ON PROBABILISTIC TRANSITION RATES USED IN MARKOV MODELS
FOR PITTING CORROSION

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ON PROBABILISTIC TRANSITION RATES USED IN MARKOV MODELS
FOR PITTING CORROSION

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Thesis

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ABSTRACT

A stochastic initiation and propagation model is developed to predict the effects of pitting corrosion on susceptible metals. The model relies upon an inhomogeneous Markov chain system in order to describe the propagation of pit depths throughout a discretized set of states. This work mainly examines the flexibility of the model with respect to the probabilistic transition rates $\lambda_i$ used in the Markov system. Depending on the form of $\lambda_i$, either an analytical or a numerical solution procedure can be used to solve the Markov system, with the numerical form of $\lambda_i$ being able to simulate a wider variety of systems, especially for dynamically changing environments. By modifying the expression of $\lambda_i$, increases or decreases, cyclical changes, or abrupt shifts in environmental corrosivity are studied. Simplifications to the model are also suggested for the sake of computational efficiency. A tool in the form of a Mathematica Computational Document is offered as an example of the model’s possible use in industry. Additionally, suggestions are made in regard to metastable pitting and situations where the metal begins in a corroded state. The model is flexible enough to handle these scenarios as long as appropriate data is available.
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CHAPTER I

INTRODUCTION

1.1 The Problem

Corrosion is the natural process of material degradation resulting from chemical reactions between a metal and the environment. All metals are susceptible to the damage of this process, and the result of such damage can be devastating if left unchecked. A metal bridge, weakened by years of corrosion, could easily collapse without proper inspection and maintenance. Inspections and replacements can be costly and inefficient, though, especially for buried pipelines. Imagine the expense involved in digging up miles of pipe only to search every inch for a defect. What can be done to control the dangerous effects of corrosion while minimizing these efforts and costs?

One answer is prevention. Preservative methods such as galvanization and coatings have been studied and used extensively. A good chef knows the importance of maintaining a film of grease on a cast-iron skillet in order to control rust. However coatings can scratch and many coatings are permeable, meaning corrosion will still, inevitably occur. Coatings are even impractical in certain situations. A mechanical part may not be able to function as intended with a coating.
A potentially more viable and economical approach of controlling corrosion is to predict the timing and severity of its effects. This is especially useful for corrosive processes that are not easily tracked. For instance, Shi and Mahadevan note how airplanes are susceptible to corrosion because the process may occur unknowingly within fuselage joints [3]. Many mathematical models have already been developed in reliability engineering to estimate the lifetime of corroding systems. One instance is Fleming’s process of using a Markov model to assess the risk of leakages in nuclear power plant piping by utilizing the results of in-service inspections [4]. However, Fleming’s model does not track the development or appearance of the corrosion. In fact, there are few models that can do so.

Fortunately with one form of corrosion, known as pitting corrosion, substantial advancements in prediction and risk-assessment have been made over the last century. During pitting corrosion – a process often seen in aluminum and its alloys – the material degrades as small holes (pits) develop and grow on its surface. Figure 1.1 shows an example of this type of corrosion.
This work is focused on a stochastic model for pitting corrosion and can predict many of the outcomes of pitting corrosion for metals placed and moved within dynamically changing environments. The model is to be the foundation for tools to be used in the corrosive risk management industry as it can be customized and adapted to given situations as needed.

1.2 Literature Review

Shibata cites that in 1933, Evans, et al., were the first to consider probability concepts in studying corrosion. By the 1960’s, Evans had made the use of statistics in corrosion a norm by dedicating a chapter to the topic in his book titled *Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications* [5]. Meanwhile in the 1950’s, Aziz [6] concluded from experimentation with aluminum and hard tap water that pitting corrosion is governed by two separate processes: 1) pit initiation and 2) pit propagation. His findings indicated that overall pit depth could be modeled by the expression $kt^{1/3}$, with $t$ referring to time and $k$ being a constant. Later experimentation with Godard convinced Aziz that pitting corrosion is a random, stochastic process, requiring the need for more advanced statistical approaches [7].

The thoughts presented by the groups governed by Evans and Aziz inspired Shibata to model pit initiation in aluminum stochastically in the 1970’s and 1980’s. Shibata and Sudo linked pitting potential, the lowest potential required to detect a current increase due to pit nucleation, to pit initiation rates [8]. Several analytical models were suggested to predict pit survival probabilities, including an exponential
distribution. Shibata further proved his model in other pit-susceptible metals such as zirconium, high-nickel alloys, and titanium [9, 10, 11], justifying his predictions by using experimental data and Monte Carlo simulations. It was later noted that pit generation should be a combination of both pit birth and pit death rates; that is, generation may not be merely exponential [12].

Shibata modeled only one portion of the pitting corrosion process, though. The other half of the problem, pit growth and propagation, wasn’t fully explored until 1989 when Provan and Rodríguez suggested a new solution procedure through the use of a Markov chain [13]. The Markov process requires the assumption that the probability of a pit growing deeper only depends on its current state – a pit’s past and the speed at which the pit grows into its current state are irrelevant to the probability calculation. This is justifiable given that a pit could stop growing at any time. By utilizing the Chapman-Kolmogorov equation, Provan and Rodríguez generated a set of ordinary differential equations and solved them numerically. These predictive results were compared with results of actual experiments. However, Valor, et al., report that the results are unreproducible [14].

In 1999, Hong combined a Poisson-distributed initiation model and Provan and Rodríguez’s Markov propagation model into one complete pitting corrosion model [15]. He was able to find an analytical solution by using constant growth rates for pit propagation. However, the rate at which a pit grows from one depth to another is not always constant over time in application. A metal’s environment is often subject to change, as with the seasons.
Valor, et al., improved on Hong and Provan’s models by suggesting a non-constant growth rate with appropriate units, stating that Provan’s model bore no physical meaning [14]. Valor was also able to find an analytical solution for her model, and even proved that the model followed extreme value statistics theory (unlike Hong’s). Extreme value statistics give validity to the model by confirming that small samples of pit depths can be extrapolated to predict larger areas of pit propagation. By the theory, extreme pit depth distributions must follow a combination of Gumbell, Cauchy, and Weibull distributions [5]. Valor’s model falls short in modeling all situations, however. Although her equations for the growth rates are non-constant, they are still not general enough to create a proper distribution (see Chapter 4). Valor also does not provide a strategy for modeling metastable pitting.

Metastable pitting refers to pits that cease growing before a critical depth is reached. On the other hand, stable pits grow without pause. If a stable pit forms immediately, that pit is said to be super-stable, a term coined by Melchers [16]. Figure 1.2 illustrates these definitions. Melchers claims that metastable pitting requires a different statistical modeling process, especially since the majority of pits are metastable [16]. This abundance of metastable pits is explained by Dornhege, et al., through the hypothesis that metastable pit formation induces nearby metastable pit formation due to the weakening of the surrounding oxide layer [17]. Melchers’s experiments conclude that early average pit depths fit best with a Poisson distribution, while later depths can be fit to a weighted normal distribution. This duo-distribution conflicts with the distributions suggested by extreme value statistics. In a second pa-
Figure 1.2: Example growth trajectories of stable and metastable pits.

per, Melchers also suggests that there is little dependence between average pit depth and extreme pit depth, questioning the use of extreme value statistics entirely [18]. Stable pits tend to grow in a similar fashion whether isolated or located near other stable pits [16]. Melchers does state a dependence between pit growth and initiation, though. The probability of a stable pit nucleating is suggested to decrease as overall pit depth increases.

Some of Melchers’ concerns are addressed in this work, but it should be noted that techniques need to be developed to better identify stable and metastable pits. Melchers claims that maximum pit depth should only be predicted from the
propagation of stable pits [16, 18]. As such, the models developed by Valor, et al., can still be used given the proper data. That is, pit data should be collected and organized into metastable and stable categories. Moayed, et al., have already begun research in this area, concluding that pit stability is directly proportional to the local solution chemistry through an expression known as the stability product [19]. All pits are said to initialize as metastable pits, but if a pit’s stability product is determined to increase linearly over time (but below a critical value), the pit may become stable.

Experimental results should also improve as imaging and science continue to develop. Pit depths can be difficult to characterize on the nano-scale, and Knight, et al., recommend the use of X-ray tomography to capture the complete profile of pitting, even within a metal [20]. Advancements in the deterministic studies of pitting corrosion may also prove to be helpful. Reis, et al., studied the chemistry behind metastable pitting and developed a Monte Carlo simulation to track the chemical mechanisms behind the corrosion process [21]. Meanwhile Cavanaugh, et al., demonstrated the use of neural networks to determine the emphasis of different environmental factors on pit growth, finding that pH and time play the biggest roles [22].

The risk assessment of pitting corrosion is also important to future steps in the overall corrosion-tracking process. A corroding pipeline can degrade through multiple stages of corrosion, each requiring a separate tool for risk assessment. However, it may be possible for the smaller predictive models of each stage to be built into a larger, combined mathematical model. For example, Shi and Mahadevan offer a multi-step approach and process to predict corrosion fatigue in airplanes. These steps include pit
nucleation, pit growth, transitioning from pitting to crack nucleation, crack growth, and fracture [3]. However, their model for pit growth is not stochastic. The results of Valor, et al., and consequently this work could be of great help in implementing Shi’s model. In turn, the safety of not only air travel, but also of other systems that suffer from corrosion-induced fracture can be improved and assured.

1.3 The Approach

The model presented here generalizes and builds upon the combined growth (Markov chain) and initiation models suggested by Hong and Valor to track and predict maximum pit depth. The previous modeling attempts are especially limited in accounting for metastable pitting and the effects of changes within a metal’s environment. For example, the state of pitting corrosion for a ship ported in a tropical environment and later moved to an arctic environment is demonstrated by this model. Other situations are also considered through the use of a newly suggested pit growth rate equation.

Some simplifications of the combined model are also offered. The model is ultimately to be used within industry and should be reasonably cost-effective in terms of computational speed. The included sample Mathematica Computational Document demonstrates the model’s industrial utility. In order to ensure the accuracy of the simplifications, the model’s results have been compared with results from Monte Carlo simulations. Additionally, the model has been curve fit to experimental data. However, data is scarce, especially outside the laboratory, over large periods of time, and for metastable and stable pitting. A call for thorough experimentation is made
to aid the continued research in this area. The work is concluded with a discussion of results and real-world applications. Limitations are explained, especially with regards to the lack of experimental data.
CHAPTER II
MODEL FORMULATION

The model is developed from the two stages of pitting corrosion mentioned by Aziz: pit initiation and pit propagation [6]. Statistical representations of each are first discussed. Then the two solutions are combined into a general model in the form of a cumulative distribution function. The cumulative distribution function calculates the probability that all pits have not grown past a certain depth at a certain time. Simplifications are made to the combined model in order to improve computation speeds. Additionally, equations for statistical approximation of maximum pit depth are derived from the cumulative distribution function. Table 2.1 summarizes and describes the variables and parameters used in the equations to follow.

