nm, "
    Print(iNumOfNodes, nodes, nm, name);
    cout << "File " << nm << " output " << endl;
 }
 // output species loop

if (outneut == 1) // calculating concentration of charge neutrality species
    { sprintf(name, neutname);
        cout << "Starting " << name << endl;
        NeutralizeCharge(neutname, nodes, iNumOfNodes, crc);
        cout << "Time period " << count1 << " " << name << " found " << endl;
        sprintf(nm, "
    Print(iNumOfNodes, nodes, nm, name);
    cout << "File " << nm << " output " << endl;
 }
 // chemical time steps

} // main

******************************************************************************
TMATLST.C  9/24/98

TMatListElem is the class of objects that are elements in the dynamically
allocated list of materials used in a run of the model. These objects
contain simply a reaction and a pointer to the next element in the list
*******************************************************************************/

#include "tmatlst.h"
#include <iostream.h>
#include <fstream.h>
#include <math.h>

TMatListElem::TMatListElem()
/*****************************/
{ material = 0;
  next = 0;
}

TMatListElem::TMatListElem(TMaterial *mat)
/*****************************/
{ material = mat;
  next = 0;
}

*******************************************************************************/
TMATLST.C  9/24/98
TMatListElem is the class of objects that are elements in the dynamically allocated list of materials used in a run of the model. These objects contain simply a reaction and a pointer to the next element in the list.

#include "tmatlst.H"
#include <iostream.h>
#include <fstream.h>
#include <math.h>

TMatListElem::TMatListElem()
{ material = 0; next = 0; }

TMatListElem::TMatListElem(TMaterial *mat)
{ material = mat; next = 0; }

In TMaterial.cpp:

TGenericMaterial::TGenericMaterial(TMatName mname, TReacListElem * rlist)
{ matname = mname; reaclist = rlist; }

double TGenericMaterial::GetChemicalFlux(TSpeciesName name, TChemistry *chemistry, double E, double T, double P)
{ double flux; TReacListElem * current;
  flux = 0;
  current = reaclist;
  while (current != 0)
  { flux = flux + current->reaction->GetFluxOfSpecies(name,chemistry,E,T,P);
    current = current->next;
  }
  return(flux);
}

double TGenericMaterial::GetNetCurrentDensity(TChemistry *chemistry, double E, double T, double P)
{ double net; TReacListElem * current;
  net = 0;
  current = reaclist;
  while (current != 0)
  { net = net + current->reaction->GetCurrentDensity(chemistry,E,T,P);
    current = current->next;
  }
  return(net);
}
current = current->next;
|
return(net);
|

In Treacio.cpp:

TGenericConst::TGenericConst (TReacName rname, TSpeciesName react1, TSpeciesName react2,
TSpeciesName prod1, TSpeciesName prod2, int stoicr1,
int stoicr2, int stoicp1, int stoicp2, int nelec,
double currconst)
/**************************************************************/
TGenericConst():This is the constructor for a class of generic reactions
with constant current. Objects of this class are created from
information read in from the GUI.
Written by Lisa DeJong last revised 8/28/98
*******************************************************************************/
{ reacname = rname;           // set the reaction name
reactant1 = react1;          // set the names of the species in the reaction
reactant2 = react2;
product1 = prod1;
product2 = prod2;
StoicReac1 = stoicr1;        // set the stoichiometric coeffs of the reaction
StoicReac2 = stoicr2;
StoicProd1 = stoicp1;
StoicProd2 = stoicp2;
NumElec = nelec;             // set the number of electrons transferred
CurrentConstant = currconst; // set the variables used to determine the current (constant)
}
double TGenericConst::GetFluxOfSpecies(TSpeciesName name, TChemistry * chemistry,
double E, double T, double P)
/**************************************************************/
GetFluxOfSpecies() : This function returns the flux of species name.
It is the redefinition of a virtual function for the TGenericConst subclass
RETURNS: The chemical flux in mol/(m^2-s)
inet            [A/m^2]
N(X) = -------- v(X) --------
nF         [eq/mol]-[C/eq]
***************************************************************/
{ double flux;
  if (StringsEqual(name,reactant1))
    { flux = (GetCurrentDensity(chemistry,E,T,P)*StoicReac1)/(NumElec*F);
    }
  else if (StringsEqual(name,reactant2))
    { flux = (GetCurrentDensity(chemistry,E,T,P)*StoicReac2)/(NumElec*F);
    }
  else if (StringsEqual(name,product1))
    { flux = (GetCurrentDensity(chemistry,E,T,P)*StoicProd1)/(NumElec*F);
    }
  else if (StringsEqual(name,product2))
    { flux = (GetCurrentDensity(chemistry,E,T,P)*StoicProd2)/(NumElec*F);
    }
  else
    { flux = 0;
    }
  return(flux);
}
double TGenericConst::AnodicCurrentDensity (TChemistry * chemistry,
double E, double T, double P)
/**************************************************************/
AnodicCurrentDensity: This function calculates the anodic current
density of the reaction. For this TGenericConst class, all of the
current will be calculated in the CathodicCurrentDensity function
so this one is set to zero.
Written by Lisa DeJong last revised 8/28/98
*******************************************************************************/
{ return(0);
}
double TGenericConst::CathodicCurrentDensity(TChemistry * chemistry,
double E, double T, double P)
/**************************************************************/
CathodicCurrentDensity: This function calculates the cathodic current
density of the reaction. For this TGenericConst class, the current
is simply a constant.
Written by Lisa DeJong last revised 8/28/98
*******************************************************************************/
{ double current;
current = CurrentConstant;
return(current);
}