2.1 Pit Initiation

At a given time, a number of pits can be distributed without a pattern across a metal’s surface. Although it is deterministically accepted that pit initiation is the result of the local breakdown of the passivation layer on a metal’s surface, the process is still considered stochastic throughout the metal [5, 14, 16, 23, 24]. As such, the number of pits per unit area of metal, pit density, can be predicted from the averaged results over an area of interest.
Although the pit initiation process seems random and varied, there are some accepted patterns. Experimental results of Elola, et al., and Cavanaugh, et al., demonstrate that the distribution of average pit density over time could range from exponential to linear, or a combination thereof [1, 25]. In general, pit density increases over time, but it could decrease as pits grow large enough to combine. The rate of pit initiation also varies by the corrosive environment and the type of metal considered. To account for this large range of scenarios, average pit density is assumed to be governed by the generalized equation

\[ APD(t) = \frac{A}{\mu} \left[ 1 - e^{-\mu t} \right] + \nu t^\beta, \]  

(2.1)

where \( A, \mu, \nu \) and \( \beta \) are parameters that could depend upon time, allowing for changes in environmental conditions to be considered. The parameters should be chosen in a way to best reflect data from literature or historical data. If the data appears to be parabolic, then equation (2.1) should be developed such that the second term is emphasized, \( \beta \approx 2 \), and the first term is deemphasized with a small value for \( A/\mu \).

Notice that \( \frac{d}{dt} APD(t) \) also represents the average rate of change of pit density, and could be fit to an alternative data set of initiation rates instead of a data set of pit distributions over time.

In order to predict future pit densities, an inhomogeneous Poisson distribution is suggested. Using equation (2.1), the probability of \( m \) pits existing in an area at time \( t \) is defined by

\[ \Pr [N(t) = m] = \frac{1}{m!} [APD(t)]^m e^{-APD(t)}, \]  

(2.2)
where $N(t)$ denotes pit density at time $t$. The Poisson distribution is used for its simplicity and for the fact that the expected value of distribution (2.2) is $APD(t)$ (equation (2.1)), which is important to simplifications made to the combined model.

A Poisson distribution is not the only distribution that can model the pit initiation process, nor is it an original idea. Shibata and Sudo, the pioneers of modeling pit initiation statistically, were some of the first to suggest the Poisson distribution along with Mears and Brown [5, 8, 12]. However, they did not offer a general expression with time dependent parameters for average pit density. On the other hand, Caleyo and Valor suggest the use of a Weibull distribution with multiple fitting parameters [14, 23, 26], similar to the parameters offered in this model. The Weibull distribution parameters cannot be fit to data as intuitively as the Poisson parameters can, though. Further initiation schemes can be found in Zhao’s thesis [27].

For some scenarios, it may be desired for equation (2.1) to represent a portion of the pit population instead of the entire population. If the initiation rates of stable and metastable pits are known, for instance, the population of metastable pits could be estimated by one curve fit of equation (2.1) while the population of stable pits could be estimated by another curve fit. These two separate equations could then be used in two separate models, and the solutions of those could be combined to predict more accurately the total distribution of pits.
2.2 Pit Propagation

An inhomogeneous Markov chain system is used to model pit growth, and has been demonstrated by others to be effective for risk analysis [13, 14, 15, 23, 26]. The Markov process outlined in this work is based upon the discretization of the metal’s thickness into \( n - 1 \) states of equal thickness, \( C \). A pit advances through the states as it grows, and two additional states are added to represent no pit growth (state 1) and pit depth exceeding the thickness of the metal (state \( n + 1 \)), for a total of \( n + 1 \) states. Figure 2.1 illustrates this discretization. A requirement for the use of the Markov chain is that the probability of the pit proceeding to the next state must depend only on the pit’s current state, and not on the rate that the pit advanced through any prior states. Because the growth of a pit is just as random a process as pit initiation, depending on many environmental factors such as solution chemistry and alloy micro-structure [14, 28], the Markov chain assumption can be made.

The system of ordinary differential equations defining the inhomogeneous Markov chain model is

\[
\frac{dP_1(t; u)}{dt} = -\lambda_1(t; u)P_1(t; u)
\]

\[
\frac{dP_i(t; u)}{dt} = -\lambda_i(t; u)P_i(t; u) + \lambda_{i-1}(t; u)P_{i-1}(t; u), \text{ for } i = 2, 3, \ldots, n. \quad (2.3)
\]

Here, \( P_i(t; u) \) is the probability of a pit that was born at time \( u \) being in state \( i \) at time \( t \). Also, \( \lambda_i(t; u) \) is the probabilistic transition rate for a pit advancing from state \( i \) to state \( i + 1 \) born at time \( u \). Furthermore, \( P_{n+1}(t; u) = 1 - \sum_{i=1}^{n} P_i \) is the probability of the pit being in the last stage. Hence, \( \sum_{i=1}^{n+1} P_i = 1. \)
Figure 2.1: Discretization of pit growth into \( n + 1 \) states. A pit in state 1 has no depth, while a pit in state \( n + 1 \) has surpassed the thickness of the metal. States \( 2, 3, \ldots, n \) each have a thickness of \( C = \frac{T}{n-1} \). The pit in the foreground is in state 3.

If the metal of interest has not experienced any corrosion, the initial conditions of \( P_1(0, u) = 1 \) and \( P_i(0, u) = 0, i = 2, 3, \ldots, n + 1 \) are applied to system (2.3). Other initial conditions, indicating an initial stage of damage, can also be used and may be estimated from any distribution of pit depths on the metal. This gives the model an aspect of adaptability, allowing for the system to be rerun and corrected with an updated distribution.

The most important aspect of system (2.3) is the transition rate, \( \lambda_i(t; u) \), for each state. The transition rates govern the accuracy of the predictability of the solution. Valor, et al., mention that the transition rates may be related to the general pit growth rate through the pit growth law [23]. The pit growth law is generally accepted to be of the form of \( D(t) = at^b \), where \( D(t) \) represents the depth of a pit.
and $a$ and $b$ are constants [24]. However, as Melchers mentions, this growth law does not properly model all situations [16], especially when using constants for $a$ and $b$. We modify the pit growth law so that

$$D(t; u) = a(t)(t - u)^{b(t)}. \quad (2.4)$$

The equation now accounts for dynamic environmental changes through the time-dependent parameters, $a$ and $b$.

Notice that each $\lambda_i$ should have units of $\text{state time}^{-1}$. With this physical meaning in mind, we deduce that $\lambda_{i-1} = \frac{dD}{D}(i - 1)$. It follows through the differentiation of equation (2.4) that

$$\lambda_{i-1}(t; u) = \left[ \frac{b(t)}{t - u} + \frac{a'(t)}{a(t)} + b'(t) \ln(t - u) \right] (i - 1) = \alpha(t; u)(i - 1). \quad (2.5)$$

The equation $\lambda_i(t; u) = \alpha(t; u)i$ is important to the analytical solution discussed in Chapter 3, but is limited in scope, especially for the singularity at $t = u$ (also discussed in Chapter 3). A different, more general, version of equation (2.5) is developed for small $C$ such that the approximation $D(t; u) \approx C(i - 1)$ can be justified. Solving equation (2.4) for $t - u$ with this approximation and then substituting the result into (2.5) yields

$$\lambda_{i-1} = \left( \frac{b(t)}{(i - 1)^{1/b(t)}} \right) - \frac{a'(t)}{a(t)} + \frac{b'(t) \ln \left( \frac{C}{a(t)} \right) + \ln(i - 1)}{b(t)} (i - 1). \quad (2.6)$$

This substitution differentiates local pit time $t - u$ from global pit time $t$ by emphasizing the time that the pit belongs to the state through the variable for state $i$. 

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instead of through the variable for time $t$. We want, after all, for $\lambda_i$ to represent the transition of a pit from state $i$ to state $i + 1$.

Equation (2.6) is the most general form of the transition rates, and should be used when considering either overall or stable pit growth. It can be adjusted to account for cyclic or changing environmental conditions through the time-dependent functions $a$ and $b$. However, the system (2.3) does not have an analytic solution unless it can be simplified to the form of $\alpha(t; u)i$. Furthermore, the equation would change if another growth law were considered. For instance, it is not likely that the growth law for metastable pits follows the $at^b$ pattern. Once technology has improved to track the growth of metastable pits and develop a growth law equation, though, the same derivation process can be followed to yield a set of probabilistic transition rates for metastable pits.

2.3 Combined Model: Initiation and Propagation

The goal of the combined model is to calculate the probability that no pit depth has exceeded a given state $i$ by time $t$. This is the probability that maximum pit depth is less than or equal to state $i$, which is a cumulative distribution function, denoted $\theta_i(t)$. Suppose that $m$ pits are generated in the interval $(0, t)$ at times $u_j$, for $j = 1, \ldots m$. Then $\theta_i(t) = \sum_{m=0}^{\infty} G(m, t)$, where $G(m, t)$ is the probability of $m$ pits initiating and all pits being in a state less than or equal to state $i$ at time $t$. Using the Kolmogorov conditional probability definition, $G(m, t)$ is also equivalent to the probability of $m$ pits initiating by time $t$ multiplied by the probability of all
pits being in a state less than or equal to state \( i \) given \( m \) initiated pits at time \( t \). The probability of \( m \) pits initiating by time \( t \) has been defined by equation (2.2) through the Poisson distribution. We can also define the probability that a pit born at time \( u_j \) is in a state less than or equal to \( i \) by time \( t \) through the solution of equation (2.3), that is

\[
F(t, i; u_j) = \sum_{k=1}^{i} P_k(t; u_j).
\]  

(2.7)

However, equation (2.7) accounts only for the probability of a single pit born at a specific time. To account for all \( m \) pits born at their respective times \( u_j \), consider the joint density function of initiation times, \( f(u_1, u_2, \ldots, u_m|N(t) = m) \). After substituting these results and equation (2.2) into the definition of \( \theta_i \), the cumulative distribution function can be written as

\[
\theta_i(t) = \sum_{m=0}^{\infty} \Pr[N(t) = m] \int_{0}^{t} \int_{0}^{u_{m-1}} \cdots \int_{0}^{u_2} \prod_{j=1}^{m} F(t, i; u_j) f du_1 \cdots du_m.
\]  

(2.8)

Note that a form for \( f \) has not been explicitly provided. As a result of simplifications made in the following section, \( f \) is not required.

2.4 Simplification of \( \theta_i(t) \)

Equation (2.8) is difficult and costly to numerically compute in its current form. The first step of our simplification process is to apply the mean value theorem for integration to each of the integrals in equation (2.8), yielding

\[
\theta_i(t) = \sum_{m=0}^{\infty} \Pr[N(t) = m] \prod_{j=1}^{m} F(t, i; v_j), \quad v_j \in [0, u_j].
\]  

(2.9)
For each \( j \), \( v_j \) is the time at which \( F \) attains its average value in the interval \([0, u_j]\), per the mean value theorem. Notice that the joint density function for initiation times has been removed since

\[
\int_0^t \int_0^{u_{m-1}} \cdots \int_0^{u_2} f(u_1, u_2, \ldots, u_m \mid N(t) = m) \, du_1 \cdots du_m = 1.
\]

However, \( \theta_i(t) \) cannot be calculated until the pit initiation times \( v_j \) are specified.

Hence, equation (2.9) is simplified further by deterministically calculating the expected number of pits and the expected value of pit initiation times, denoted through the function \( E(\cdot) \). Equation (2.1) for average pit density represents the expected number of pits developed using the Poisson distribution initiation process (equation (2.2)), and its inverse can be used to estimate the pit initiation times such that \( APD(E(u_j)) = j \). Now the cumulative probability that the maximum pit depth is less than or equal to state \( i \) becomes

\[
\theta_i(t) \approx \prod_{j=1}^{\lfloor APD(t) \rfloor} F(i, t; E(u_j)), \tag{2.10}
\]

where \( \lfloor \cdot \rfloor \) is the floor function, truncating the result to an integer. A result of these same assumptions yields an equation for the probability mass distribution of all pits within each stage, written as

\[
PMF(i, t) = \sum_{j=1}^{\lfloor APD(t) \rfloor} P_i(t, u_j). \tag{2.11}
\]

Using the simplified equations (2.10) and (2.11), the speed of calculating the combined model now depends upon the speed that the Markov chain system of equations (2.3) is solved for \( P_i(t; u_j) \), with \( j = 1, 2, \ldots, \lfloor APD(t) \rfloor \). The equivalence of the approximations made to equation (2.8) by equation (2.10) have been justified.
using Monte Carlo simulations [29]. This simulation procedure is briefly discussed in Chapter 3.

Other simplification schemes could prove to be more accurate for different forms of \( \lambda_i \), especially Hong’s simplified cumulative density function expression for constant \( \lambda_i \) [15]. However, since complicated forms of \( \lambda_i \) are to be used in the case studies to follow, equation (2.10) suffices.

2.5 Maximum Pit Depth Statistics

The function \( \theta_i(t) \) is used to calculate the frequency distribution of maximum pit depth, which in turn is used to find mean maximum pit depth and variance. The probability that the maximum pit depth is in state \( i \) at time \( t \) is calculated by the difference

\[
PMF_M(i, t) = \theta_i - \theta_{i-1}.\tag{2.12}
\]

Furthermore, the predicted state of the mean maximum pit is calculated as

\[
MMPD(t) = \sum_{i=1}^{n} iPMF_M(i, t),\tag{2.13}
\]

and the variance from this mean is computed as

\[
\sigma^2(t) = \sum_{i=1}^{n} i^2 PMF_M(i, t) - [MMPD(t)]^2.\tag{2.14}
\]

In the case studies that follow in Chapter 4 and 5, these statistics are utilized to demonstrate the reliability of the model’s results. An additional statistic showing the distribution of all pits is also used.
Table 2.1: List of variables and parameters derived within Chapter 2.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Equation Usage</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$</td>
<td>various</td>
<td>global time</td>
</tr>
<tr>
<td>$u, u_j$</td>
<td>various</td>
<td>local pit initiation time</td>
</tr>
<tr>
<td>$APD(t)$</td>
<td>2.1, 2.2, 2.10</td>
<td>average pit density (number of pits per unit area)</td>
</tr>
<tr>
<td>$A, \mu, \nu, \beta$</td>
<td>2.1</td>
<td>fitting parameters for $APD(t)$; possibly time dependent</td>
</tr>
<tr>
<td>$Pr[N(t) = m]$</td>
<td>2.2, 2.8, 2.9</td>
<td>probability that $m$ pits have initiated by time $t$</td>
</tr>
<tr>
<td>$i$</td>
<td>various</td>
<td>state</td>
</tr>
<tr>
<td>$C$</td>
<td>2.5</td>
<td>depth per state, a constant</td>
</tr>
<tr>
<td>$\lambda_i$</td>
<td>2.3, 2.5, 2.6</td>
<td>probabilistic growth rate from state $i$ to state $i + 1$</td>
</tr>
<tr>
<td>$P_i(t; u)$</td>
<td>2.3, 2.7</td>
<td>probability of a pit initiated at time $u$ being in state $i$ at time $t$</td>
</tr>
<tr>
<td>$D(t; u)$</td>
<td>2.4</td>
<td>pit growth law; depth at time $t$ of a pit initiated at time $u$</td>
</tr>
<tr>
<td>$a, b$</td>
<td>2.4, 2.5, 2.6</td>
<td>fitting parameters for $\lambda_i$; possibly time dependent</td>
</tr>
<tr>
<td>$\alpha(t)$</td>
<td>2.6</td>
<td>parameter for pit transition rate equation (used in analytical solution)</td>
</tr>
<tr>
<td>$\theta_i(t)$</td>
<td>2.8, 2.9, 2.10, 2.13</td>
<td>pit depth cumulative distribution function: probability that maximum pit depth is less than or equal to state $i$ at time $t$</td>
</tr>
<tr>
<td>$F(t, i; u)$</td>
<td>2.7, 2.8, 2.9, 2.10</td>
<td>probability that a pit initiated at time $u$ is in a state less than or equal to $i$ at time $t$</td>
</tr>
<tr>
<td>$E(\cdot)$</td>
<td>2.10</td>
<td>expected value function</td>
</tr>
<tr>
<td>$PMF(i, t)$</td>
<td>2.11</td>
<td>probability mass function: percentage of pits in state $i$ at time $t$</td>
</tr>
<tr>
<td>$MMPD$</td>
<td>2.13, 2.14</td>
<td>mean maximum pit depth</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>2.14</td>
<td>variance in maximum pit depth</td>
</tr>
</tbody>
</table>
CHAPTER III
SOLUTION PROCEDURES

Two procedures are outlined for assembling and solving system (2.3): an analytical solution procedure and a numerical solution procedure. The results of either procedure are used to evaluate \( \theta_i \) straightforwardly. The Monte Carlo simulation procedure also generates a result for \( \theta_i \) and is briefly discussed below, although it is not used in the case studies in Chapters 4 and 5. Additionally, the limitations of each procedure are explained, and comments about the model’s capacity for metastable pitting and adaptability are made.

3.1 Initial Setup and Required Inputs

All three procedures require the initial development of equations (2.1) and (2.4) before a solution can be generated. Whether or not data is available for the metal and environment of interest, values or time dependent formulas must be provided for the parameters \( A, \mu, \nu, \beta, a, \) and \( b \). Approximations may be made at first if data is not available because the model can be updated and rerun at a later time with newer, more accurate information.

Typical data required for the fitting process of equation (2.1) should include average pit densities over time, while the data for equation (2.4) should include av-
average pit depth (or stable pit depth) over time. If the parameters of the growth law are available, they can be directly substituted into either equation (2.5) or (2.6), and equation (2.4) would not need to be fit to data. MATLAB’s \texttt{fminsearch} function and the least squares method can be used to curve fit equations (2.1) and (2.4) by evaluating the appropriate values for $A$, $\mu$, $\nu$, $\beta$, $a$, and $b$, or these parameters may be chosen by hand. Alternatively, if data for maximum pit depth over time is available, the parameters in either equation (2.5) or (2.6) can be retroactively determined by utilizing the least squares method and \texttt{fminsearch} on equation (2.13). This last approached is demonstrated in Chapter 4.

The procedures also require an initial distribution of pit depths to determine the initial conditions of system (2.3). If the metal is undamaged and without an initial pitting distribution, one should set $P_i(0, u) = 1$ and $P_i(0, u) = 0$ for $i = 2, 3, \ldots, n+1$. Otherwise, the metal is initially damaged and the initial probabilities can be estimated from the starting distribution. System (2.3) also requires a time domain. If $\tau$ is the desired stopping time of the model predictions, then system (2.3) must be solved over the domain $[u_j, \tau]$ for each unique pit initiation time $u_j$ in order to generate $P_i(t, u_j)$ for each expected pit $j = 1, 2, \ldots, m$. Once $P_i$ has been calculated, the combined model described by equation (2.10) and statistical derivations can be computed.

Lastly, the analytical and numerical solutions require the expected number of pits and pit initiation times. These are evaluated from equation (2.1). Suppose $\overline{APD}(t)$ is the result of curve fitting equation (2.1) to a data set. If the model is to be run until time $\tau$, the expected number of total pits is $m = \lfloor \overline{APD}(\tau) \rfloor$, where
is the floor function, truncating the result to an integer. Then the pit birth times \( u_j \) for \( j = 1, 2, \ldots, m \) are found by solving the equation \( \overline{APD}(u_j) = j \) for \( u_j \).

Numerically, this can be done using MATLAB’s \texttt{fzero} function with the equation \( \overline{APD}(u_j) - j = 0 \). Alternatively, if a small grid of times is chosen, \( APD \) can be calculated across the grid, and expected birth times can be estimated to the nearest gridstep. In either case, if a birth time is calculated to be smaller than the starting time \( t_s \) of the pitting corrosion process, then the birth time should be set to \( t_s \), and the initial conditions should be adjusted if the pit is expected to be in a certain state at the model’s starting time. Physically, this represents a pit forming before the simulation’s starting time, and setting the value to \( t_s \) prevents any computational complications resulting from the birth time being outside the time domain of interest.

In general, \( t_s \leq u_j \leq \tau \) for all \( j = 1, 2, \ldots, m \).

### 3.2 Analytical Solution

Parzen [30] has shown that an analytical solution exists to system (2.3) if \( \lambda_i(t; u) = \alpha(t; u)i \) as in equation (2.5). For an initially undamaged metal that begins the pitting corrosion process with starting time \( t_s \), the resulting probability of a pit born at time \( u \) being in state \( i \) at time \( t \) can be calculated directly as

\[
P_i(t; u) = e^{-\rho(t; u)} \left( 1 - e^{-\rho(t; u)} \right)^{i-1}, \tag{3.1}
\]

where

\[
\rho(t; u) = \int_u^t \alpha(\tau; t_s) d\tau = \ln[D(t; t_s)] - \ln[D(u; t_s)]. \tag{3.2}
\]
The result of the integrated expression of equation (3.2) follows from the fact that
\[ \alpha(t; u) = \frac{dD}{dt}, \] as derived in equation (2.5). A more general form of equation (3.1) also exists to account for any set of initial conditions, which is more useful for models of metals that begin in a damaged state (see [23]).

A drawback of using the analytical solution is that equation (3.2) has a singularity when \( D = 0 \). The singularity would not exist if all pits formed with a certain depth (in a state greater than 1) so that \( t \neq 0 \). In this scenario, \( P_1(u; u) = 0 \). Nonetheless, the singularity can be addressed by slightly altering equation (2.4) into

\[
D(t; u, \epsilon) = a(t)(t - u + \epsilon)^{b(t)},
\]

where \( \epsilon \) is small and \( \epsilon > 0 \). Equation (2.5) would also change to

\[
\lambda_i(t; u, \epsilon) = \left[ \frac{b(t)}{t - u + \epsilon} + \frac{a'(t)}{a(t)} + b'(t) \ln(t - u + \epsilon) \right] i = \alpha(t; u, \epsilon)i.
\]

The modification to account for the singularity requires an extra parameter, \( \epsilon \), to be fit with the data. It also does not completely remove the instability surrounding the singularity – solution can be very elastic with respect to \( \epsilon \).

Another downside is that the analytical solution was derived only for transition rates of the form \( \lambda_i = \alpha i \). Though physically sound, solutions resulting from rates of this form may not produce accurate pit depth distributions, as shown through the example in Chapter 4. Furthermore, if the \( a(t) \) parameter in equation (3.3) is constant, it has no effect on the solution due to the logarithmic subtraction in equation (3.1). The more general equation (2.6) for \( \lambda_i \) can account for a greater variety of
pitting scenarios but requires a numerical solution procedure when used in the system of ordinary differential equations (2.3).

3.3 Numerical Solution

A numerical solution of system (2.3) exists for any form of \( \lambda_i \) and can be benchmarked by the analytical solution when \( \lambda_i = \alpha i \). One simply solves the system of ordinary differential equations using a numerical solver such as the Runge-Kutta method. MATLAB’s \texttt{ode45} function is used to generate most numerical results, while \texttt{ode15s} is used for stiff cases in Chapter 5. The drawback is that system (2.3) must be solved at most \( m \) times, where \( m \) is the expected number of pits at the model’s ending time \( \tau \). Each unique pit initiation time \( u_j \) requires a solution \( P_i(t, u_j) \) over the domain \([u_j, \tau]\). Because the repeated runs of the differential solver slow down computational speed, the analytical solution is favored over the numerical solution when \( \lambda_i = \alpha i \).