tGenericLine::TGenericLine(TReacName rname, TSpeciesName react1, TSpeciesName react2, TSpeciesName prod1, TSpeciesName prod2, int stoicr1, int stoicr2, int stoicp1, int stoicp2, int nelec, double m, double b)

/**********************************************************************
TGenericLine():This is the constructor for a class of generic reactions
with a Tafel current/potential relationship (potential vs. log(current)
is linear). Objects of this class are created from information read
in from the GUI.
Written by Lisa DeJong last revised 8/28/98
***********************************************************************/
{
  reacname = rname;  // set the reaction name
  reactant1 = react1;  // set the names of the species in the reaction
  reactant2 = react2;
  product1 = prod1;
  product2 = prod2;
  StoicReact1 = stoicr1;  // set the stoichiometric coeffs of the reaction
  StoicReact2 = stoicr2;
  StoicProd1 = stoicp1;
  StoicProd2 = stoicp2;
  NumElec = nelec;  // set the number of electrons transferred
  slope = m;      // set the variables used to determine the current (line)
  intercept = b;
}

double TGenericLine::GetFluxOfSpecies(TSpeciesName name, TChemistry * chemistry, double E, double T, double P)

/*********************************************************************
GetFluxOfSpecies() : This function returns the flux of species name.
It is the redefinition of a virtual function for the TGenericLine subclass
RETURNS: The chemical flux in mol/(m^2-s) (m^2-A/m^2)
inet            [A/m^2]
N(X) =  ---- v(X)   ---------------
  nF         [eq/mol]-[C/eq]
***********************************************************************/
{
  double flux;
  if (StringsEqual(name,reactant1))
    (flux = (GetCurrentDensity(chemistry,E,T,P)*StoicReact1)/(NumElec*F));
  else if (StringsEqual(name,reactant2))
    (flux = (GetCurrentDensity(chemistry,E,T,P)*StoicReact2)/(NumElec*F));
  else if (StringsEqual(name,product1))
    (flux = (GetCurrentDensity(chemistry,E,T,P)*StoicProd1)/(NumElec*F));
  else if (StringsEqual(name,product2))
    (flux = (GetCurrentDensity(chemistry,E,T,P)*StoicProd2)/(NumElec*F));
  else
    (flux = 0);
  return(flux);
}

double TGenericLine::AnodicCurrentDensity(TChemistry * chemistry, double E, double T, double P)

/***********************************************************************
AnodicCurrentDensity: This function calculates the anodic current
density of the reaction. For this TGenericLine class, all of the
current will be calculated in the CathodicCurrentDensity function
so this one is set to zero.
Written by Lisa DeJong  last revised 8/28/98
***********************************************************************
{
  return(0);
}

double TGenericLine::CathodicCurrentDensity(TChemistry * chemistry, double E, double T, double P)