3.4 Monte Carlo Simulations

A Monte Carlo simulation uses random number generation and the initiation and propagation models to evaluate a solution to equation (2.8), and consequently equation (2.13). Unfortunately, these simulations must be run many times, which can be very time consuming. The benefit, however, is that any form of \( \lambda_i \) may be used with the Monte Carlo procedure, and that the resulting evaluation of \( \theta_i \) may be benchmarked against the (analytically or numerically computed) simplified solution for \( \theta_i \).
The Monte Carlo simulation procedure is not run alongside the results in the following case studies because (1) the use of equation (2.10) is more convenient and (2) the use of equation (2.10) over the results of the Monte Carlo procedure has already been supported by previous work [29]. More information about using the procedure is established in [29] and the work of Prados, et al. [31].

3.5 Solutions Considering Metastable Pitting

The solution procedures outlined above are designed to predict maximum pit depth distributions. When metastable pitting is to be considered alone or as a part of the pit population, certain precautions, assumptions, and adjustments should be made in order to generate a proper solution.

One adjustment is to absorb the advancement of metastable pits into the overall pit depth equation (2.4). Though the mechanics of metastable pitting are not accounted for, the final solution would be affected by the reduced growth rates associated with metastable pitting. This is not likely the best option, however. Melchers mentions that the deepest pits are stable, not metastable [16]. If the goal is to predict the pit depth distribution of the deepest pits, then it is better to fit equations (2.1) and (2.4) only to data for stable pit initiation and growth, ignoring data on metastable pitting entirely.

If the propagation law of metastable pitting is known, a more accurate approach is to solve an additional model for only metastable pits and combine the results to a model solved for only stable pits. However, if the propagation law for metastable
pitting does not fit the form of equation (2.4), $\lambda_i$ would need to be re-derived using the process described in Chapter 2. Alternatively, a single model could be solved using a piecewise function for $\lambda_i$ of the form

$$
\lambda_i(t; u) = \begin{cases} 
\text{overall pit transition rate (accounting for metastable pits) for } 1 \leq i < k \\
\text{stable pit transition rate for } k \leq i \leq n,
\end{cases}
$$

where $k$ is the critical state corresponding to the critical pit depth for the metal of interest. As described by Galvele, pits reaching the critical depth remain stable and continue to grow [32]. Hence, $\lambda_{k-1}(t; u)$ can be termed the critical transition rate because it is responsible for determining whether or not a pit initiated at time $u$ remains stable, by transitioning from metastable state $k - 1$ to stable state $k$. 

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CHAPTER IV
FITTING THE MODEL TO EXPERIMENTAL DATA

To demonstrate the model’s capabilities and highlight the thought process behind the solution procedures, a fitted model is built for a sample set of data taken from the field observations of Elola, et al. [1]. Elola’s experiment consisted of monitoring the pit depths and densities of several aluminum alloy (UNS A91050) plates throughout various regions of Spain for 48 months. Pit depths were measured using a micrometric screw on an optical microscope and were averaged into frequency distributions. Although samples within five locations of Spain were recorded, only the data of the plates observed in Bilbao, an urban-industrial city with an Atlantic climate, are used in the following model development.

The first step is to establish how the pits initiate. The average pit density data listed in Table 4.1 for the Bilbao samples are first estimated from Elola’s Figure 2 [1]. Then, equation (2.1) is curve fit to the data in Table 4.1. The values of the resulting parameters are shown in Table 4.2. Elola, however, suggests a linear fit for average pit density such that \( APD(t) = 3t + 5 \). The generality of equation (2.1) can account for this scenario by using the parameter values in Table 4.3. Notice that 5 pits are initiated at time \( t = 0 \) using the linear approach. A plot of the pit density data and the two different models for average pit density are displayed in Figure 4.1.
Figure 4.1: Results of curve fitting experimental data for average pit density to equation (2.1). One model uses the linear expression $APD(t) = 3t + 5$ suggested by Elola, et al. [1], with parameters for equation (2.1) listed in Table 4.3, while another model uses the parameters listed in Table 4.2.

Table 4.1: Data of average pit density over time for aluminum alloy (UNS A91050) plates that corroded in Bilbao, Spain over 48 months. The values are estimated from Figure 2 in [1].

<table>
<thead>
<tr>
<th>Time (months)</th>
<th>0</th>
<th>6</th>
<th>13</th>
<th>24</th>
<th>36</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pit Density (number per cm$^2$)</td>
<td>0</td>
<td>10</td>
<td>40</td>
<td>75</td>
<td>135</td>
<td>130</td>
</tr>
</tbody>
</table>

Once an equation for average pit density is established, the expected number of pits and the expected pit initiation times are calculated. The model is run until
Table 4.2: Resulting parameter values from curve fitting equation (2.1) to the experimental data from Elola, et al., that is listed in Table 4.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$A$</th>
<th>$\mu$</th>
<th>$\nu$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>1</td>
<td>0.05</td>
<td>2.5</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4.3: Parameter values of equation (2.1) such that $APD(t) \approx 3t + 5$, a linear fit suggested by Elola, et al. [1].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$A$</th>
<th>$\mu$</th>
<th>$\nu$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>$5\mu$</td>
<td>large</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

$\tau = 48$ months in accordance with Elola’s experiments, and hence, $m = 138$ pits are expected to form by time $\tau$ when using the parameters in Table 4.2 for $APD$.

Similarly, $m = 149$ pits are expected to form if the linear fit of equation (2.1) is used with the parameters listed in Table 4.3. The pit initiation times $u_j$ for $j = 1, 2, \ldots, m$ are also calculated, and any initiation times less than the model’s starting time $t_s$ are replaced by the value of $t_s$, here set to 0.

Next we consider pit propagation. Elola, et al., supply data for pit growth in the form of an equation for average pit depth (in their Table 5), an equation for maximum pit depth (in their Table 4), and a distribution of all pit depths for $t \in \{6, 13, 24, 36, 48\}$ (in their Figure 6) [1]. Because the histogram in Elola’s Figure 6 shows pit density for 12 different depths, the metal is discretized into 13 states. Instead of using Elola’s equation for average pit depth, we develop $\lambda_i$ by matching
the model’s solution in the form of the mean maximum pit depth equation (2.13) to Elola’s expression for maximum pit depth. Three attempts at forming $\lambda_i$ follow.

At first it is assumed that $\lambda_i = \frac{b}{t-u+\epsilon}i$, where $b$ and $\epsilon$ are constants and $\epsilon > 0$. This directly follows from equation (3.4). Using the parameters for equation (2.1) from Table 4.2 for the pit initiation process, the curve fit of this form of $\lambda_i$ yields $b \approx 0.4638$ and $\epsilon \approx 0$. The fact that $\epsilon \approx 0$ shows that the numerical curve fit procedure failed because the singularity still exists in the solution. Figure 4.2 shows how mismatched this case’s mean maximum pit depth is when compared to Elola’s experimental mean maximum pit depth.

The next case attempts to address the failure of the curve fit by adjusting the parameters of the average pit density equation to match Elola’s linear expression, $APD(t) = 3t + 5$. If the same form of $\lambda_i = \frac{b}{t-u+\epsilon}i$ is used, then the results of the curve fitting procedure are that $b = 0.2177$ and $\epsilon = 0.0064$. Figure 4.3 shows that the match between the resulting mean maximum pit depth with Elola’s experimental mean maximum pit depth is much better (as compared to Figure 4.2). However, on inspection of additional results, such as the predicted distribution of pits from equation (2.11) in Figure 4.4, it is concluded that $\lambda_i = \frac{b}{t-u+\epsilon}i$ is not an appropriate model for the pit transition rates. The model does not capture the complex distribution of pit depths seen in Elola’s Figure 6.

In a final attempt, we model the situation using a more complex form of $\lambda_i$ in order to generate a better data fit for the distribution of pit depths. Let average pit density be governed by equation (2.1) with parameters from Table 4.2, and let
Figure 4.2: Mean maximum pit depth results from equation (2.13) for $\lambda_i = \frac{b}{t-u+\epsilon}i$, $b \approx 0.4638$, $\epsilon \approx 0$. Equation (2.1) uses the parameters in Table 4.2. The curve fitting process failed, yielding a result that doesn’t match well to Elola’s results.

The transition rates be modeled by $\lambda_i = \frac{k}{\beta_0 + b_1 t}i$. Notice that $\lambda_i$ is an approximation of (2.6) which holds if $b_1$ is small. The results of the curve fitting procedure justify the approximation with $k \approx 20$, $b_0 \approx 2.0145$, and $b_1 \approx 0.0456$. Mean maximum pit depth and pit depth distribution plots are shown in Figures 4.5 and 4.6 respectively. Although the curve fit of mean maximum pit depth in Figure 4.5 is not as close as the results in Figure 4.3, the histogram of pit density across the stages matches better with Elola’s Figure 6. One can even see how the average depth of the pits
Figure 4.3: Mean maximum pit depth results from equation (2.13) for when \( \lambda_i = \frac{b}{t-u+\epsilon} \), \( b \approx 0.2177 \), \( \epsilon \approx 0.0064 \), and \( APD(t) = 3t + 5 \). The curve fitting process succeeded with this form of \( APD \), and the curves appear to be very close.

increases slightly as time increases. Even better results could be obtained if a more complicated form of \( \lambda_i \) was chosen. Particularly, the pits should advance through the stages slightly faster as time increases.

The results of the last model show how important it is to consider the predicted distribution of pit depths when fitting the model to actual data. Although equation (2.5) is theoretically justified and can produce great results for mean maximum pit depth, it cannot capture the local pit growth per stage like equation (2.6)
Figure 4.4: Resulting distribution of pits from equation (2.11) for when $\lambda_i = \frac{b}{t - u + \epsilon}$, $b \approx 0.2177$, $\epsilon \approx 0.0064$, and $APD(t) = 3t + 5$. These results were scaled logarithmically to match the reported results of Elola et al. [1]. However, the figure does not match Elola’s results, signifying that further adjustments must be made to the model.

can. The local pit time substitution that was made in the derivation of equation (2.6) causes this distinction. Consequently, equation (2.6) should be the model of choice for the pit transition rates, and is used exclusively in the following case studies.
Figure 4.5: Mean maximum pit depth results for retroactively curve fitting $\lambda_i = \frac{k}{b_0 + b_1 t_i}$ through equation (2.13) to an expression for mean maximum pit depth provided by Elola, et al. [1]. The average pit density model with parameters in Table 4.2 was also used. The values of $k \approx 20$, $b_0 \approx 3.0145$, and $b_1 \approx 0.0456$ result from the curve fit.
Figure 4.6: Resulting depth distribution of pits from equation (2.11) for when $\lambda_i = \frac{k}{b_0 + b_1 t_i}$, $k \approx 20$, $b_0 \approx 3.0145$, $b_1 \approx 0.0456$, and equation (2.1) is fit to the parameters in Table 4.2. The figure matches decently with Elola’s Figure 6, and captures how the majority of pits are deepening as time increases.
CHAPTER V
CASE STUDIES

Each case below uses equation (2.1) for the pit initiation process and equation (2.6) for the transition rates of the pit propagation process. The parameters of each equation are slightly varied in each case, and the set of ordinary differential equations (2.3) is solved numerically assuming that the metal begins in an uncorroded state. Results of the distribution of pits within each state (2.11) and the expected state of maximum pit depth (2.13) are displayed and analyzed.

5.1 Case 0: Base Case

Table 5.1: Base case parameters used in equations (2.1) and (2.6).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$A$</th>
<th>$\mu$</th>
<th>$\nu$</th>
<th>$\beta$</th>
<th>$a$</th>
<th>$b$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>0</td>
<td>arbitrary</td>
<td>2.1</td>
<td>1</td>
<td>1</td>
<td>0.3</td>
<td>0.25</td>
</tr>
</tbody>
</table>

For the base case, we predict the resulting corrosion within the first 5 $\mu m$ of a hypothetical metal over a time period of 48 months (4 years). The metal is discretized into 20 states of equal depth $C = 0.25 \mu m$ so that there are 22 pitting states in total. Recall that a pit in state 1 has no depth, a pit in state 2 has a depth between 0 and 0.25 $\mu m$, a pit in state 21 has a depth between 4.75 and 5 $\mu m$, and a
pit in state 22 has a depth greater than or equal to 5 µm. We govern the pit initiation process by a linear average pit density function with parameters listed in Table (5.1). By ending time \( \tau = 48 \), 100 pits are expected to form per unit of area on average. For the pit propagation process, we use constant values for \( a \) and \( b \), also listed in Table (5.1). The resulting distribution of pits within each state is displayed in Figure 5.1 while the expected state of maximum pit depth over time is shown in Figure 5.2. The MATLAB code used to generate these results can be referenced in Appendix A.

Figure 5.1: Distribution of pits within each state from equation (2.11) for the base case (initiation and growth parameters are listed in Table 5.1).
Figure 5.2: Average state of maximum pit depth over time from equation (2.13) for the base case with one standard deviation $\sigma$ of error bars. Initiation and growth parameters are listed in Table 5.1.

5.2 Case 1: Superlinear and Sublinear Pit Initiation

In this case, the parameters of the average pit density equation (2.1) are modified from the base case to examine the effects of superlinear and sublinear pit initiation. For control, the pit propagation scheme is defined by the same scheme used in Case 0. Table 5.2 shows the parameters that are used to produce both the superlinear and sublinear scenarios, while Figure 5.3 visualizes the pit initiation procedures.
Table 5.2: Case 1 parameters for superlinear and sublinear pit initiation, used in equation (2.1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$A$</th>
<th>$\mu$</th>
<th>$\nu$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superlinear Values</td>
<td>10.1636</td>
<td>0.1</td>
<td>0</td>
<td>arbitrary</td>
</tr>
<tr>
<td>Sublinear Values</td>
<td>0.0836442</td>
<td>-0.1</td>
<td>0</td>
<td>arbitrary</td>
</tr>
</tbody>
</table>

In the superlinear subcase, the majority of the pits form by the 24th month. Compared to the base case, the distributions of pits within the states have larger peaks, as seen in Figure 5.4. This is explained by the higher number of pits being initiated at earlier times. The average state of maximum pit depth is also larger by a nearly constant amount, as seen in Figure 5.6.

On the other hand, the sublinear subcase produces the majority of the 100 pits after the 24th month. Compared to the base case, the sublinear distributions have shallower peaks because of the lower number of pits at earlier times (see Figure 5.5). The expected state of maximum pit depth remains at 1 in Figure 5.6 for the sublinear subcase until a sufficient number of pits initiate (by $t \approx 8$) to cause the state of maximum pit depth to increase. This causes the average state of maximum pit depth to be lower than in the base and superlinear cases by a nearly constant amount.
Figure 5.3: Average pit density over time for the superlinear and sublinear subcases. Parameter values for the average pit density equation (2.1) can be found in Table 5.2.

Figure 5.4: Distribution of pits within states for the superlinear subcase. Compared to the base case, the pits are more concentrated and each distribution is shifted slightly to the right (signifying deeper pits).
Figure 5.5: Distribution of pits within states for the sublinear subcase. Compared to the base case, the pits are less concentrated and each distribution is shifted slightly to the left (signifying shallower pits).

Figure 5.6: Average state of maximum pit depth over time for the superlinear and sublinear cases. Having more pits initiate at earlier times increases the average state of maximum pit depth. The expected state of maximum pit depth is 1 for the sublinear case until a sufficient number of pits initiate to affect it.
5.3 Case 2: Aggressiveness of Pit Propagation

For the second case, the parameters $a$ and $b$ are modified within the transition rate equation (2.6) to study the effects of pit growth on maximum pit depth and the distribution of pit depths. For control, pit initiation is defined by the same scheme as in Case 0. Table 5.3 shows how $a$ and $b$ are varied for the following four subcases.

Table 5.3: The propagation parameters used in equation (2.6) for the four subcases of Case 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increased $a$</td>
<td>1.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Decreased $a$</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Increased $b$</td>
<td>1</td>
<td>0.36</td>
</tr>
<tr>
<td>Decreased $b$</td>
<td>1</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The resulting plots of the expected state of maximum pit depth over time for each subcase are displayed in Figure 5.7. The state of maximum pit depth increases at a faster rate over time for the subcases where either $a$ or $b$ are increased. This is an expected result given that the transition rates between the states have increased in both these subcases. Likewise, the state of maximum pit depth decreases at a faster rate over time for the subcases where either $a$ or $b$ are decreased.

Figure 5.8 shows the distributions of pits within each state for each subcase. If either $a$ or $b$ increases, the distributions are shifted to the right – the larger transition
rates cause the pits to be deeper. On the other hand, if $a$ or $b$ decreases, the pits stay longer in states corresponding to shallower depths.

Figure 5.7: Expected state of maximum pit depth over time for the four subcases of Case 2. Parameters for pit propagation are listed in Table 5.3.
Figure 5.8: Distribution of pit densities through each state over time for Case 2. Increasing either $a$ or $b$ produces similar results – the pits in general reside in states corresponding to deeper depths. Likewise, decreasing either $a$ or $b$ causes the pits to reside longer in states corresponding to more shallow depths.

5.4 Case 3: Representation of Environmental Scenarios

For the third case (and the following subcases), time dependent expressions for the parameters $a$ and $b$ of equation (2.6) are considered to demonstrate the model’s capacity to represent environmentally changing scenarios.
5.4.1 Subcase 1: Linear Transition Rates

At first we consider an environment of gradually increasing or decreasing corrosivity. This could represent steady climate change or the environment of a newly industrialized town as its concentrations of pollutants begin to rise. To model these scenarios, a linear equation for $b$ is chosen, keeping $a$ constant. With $a = 1$ and $b = b_0 + b_1 t$, equation (2.6) becomes

$$
\lambda_i = \left( \frac{b_0 + b_1 t}{(C_i)^{a_0 + a_1 t}} + \frac{b_1}{b_0 + b_1 t} \ln (C_i) \right) i, \tag{5.1}
$$

where $C = 0.25$ (from the base case).

By substituting $b_0 = 0.3$ and $b_1 = \frac{0.06}{48}$ into equation (5.1), we model a case of gradually increasing corrosivity. Note that the value of $b$ increases at a constant rate from the value used in Case 0 ($b = 0.3$) to the value used in the third subcase of Case 2 ($b = 0.36$) over 48 months. The resulting distributions of pit depths are displayed in Figure 5.9. At early times, the distributions look similar to the base case distributions. Then, they gradually move towards the distributions for the case with the increased value for $b$. At later times, this case is even more corrosive than the case with constant $b = 0.36$, which is seen in Figure 5.11. This is because there is a second term present in equation (5.1) that is not present in the case for constant $b$, since the derivative of a constant is 0. The second term increases the value of $\lambda_i$ to be more than the value of $\lambda_i$ in the case for constant $b$ at later times.

By letting $b_1 = -\frac{0.06}{48}$, we also model a case of gradually decreasing corrosive conditions. Here, the value of $b$ decreases at a constant rate from the value used
Figure 5.9: Distribution of pit densities through each state over time for $b = 0.3 + \frac{0.06}{48}t$. These results are compared to the base case, $b = 0.3$, and the increased $b$ case, $b = 0.36$.

in Case 0 ($b = 0.3$) to the value used in the fourth subcase of Case 2 ($b = 0.24$).

Similar to the linearly increasing case, the distributions hug closely to the base case distributions at early times and move gradually to the distributions of the case with the decreased value for $b$ at later times in Figure 5.10. Due to the second term of equation (5.1), the mean state of maximum pit depth drops lower at later times than the mean state of maximum pit depth for the case with decreased, constant $b$ (see Figure 5.11). In fact, the plot of the average state of maximum pit depth is no longer
strictly increasing over the whole time interval. The larger number of pits in lower states at later times causes the average to shift downwards.

Similar cases were run by making $a$ linear and keeping $b$ constant. The cases for linear $a$ produced similar results to the above cases for linear $b$, just as $a$ and $b$ behave similarly in Case 2. This gives some justification for the removal of $a$ in the analytical solution, mentioned in Chapter 3.

Figure 5.10: Distribution of pit densities through each state over time for $b = 0.3 - 0.06t$. These results are compared to the base case, $b = 0.3$, and the decreased $b$ case, $b = 0.24$. 

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Figure 5.11: Average state of maximum pit depth over time for both the linearly increasing case, $b = 0.3 + 0.0648t$, and the linearly decreasing case, $b = 0.3 - 0.0648t$.

5.4.2 Subcase 2: Sinusoidal Transition Rates

Next we consider a cyclically changing environment. For instance, the cycle of seasons should have some impact on the corrosiveness of a metal’s surroundings. We first attempt to model seasonal change by letting $b = 0.3 + 0.06 \sin\left(\frac{2\pi}{12}t\right)$. Here, $b$ oscillates between the values 0.24 (the decreased value of $b$ in Case 2) and 0.36 (the increased value of $b$ in Case 2) on a yearly cycle. Substituting this equation for $b$ into equation
(2.6) along with the other base case parameters \((a = 1 \text{ and } C = 0.25)\) yields

\[
\lambda_i = \left( \frac{0.3 + 0.06 \sin\left(\frac{2\pi}{12} t\right)}{0.3 + 0.06 \sin\left(\frac{2\pi}{12} t\right)} \right) + \frac{0.01 \cos\left(\frac{2\pi}{12} t\right) \ln \left(0.25i\right)}{0.3 + 0.06 \sin\left(\frac{2\pi}{12} t\right)} i. \tag{5.2}
\]

However, numerical solutions to system (2.3) with this form of \(\lambda_i\) are unstable. At certain times and states, the second term of equation (5.2) can have too large of a magnitude and cause \(\lambda_i\) to be negative. If the sinusoidal change is small, however, the second term can be ignored, so that equation (5.2) can be written as

\[
\lambda_i = \left( \frac{0.3 + 0.06 \sin\left(\frac{2\pi}{12} t\right)}{0.3 + 0.06 \sin\left(\frac{2\pi}{12} t\right)} \right) i. \tag{5.3}
\]

This simplification is justified given that seasonal change should not have too large of an impact on the corrosiveness of the metal’s surroundings.

Using equation (5.3) yields results when solving system (2.3) and equations (2.11) and (2.13). In Figure 5.12, the distributions are close to the base case distributions, but shifted slightly to the right since the corrosivity of the environment initially increased for the first six months. Figure 5.13 gives a better picture of how the cyclical rates affect the state of maximum pit depth over time, showing a stair-like pattern. Similar results can be achieved by making \(a\) sinusoidal and \(b\) constant.
Figure 5.12: Distribution of pit densities through each state over time for the cyclical case of $b = 0.3 + 0.06 \sin\left(\frac{2\pi}{12}t\right)$ and $b' \approx 0$. These results are compared to the base case, $b = 0.3$. 
Figure 5.13: Average state of maximum pit depth over time for sinusoidal $b = 0.3 + 0.06 \sin \left( \frac{2\pi}{12} t \right)$ and $b' \approx 0$.