/***********************************************************************
CathodicCurrentDensity: This function calculates the cathodic current
density of the reaction. For this TGenericLine class, the potential vs. log(current) relationship is linear (Tafel).
Written by Lisa DeJong  last revised 8/28/98
***********************************************************************
{
  double current, exponent;
  exponent = slope * E + intercept;
  current = pow(10,exponent);
  return(current);
}

tGenericPoly::TGenericPoly(TReacName rname, TSpeciesName react1, TSpeciesName react2,
TSpeciesName prod1, TSpeciesName prod2, int stoicr1,
int stoicr2, int stoipc1, int stoipc2, int nelec,
double c0, double c1, double c2, double c3, double c4,
double c5, double c6, double c7, double c8, double c9,
double c10
}

 /**********************************************************************
TGenericPoly::TGenericPoly():This is the constructor for a class of generic
reactions
with a polynomial current/potential relationship (potential vs. log(current)
is represented as a tenth order polynomial). Objects of this class are
created from information read in from the GUI.
Written by Lisa DeJong last revised 8/28/98
**************************************************************************/

{ reacname = rname;             // set the reaction name
reactant1 = react1;           // set the names of the species in the reaction
reactant2 = react2;
product1 = prod1;
product2 = prod2;
StoicReac1 = stoicr1;         // set the stoichiometric coeffs of the reaction
StoicReac2 = stoicr2;
StoicProd1 = stoipc1;
StoicProd2 = stoipc2;
NumElec = nelec;              // set the number of electrons transferred
coef0 = c0;      // set the variables used to determine the current (polynomial)
coef1 = c1;
coef2 = c2;
coef3 = c3;
coef4 = c4;
coef5 = c5;
coef6 = c6;
coef7 = c7;
coef8 = c8;
coef9 = c9;
coef10 = c10;
}

double TGenericPoly::GetFluxOfSpecies(TSpeciesName name, TChemistry * chemistry,
double E, double T, double P)
/*********************************************************************
GetFluxOfSpecies() : This function returns the flux of species name.
It is the redefinition of a virtual function for the TGenericPoly subclass
RETURNS: The chemical flux in mol/(m^2-s)
inet            [A/m^2]
N(X) = ---- v(X)   ---------------
nF         [eq/mol]-[C/eq]
**********************************************************************/

{ double flux;
if (StringsEqual(name,reactant1))
{ flux = (GetCurrentDensity(chemistry,E,T,P)*StoicReac1)/(NumElec*F);
}
else if (StringsEqual(name,reactant2))
{ flux = (GetCurrentDensity(chemistry,E,T,P)*StoicReac2)/(NumElec*F);
}
else if (StringsEqual(name,product1))
{ flux = (GetCurrentDensity(chemistry,E,T,P)*StoicProd1)/(NumElec*F);
}
else if (StringsEqual(name,product2))
{ flux = (GetCurrentDensity(chemistry,E,T,P)*StoicProd2)/(NumElec*F);
}
else
{ flux = 0;
}
return(flux);
}

double TGenericPoly::AnodicCurrentDensity(TChemistry * chemistry,
double E, double T, double P)
/*********************************************************************
AnodicCurrentDensity: This function calculates the anodic current
density of the reaction. For this TGenericPoly class, all of the
current will be calculated in the CathodicCurrentDensity function
so this one is set to zero.
Written by Lisa DeJong  last revised 8/28/98
**********************************************************************/

{return(0);}

double TGenericPoly::CathodicCurrentDensity(TChemistry * chemistry,
double E, double T, double P)
/*********************************************************************
CathodicCurrentDensity: This function calculates the cathodic current
density of the reaction. For this TGenericPoly class, the potential
vs. log(current) relationship is represented as a tenth order polynomial
Written by Lisa DeJong  last revised 8/28/98
**********************************************************************/

{ double current, exponent;
  exponent = coef0 + coef1*E + coef2*pow(E,2) + coef3*pow(E,3) + coef4*pow(E,4) +

\[ \text{coef5} \cdot \text{pow(E,5)} + \text{coef6} \cdot \text{pow(E,6)} + \text{coef7} \cdot \text{pow(E,7)} + \text{coef8} \cdot \text{pow(E,8)} + \\
\text{coef9} \cdot \text{pow(E,9)} + \text{coef10} \cdot \text{pow(E,10)}; \]

\[
\text{current} = \text{pow(10, exponent)};
\]

\[
\text{return(current);}
\]