5.4.3 Subcase 3: Hyperbolic Tangential Transition Rates

This last subcase models an abruptly changing environment. If the metal is moved from an arid climate to a more corrosive marine climate (or vice versa), the transition rates should reflect the changing environmental scenarios. We use the hyperbolic tangent function to model these jump-like transitions.
To simulate an abrupt increase in corrosive conditions, suppose $b = 0.3 + 0.06 \tanh(100(t - 12))$. Here, $b = 0.24$ for the first twelve months, which is the decreased $b$ subcase of Case 2. Afterwards, $b$ is quickly increased to $b = 0.36$ (the increased $b$ value of Case 2) for the remaining three years. Notice that the derivative of $b$ with respect to time, $b' = 6 \sech^2(100(t - 12))$, is approximately 0 except near $t = 12$. Because the sudden change near $t = 12$ causes numerical instability, we let $b' = 0$ in equation (2.6) when solving system (2.3).

When using this form of $b$, a stiff set of equations for $\lambda_i$ is generated due to the sudden change at the 12th month. This is addressed by solving system (2.3) with the MATLAB function `ode15s` in place of `ode45`. The resulting distributions of pits within the stages in Figure 5.14 exactly match the distributions for the decreased $b$ subcase of Case 2 for the 6th and the 12th month. Afterwards, the distributions appear more like the distributions of the increased $b$ subcase of Case 2. The same pattern can be observed in the plot of average state of pit depth over time (in Figure 5.15). At first the plot matches the plot for the decreased $b$ case, and then begins to increase up to the plot of the increased $b$ case after the 12th month.

With $b = 0.3 - 0.06 \tanh(100(t - 12))$, we also model an abrupt decrease in corrosivity, which changes $b$ from 0.36 to 0.24 after the 12th month. This could simulate coating a metal in order to hamper future corrosion. Figure 5.16 shows how the distributions of pits within the states match the distributions for the case of $b = 0.36$ for 6th and 12th month. Afterwards, the distributions change appearance to
Figure 5.14: Distribution of pit densities through each state for the abruptly increasing corrosivity case using $b = 0.3 + 0.06 \tanh(100(t - 12))$ and $b' = 0$. The value of $b$ changes from 0.24 to 0.36 after the 12th month.

match the distributions for $b = 0.24$. Figure 5.17 also shows how the rate of increase in the average state of maximum pit depth abruptly decreases after the 12th month.
Figure 5.15: Average state of maximum pit depth over time for the abruptly increasing corrosivity case using $b = 0.3 + 0.06 \tanh(100(t - 12))$ and $b' = 0$. The value of $b$ changes from 0.24 to 0.36 after the 12th month.
Figure 5.16: Distribution of pit densities through each state for the abruptly decreasing corrosivity case using $b = 0.3 - 0.06 \tanh(100(t - 12))$ and $b' = 0$. The value of $b$ changes from 0.36 to 0.24 after the 12th month.
Figure 5.17: Average state of maximum pit depth over time for the abruptly decreasing corrosivity case using $b = 0.3 - 0.06 \tanh(100(t - 12))$ and $b' = 0$. The value of $b$ changes from 0.36 to 0.24 after the 12th month.
CHAPTER VI
THE MODEL AS A TOOL

The model can be used without a complete understanding of its development – the user simply needs to manipulate the parameters in the initiation and growth equations ((2.1) and (2.4) respectively) to match the model’s output to a known set of data. Then, the model can extrapolate and predict future pit depth distributions and mean maximum pit depth. To demonstrate and facilitate this process, an interactive Mathematica Computable Document for the analytical solution is presented (displayed in Figure 6.1). Mathematica’s Computable Document Format (CDF) allows for the creation of dynamic user interfaces that update on specified event changes. For instance, the tool will recalculate the model and re-plot the solutions within the right column after modifying any of the parameter values listed within the left column of Figure 6.1 and pressing the “Update Figures” button. This allows for quick, user friendly, parameter studies to be made, making the tool an asset to any industry that manages pitting corrosion.

Each section within the left column of the interactive tool affects the model in some way. The “Model Parameters” section allows the user to change the model’s starting time, end time, units, and depth discretization by either using the decrement/increment buttons or typing a new value into the text box. However, the plots
Figure 6.1: Mathematica Computable Document for the analytical model. If any parameter within the left column is changed, the graphs within the right column are updated whenever the “Update Figures” button is pressed.
to the right will not appear correctly (after pressing the “Update Figures” button) if an invalid scenario is requested, such as setting Start Time = End Time. The user should also be careful about modifying the units because the parameters within the “Pit Initiation” and “Pit Propagation” sections inherently depend on the units and are not updated when the units are changed. The user additionally has the option of modifying the “Timestep” parameter, which directly affects the speed at which the model calculations are made or inversely affects the accuracy of the “Expected Mean Maximum Pit Depth” plot. The tool enforces that the start time, end time, and plot times are rounded to the nearest timestep.

Within the “Pit Initiation” and “Pit Propagation” sections, the user can choose the desired form of equations (2.1) and (2.4) respectively from the drop-down menus, and the parameters underneath will dynamically update (see Figure 6.2). Note that the “Average Pit Density” figure is only affected by the pit initiation parameters. On the other hand, both sets of parameters may change the “Expected Mean Maximum Pit Depth” and “Distribution of Pit Depths” figures.

Lastly, the “Distribution Settings” area allows for more plots to be made on the “Distribution of Pit Depths” figure, up to a maximum of five. Figure 6.3 illustrates how changing the “Number of Plots” parameter will dynamically create more “Plot Times” boxes. The user should keep in mind that the “End Time” parameter must be larger than any of the desired “Distribution of Pit Depths” plot times in order for the plot to properly display. Also, if the x-axis of the “Distribution of Pit Depths”
Figure 6.2: Different equations may be selected for the initiation (a) and growth (b) models through the respective drop-down menus. Both the parameter selection area and graphs will update whenever a new equation is chosen and the “Update Figures” button is pressed. For comparison, the equations and parameter listed here are different than those in Figure 6.1.

If the figure is to be changed, the “Maximum Depth” Parameter underneath the “Model Parameters” section should be modified.

The tool demonstrated here was created as a proof of concept and is not intended for immediate industrial use. Certain licensing agreements must be made with Mathematica if the CDF is to be sold or commercially used. Also, the tool is restricted to calculating only the analytical model results, which are limited in comparison to the numerical results, as discussed in Chapter 4. Future work could improve the tool by implementing the numerical solution procedure, which would in turn allow additional equations to be used for depth in the “Pit Propagation” section, leading to more accurate distribution results. The Computable Document

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Figure 6.3: The “Distribution Settings” allow the user to change the appearance of the “Distribution of Pit Depths” figure. The number of distributions and the time of each distribution may be modified. Notice how more plots have been added here than in Figure 6.1.

could also be improved in computational efficiency. With a “Timestep” value of 1, nearly 2 seconds elapse whenever the figures are updated. This sluggishness could be explained by the overhead generated by the Mathematica Language and compiler, and perhaps a tool written in a C-based language could prove to be more responsive. Notwithstanding the forgoing warnings, the code used to generate the tool is available in Appendix B.
CHAPTER VII
CONCLUSIONS AND FUTURE WORK

A stochastic initiation and propagation model was developed to predict the effects of pitting corrosion on susceptible metals. The model relies upon an inhomogeneous Markov chain system (2.3) in order to describe the propagation of pit depths throughout a discretized set of states. The main focus of this work was to examine the flexibility of the model with respect to the probabilistic transition rates $\lambda_i$ used in the Markov system. A generalized form of $\lambda_i$ is displayed in equation (2.6), and depending on the form of $\lambda_i$, either an analytical or a numerical solution procedure can be used to solve the Markov system.

The numerical form of $\lambda_i$ offers a wider variety of results, especially for dynamically changing environments. Since the derivation of $\lambda_i$ depends upon the pit growth law (equation (2.4)), changes in the possibly time-dependent parameters $a$ and $b$ were studied. It was shown that the expression used for either $a$ or $b$ can be modified to account for gradual increases or decreases, cyclical changes, or abrupt shifts in environmental corrosivity. Both $a$ and $b$ appear to have similar effects on the distribution of pit depths throughout the states and on the expected state of maximum pit depth over time. However, the numerical results are unstable when $\lambda_i$ is negative.
Simplifications to the model were also suggested so that computational speed could be increased. The original intent of the model was to track and predict pitting corrosion in difficult to inspect places, such as buried pipeline, enclosed mechanical pieces, and airplane fuselages. As such, the model should run in a reasonable amount of time so that it can be fit easily to actual data. A tool in the form of a Mathematica Computational Document was created using the analytical form of $\lambda_i$ to stress the industrial importance and utility of the model. The behind-the-scenes computations rely on a simple user interface.

Additionally, suggestions were offered in regard to metastable pitting and situations where the metal begins in a corroded state. The model is flexible enough to handle these scenarios as long as appropriate data is available, and can be updated as new data becomes available. It is important for pitting corrosion research to continue to develop so that a better understanding and pool of data for metastable and stable pitting can be obtained.

Future work could improve the model in several ways. Once data becomes available, case studies on using the model with metastable growth should be made. Another improvement is noticeable from the fact that pits do not always grow in isolation. Once pits become wide enough, several may combine to form an even larger pit. Because this process could affect the pit initiation and propagation procedures, the model should be adjusted to account for it. Finally, the model can be improved by adding more physical meaning to the parameters in equations (2.1) and (2.13). Shibata has already mentioned a model for the pit initiation process dependent upon
pitting potential [5]. The parameters used in our model should not only depend on this pitting potential, but should also depend on actual potential, chemical concentrations, temperature, and stochastic properties such as metal and film defects.


APPENDICES
APPENDIX A
MATLAB CODE

Below is the MATLAB code that was used to generate the results for the base case in Chapter 5. By modifying some of the parameter values, the same code was used to produce all the results in Chapters 4 and 5. Included are methods for both the numerical and analytical solutions. If an fminsearch run is to be made, the entire pitting function should be modified to accept the appropriate curve fitting parameters.

```matlab
function case0
    % Michael Workman, mrw39@zips.uakron.edu, 3/13/14

    %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
    % PARAMETERS
    %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
    T = 5; % plate thickness
    N = 21; % state of failure
    stages = 1:1:N;
    C = T./(N-1); % thickness per state
    t_s = 0;
    tau = 48;
    dt = .001;
    t = t_s:dt:tau;
    nmax = length(t);

    % Average Pit Density, APD
    A = @(t) 0;
    mu = @(t) .05;
    nu = @(t) 2.1;
    beta = @(t) 1;
    APD = @(t) A(t)./mu(t).*(1-exp(-mu(t).*t))+nu(t).*t.^beta(t);
```
% OUTPUTTING CODE

% CALCULATIONS

btimes = calc_birthtimes(APD);
P = P_num(btimes);
F = F_(P);
theta = theta_(F);
pmf = pmf_(theta);
MMPD = MMPD_(pmf);
sigma = std_dev_(pmf, MMPD);
all_pdf = all_pmf_(P);
adj_stages = [0 stages];
padding = zeros(nmax,1);
hist = [padding all_pdf];

% PRINTING

% Output file names:
% tagMpS
% tagM Markov MMPD
% tagMmS
% tagHist6 6m Histogram
% tagHist12 12m Histogram
% tagHist24 24m Histogram
% tagHist36 36m Histogram
% tagHist48 48m Histogram

tag = 'case0';

APD_ID = fopen([tag 'A.dat'], 'w');
MpsS_ID = fopen([tag 'MpS.dat'], 'w');
M_ID = fopen([tag 'M.dat'], 'w');
MmS_ID = fopen([tag 'MmS.dat'], 'w');
Hist6_ID = fopen([tag 'Hist6.dat'], 'w');
Hist12_ID = fopen([tag 'Hist12.dat'], 'w');
Hist24_ID = fopen([tag 'Hist24.dat'], 'w');
Hist36_ID = fopen([tag 'Hist36.dat'], 'w');
Hist48_ID = fopen([tag 'Hist48.dat'], 'w');

fprintf(APD_ID, '%f %f
', [t; APD(t)]);
fprintf(MpS_ID, '%f %f
', [t; (MMPD + sigma)]);
fprintf(M_ID, '%f %f
', [t; MMPD]);
fprintf(MmS_ID, '%f %f
', [t; (MMPD - sigma)]);
fprintf(Hist6_ID, '%f %f
', [adj_stages; hist(6/dt+1,:)])
fprintf(Hist12_ID, '%f %f
', [adj_stages; hist(12/dt+1,:)])
fprintf(Hist24_ID, '%f %f
', [adj_stages; hist(24/dt+1,:)])
fprintf(Hist36_ID, '%f %f
', [adj_stages; hist(36/dt+1,:)])
fprintf(Hist48_ID, '%f %f
', [adj_stages; hist(48/dt+1,:)])

fclose(APD_ID);
fclose(MpS_ID);
fclose(M_ID);
fclose(MmS_ID);
fclose(Hist6_ID);
fclose(Hist12_ID);
fclose(Hist24_ID);
fclose(Hist36_ID);
fclose(Hist48_ID);

%%%%%%%%%%
% PLOTTING %
%%%%%%%%%%

figure(1)
plot(t, APD(t))

figure(2)
plot(t, MMPD - sigma, t, MMPD, t, MMPD + sigma)

figure(4)
plot(adj_stages, hist(6/dt+1,:), adj_stages, hist(12/dt+1,:), ... 
adj_stages, hist(24/dt+1,:), ... 
adj_stages, hist(36/dt+1,:), adj_stages, hist(48/dt+1,:))
legend('6m', '12m', '24m', '36m', '48m')

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Functions
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Birth Times for pit_1 to pit_max
function b = calc_birthtimes(APD)
    fprintf('Calculating Initiation Times\n');
    mmax = floor(APD(t(nmax)));
    b = zeros(mmax,1);
    for m = 1:mmax
        % find the solution of APD = m
        APDz = @(t) APD(t) - m;
        btime = max(fzero(APDz,0),t(1));
        b(m) = btime;
    end
end

% Valor Analytic P(t_n, u_n, i)
function P = P_ana(btimes)
    fprintf('Calculating P\n');
    b = input(1);
    eps = input(2);
    D = @(t,u) (t-u+eps).^b;
    rho = @(t,u) log(D(t,t_s)) - log(D(u,t_s));
    [t_,u_,s_] = ndgrid(t,btimes,stages);
    P = exp(-rho(t_,u_)).*(1-exp(-rho(t_,u_))).^(s_-1); 
    P(:,:,N) = 1 + P(:,:,N) - sum(P,3);
end

% Numerical P: Find P(t_n,u_j,i) the prob of pit being in
% state i at time t with birth time u
function P_num = P_num(btimes)
    fprintf('Calculating P\n');
    a = @(t) 1;
    b = @(t) .3;
    a_prime = @(t) 0;
    b_prime = @(t) 0;
    lambda = @(t, i) i.*(b(t)/(C.*i./a(t)).^(1./b(t))) + ...
        a_prime(t)./a(t) + ...
        b_prime(t).*log((C.*i./a(t)).^(1./b(t))));
    m = length(btimes);
    P_num = zeros(nmax,m,N);
    P0 = zeros(N,1);
    P0(1) = 1;
opt = odeset('RelTol',1e-4,'AbsTol',1e-4);

for n = 1:m
    if (n > 2 && btimes(n) == btimes(n-1))
        P_num(:,n,:) = P_num(:,n-1,:);
    elseif btimes(n) == t(nmax)
        P_num(nmax,n,:) = P0;
    else
        tspan = [btimes(n) t(nmax)];
        [ttemp,Ptemp] = ode45(@markov,tspan,P0,opt);
        P_u = interp1(ttemp,Ptemp,t);
        P_num(:, n, :) = P_u;
    end
end
P_num(:, ,N) = 1 + P_num(:, ,N) - sum(P_num,3);

% Markov System
function y = markov(t,p)
    N = length(stages);
    y = zeros(N,1);
    y(1) = -lambda(t,1)*p(1);
    for k=2:N
        y(k) = lambda(t,k-1)*p(k-1) - lambda(t,k)*p(k);
    end
end

% Calculate F(t_n,u_j,i), the prob of one pit being in state i or below
function f = F_(P)
    fprintf('Calculating F\n');
    f = cumsum(P,3); % cumulative sum over the stages
end

% theta(t_n,i): prob of all pits being in stage i or below
function thet = theta_(F)
    fprintf('Calculating Theta\n');
    thet = zeros(nmax,N);
    for n = 1:nmax
        mmax = floor(APD(t(n)));
        thet(n,:) = prod(F(n,1:mmax,:),2);
    end
end

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% pdf(t_n,i): distribution of largest pits within stages
function p = pmf_(theta)
    p = zeros(nmax,N);
    p(:,1) = theta(:,1);
    for i = 2:N
        p(:,i) = theta(:,i)-theta(:,i-1);
    end
end

% pdf(t_n,i): distribution of all pits within stages
function p = all_pmf_(P)
    fprintf('Calculating Histogram\n');
    p = zeros(nmax,N);
    for n = 1:nmax
        mmax = floor(APD(t(n)));
        p(n,:) = sum(P(n,1:mmax,:),2);
    end
end

% MMPD(t_n): mean max pit depth
function m = MMPD_(pmf)
    fprintf('Calculating MMPD\n');
    [blank,S] = ndgrid(t,stages);
    m = sum(S.*pmf,2);
end

function sigma = std_dev_(pmf, MMPD)
    fprintf('Calculating Std Deviation\n');
    [blank,S] = ndgrid(t,stages);
    sigma = sum((S.^2).*pmf,2)-MMPD.^2;
end
end
APPENDIX B

COMPUTABLE DOCUMENT CODE

Below is the code used to generate the Computable Document for the analytical model mentioned in Chapter 6:

(* Michael Workman, mrw39@zips.uakron.edu, 3/08/14 *)

DynamicModule[{
  (* Changeable Parameters *)
  NumberOfStates = 20, tstart = 0.,
  tau = 48., timestep = 1,
  MaximumDepth = 12,
  DepthPerState = 1,

  TimeUnits = {"years", "months"},
  TimeSelector = 2,

  DepthUnits = {"cm", "\[Mu]m", "nm"},
  DepthSelector = 2,

  APDFunc = 1,
  A = 1., \[Mu] = .05, \[Nu] = 2.5, \[Beta] = 1.,
  m = 2.5, c = 5,

  DepthFunc = 1,
  a = 1, b = .2177, eps = .0064,
  a1 = 0, b1 = 0,

  NumPlots = 2, HistPlotTimes = {6, 12, 0, 0, 0},

  (* Plots *)
  APDPPlot = "", PMFPlot = "", MMPDPlot = "",

  (* Temporary Variables for Output Generation *)
  ModelParam,

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(* Equations *)

First, let's define the functions and parameters.

\[ APD[t_] := \] If[APDFunc == 1, \(A/\mu*(1 - e^{(-\mu*t)}) + \nu*t^\beta\), 
\(m*t + c\)];

\[ BinarySearch[list_?(Length[#] > 0 &), val_?NumericQ] := Module[ 
{lo = 1, mid, hi = Length[list], ele},
While[lo <= hi,
If[(ele = list[[mid = Floor[(lo + hi)/2]]]) == val, Return[mid];
If[ele > val, hi = mid - 1, lo = mid + 1];
Return[lo - 1/2]];\]

\[ UpdateFigs[] := DynamicModule[ 
{PitDensities, step = .01, NumberOfPits, BirthTimes, temp, time,
NumberOfTimesteps, GrowthLawDivisionMatrix, P, PMF, F, \[Theta],
MaxPMF, MMPD, \[Sigma]},
{APDPlot = Style["Calculating...", FontSize -> 16, Bold, FontColor -> Red],
PMFPPlot = "", MMPDPlot = ""};

PitDensities = Table[APD[t], {t, tstart, tau, step}];
NumberOfPits = Floor[PitDensities[[Length[PitDensities]]]]; 
BirthTimes = Table[tstart +
step*If[(temp = Floor[BinarySearch[PitDensities, j]]) == 0, 1, 
\(temp\) - 1], {j, NumberOfPits}];

time = Range[tstart, tau, timestep];
NumberOfTimesteps = Length[time];
GrowthLawDivisionMatrix = If[DepthFunc == 1, 
Table[((BirthTimes[[j]] - tstart + eps)/(t - tstart + eps))^b, {t, tstart, tau, timestep}, {j, NumberOfPits}],
Table[((a + 

---

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---
\[
a_1 \times \text{BirthTimes}[[j]] \times ((\text{BirthTimes}[[j]] - \text{tstart} + \text{eps})^{(b + b_1 \times \text{BirthTimes}[[j]])} / ((a + a_1 \times t)^{(b + b_1 \times t)}), \{t, \text{tstart}, \tau, \text{timestep}\}, \{j, \text{NumberOfPits}\})
\]

\[
P = \text{Table}[\begin{cases} 
0, & \text{if } \text{time}[[n]] < \text{BirthTimes}[[j]] \\
\text{GrowthLawDivisionMatrix}[[n, \ j]] \times (1 - \text{GrowthLawDivisionMatrix}[[n, j]])^{(i - 1)}, & \text{if } \text{time}[[n]] > \text{BirthTimes}[[j]] \\
0, & \text{if } i \neq 1, 0, 1 \end{cases}], \\
\{n, \text{NumberOfTimesteps}\}, \{j, \text{NumberOfPits}\}, \{i, \text{NumberOfStates}\};
\]

\[
P[[\text{All}, \text{All}, \text{NumberOfStates}]] = \\
\text{Table}[1 - \text{Total}[P[[n, j, 1 ;; \text{NumberOfPits} - 1]]], \\
\{n, \text{NumberOfTimesteps}\}, \{j, \text{NumberOfPits}\};
\]

\[
\text{PMF} = \text{Table}[ \\
\text{Total}[P[[n, 1 ;; \text{Floor}[\text{APD}[[\text{time}[[n]]]]], i]]], \\
\{n, \text{NumberOfTimesteps}\}, \{i, \text{NumberOfStates}\};
\]

\[
F = \text{Table}[ \\
\text{Total}[P[[n, j, 1 ;; i]]], \\
\{n, \text{NumberOfTimesteps}\}, \{j, \text{NumberOfPits}\}, \{i, \text{NumberOfStates}\};
\]

\[
\theta = \text{Table}\left[ \text{Apply}[\text{Times}, F[[n, 1 ;; \text{Floor}[\text{APD}[[\text{time}[[n]]]]], i]]] \right], \\
\{n, \text{NumberOfTimesteps}\}, \{i, \text{NumberOfStates}\};
\]

\[
\text{MaxPMF} = \text{Table}\left[ \\
\text{If}[i == 1, \theta[[\text{All}, 1]], \theta[[\text{All}, i]] - \theta[[\text{All}, i - 1]]], \\
\{i, \text{NumberOfStates}\}; (*\text{CARE: MaxPMF}[[i,t]] \text{ instead of } t,i*)
\]

\[
\text{MMPD} = \text{Sum}[i * \text{MaxPMF}[[i, \text{All}]], \{i, \text{NumberOfStates}\}];
\]

\[
\sigma = \text{Sqrt}[\text{Sum}[(i^2) * \text{MaxPMF}[[i, \text{All}]], \{i, 1, \text{NumberOfStates}\}] - \\
\text{MMPD}[[\text{All}]]^2];
\]

(* Plot assignment is returned *)

\[
\{
\text{APDPlot} = \\
\text{Plot}[\text{APD}[t], \{t, \text{tstart}, \tau\}, \text{AxesLabel} \rightarrow \{\text{Text}[\text{Style["time (" \leftrightarrow \text{TimeUnits}[[\text{TimeSelector}]] \leftrightarrow ")", \text{FontSize} \rightarrow 12]], \\
\text{Text}[\text{Style["density", \text{FontSize} \rightarrow 12]]}, \\
\text{PlotLabel} \rightarrow \text{Style["Average Pit Density", \text{FontSize} \rightarrow 16, \text{Bold}], \\
\text{ImageSize} \rightarrow 350],
\}
\]

\[
\text{MMPDPlot} =
\]

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ListLinePlot[{Transpose[{time, DepthPerState*(MMPD + \[Sigma])}], Transpose[{time, DepthPerState*MMPD}], Transpose[{time, DepthPerState*(MMPD - \[Sigma])}]}, AxesLabel -> {Text[Style["time (" <> TimeUnits[[TimeSelector]] <> ")", FontSize -> 12]], Text[Style["depth (" <> DepthUnits[[DepthSelector]] <> ")", FontSize -> 12]]}, PlotLabel -> Style["Mean Maximum Pit Depth", FontSize -> 16, Bold], PlotLegends -> LineLegend[ Automatic, {"MMPD+\[Sigma]", "MMPD", "MMPD-\[Sigma]"}], ImageSize -> 350], PMFPlot = ListLinePlot[Table[ Transpose[{Range[0, (NumberOfStates - 1)*DepthPerState, DepthPerState], PMF[[HistPlotTimes[[i]]/timestep - tstart/timestep + 1, All]]}], {i, 1, NumPlots}]], PlotRange -> {{0, MaximumDepth}, {0, Max[Table[APD[HistPlotTimes[[i]]], {i, 1, NumPlots}]]}}, AxesLabel -> {Text[Style["depth (" <> DepthUnits[[DepthSelector]] <> ")", FontSize -> 12]], Text[Style["density", FontSize -> 12]]}, PlotLabel -> Style["Distribution of Pit Depths", FontSize -> 16, Bold], PlotLegends -> LineLegend[Automatic, HistPlotTimes, LegendLabel -> Text["Time (" <> TimeUnits[[TimeSelector]] <> ")"]], ImageSize -> 350], (* Interface Organization *) ModelParam = Column[{ Text[Style["Model Parameters", Bold, FontSize -> 16]], Row[{InputField[Dynamic[MaximumDepth], FieldSize -> 4],}]}]
timestep /= 10, Enabled -> Dynamic[timestep > 0],
ImageSize -> {20, 20},
Button[Text[Style["+", Bold, FontSize -> 16]], timestep *= 10,
ImageSize -> {20, 20}],
Dynamic[Text["Timestep " <> "(" <> TimeUnits[[TimeSelector]] <> ")")]]},
Spacer[2]],
Row[{PopupMenu[Dynamic[TimeSelector],
Table[i -> TimeUnits[[i]], {i, Length[TimeUnits]}], Text["Units of Time"], Spacer[2]],
Row[{PopupMenu[Dynamic[DepthSelector],
Table[i -> DepthUnits[[i]], {i, Length[DepthUnits]}],
ImageSize -> {70, 20}], Text["Units of Depth"], Spacer[2]]}, Alignment -> Left, Spacings -> 1];

InitParam = Column[{Text[Style["Pit Initiation", Bold, FontSize -> 16]],
PopupMenu[
Dynamic[APDFunc], {1 -> 
"APD(t)=\!\!\\\*FractionBox[\(A\\ 1 - \(e\\ -([Mu]t)\\)\), [Mu]]+\!\!\\\*SuperscriptBox[\(\[Nu]t\), \[Beta]]", 2 -> "APD(t)=mt+c"}],
Dynamic[
Column[If[APDFunc == 1, GeneralInitParam, LinearInitParam]]
}, Alignment -> Left, Spacings -> 1];

GeneralInitParam = {Row[{InputField[Dynamic[A], FieldSize -> 4],
Row[{Button[Text[Style["-", Bold, FontSize -> 16]], A -= .1,
ImageSize -> {20, 20}],
Button[Text[Style["+", Bold, FontSize -> 16]], A += .1,
ImageSize -> {20, 20}]]}, Text["A"], Spacer[2]],
Row[{InputField[Dynamic[[Mu]], FieldSize -> 4],
Row[{Button[Text[Style["-", Bold, FontSize -> 16]], [[Mu]] -= .1,
ImageSize -> {20, 20}],
Button[Text[Style["+", Bold, FontSize -> 16]], [[Mu]] += .1,
ImageSize -> {20, 20}]]}, Text["\[Mu]"], Spacer[2]],
Row[{InputField[Dynamic[[Nu]], FieldSize -> 4],
Row[{Button[Text[Style["-", Bold, FontSize -> 16]], [[Nu]] -= .1,
ImageSize -> {20, 20}],
Button[Text[Style["+", Bold, FontSize -> 16]], [[Nu]] += .1,
ImageSize -> {20, 20}]]}, Text["\[Nu]"], Spacer[2]],
Row[{InputField[Dynamic[\[Beta]], FieldSize -> 4],
Row[{Button[Text[Style["-", Bold, FontSize -> 16]], \[Beta] -= .1,
ImageSize -> {20, 20}],
Button[Text[Style["+", Bold, FontSize -> 16]], \[Beta] += .1,
ImageSize -> {20, 20}]]}, Text["\[Beta]"], Spacer[2]]}, Alignment -> Left, Spacings -> 1];
Row[{InputField[Dynamic[\[Beta]], FieldSize -> 4],
    Row[{Button[
        Text[Style["-", Bold, FontSize -> 16]], \[Beta] -= .1,
        ImageSize -> {20, 20},
        Button[Text[Style["+", Bold, FontSize -> 16]], \[Beta] += .1,
        ImageSize -> {20, 20}]], Text["\[Beta]"], Spacer[2]]};

LinearInitParam = {Row[{InputField[Dynamic[m], FieldSize -> 4],
    Row[{Button[Text[Style["-", Bold, FontSize -> 16]], m -= .1,
        Enabled -> Dynamic[m > 0], ImageSize -> {20, 20},
        Button[Text[Style["+", Bold, FontSize -> 16]], m += .1,
        ImageSize -> {20, 20}]], Text["m"], Spacer[2]],
    Row[{InputField[Dynamic[c], FieldSize -> 4],
        Row[{Button[Text[Style["-", Bold, FontSize -> 16]], c -= .1,
            ImageSize -> {20, 20},
            Button[Text[Style["+", Bold, FontSize -> 16]], c += .1,
            ImageSize -> {20, 20}]]}, Text["c"], Spacer[2]]];

GrowthParam = Column[
    Text[Style["Pit Propagation", Bold, FontSize -> 16]],
    PopupMenu[
        Dynamic[DepthFunc], {1 ->
            "D(t;u)=a(t-u+\[Epsilon]\[SuperscriptBox[\(\(\), b)\)]]",
            2 -> "D(t;u)=(a+\[SubscriptBox[\(a\), 1]) t)(t-u+\[Epsilon]\[SuperscriptBox[\(\(\), b +\[SubscriptBox[\(b\), 1]] t)\])"}],
        Dynamic[
            Column[If[DepthFunc == 1, ConstGrowthParam, LinearGrowthParam]]
        }, Alignment -> Left, Spacings -> 1];

ConstGrowthParam = {Row[{InputField[Dynamic[a], FieldSize -> 4],
    Row[{Button[Text[Style["-", Bold, FontSize -> 16]], a -= .1,
        ImageSize -> {20, 20},
        Button[Text[Style["+", Bold, FontSize -> 16]], a += .1,
        ImageSize -> {20, 20}]], Text["a"], Spacer[2]],
    Row[{InputField[Dynamic[b], FieldSize -> 4],
        Row[{Button[Text[Style["-", Bold, FontSize -> 16]], b -= .1,
            Enabled -> Dynamic[b > 0], ImageSize -> {20, 20},
            Button[Text[Style["+", Bold, FontSize -> 16]], b += .1,
            ImageSize -> {20, 20}]], Text["b"], Spacer[2]],
        Row[{InputField[Dynamic[\[Epsilon], (\[Epsilon] = Abs[\[#]]) &], FieldSize -> 4],
            Row[{Button[Text[Style["-", Bold, FontSize -> 16]], \[Epsilon] -= .1,
                Enabled -> Dynamic[\[Epsilon] > 0], ImageSize -> {20, 20},
                Button[Text[Style["+", Bold, FontSize -> 16]], \[Epsilon] += .1,
                ImageSize -> {20, 20}]], Text["\[Epsilon]"], Spacer[2]]};

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LinearGrowthParam = {
  Row[{InputField[Dynamic[a], FieldSize -> 4],
    Row[{Button[Text[Style["-", Bold, FontSize -> 16]], a -= .1,
          ImageSize -> {20, 20}],
          Button[Text[Style["+", Bold, FontSize -> 16]], a += .1,
                ImageSize -> {20, 20}], Text["a"], Spacer[2]],
    Row[{InputField[Dynamic[a1], FieldSize -> 4],
      Row[{Button[Text[Style["-", Bold, FontSize -> 16]], a1 -= .1,
            ImageSize -> {20, 20}],
            Button[Text[Style["+", Bold, FontSize -> 16]], a1 += .1,
                  ImageSize -> {20, 20}], Text["a_\textsubscript{1}"], Spacer[2]],
      Row[{InputField[Dynamic[b], FieldSize -> 4],
        Row[{Button[Text[Style["-", Bold, FontSize -> 16]], b -= .1,
                Enabled->Dynamic[b>0], ImageSize -> {20, 20}],
                Button[Text[Style["+", Bold, FontSize -> 16]], b += .1,
                      ImageSize -> {20, 20}], Text["b"], Spacer[2]],
        Row[{InputField[Dynamic[b1], FieldSize -> 4],
          Row[{Button[Text[Style["-", Bold, FontSize -> 16]], b1 -= .1,
                ImageSize -> {20, 20}],
                Button[Text[Style["+", Bold, FontSize -> 16]], b1 += .1,
                      ImageSize -> {20, 20}], Text["b_\textsubscript{1}"], Spacer[2]],
          Row[{InputField[Dynamic[eps, (eps = Abs[#]) &], FieldSize -> 4],
            Row[{Button[Text[Style["-", Bold, FontSize -> 16]], eps -= .1,
            Enabled -> Dynamic[eps > 0], ImageSize -> {20, 20}],
            Button[Text[Style["+", Bold, FontSize -> 16]], eps += .1,
                      ImageSize -> {20, 20}], Text["\textepsilon"]}, Spacer[2]]
        }]
    }]
  
DistParam = Column[{
  Text[Style["Distribution Settings", Bold, FontSize -> 16]],
  Row[{Text["Number of Plots:"],
        InputField[
          Dynamic[NumPlots, (NumPlots = Max[1, Min[5, Round[#]]]) &],
          FieldSize -> 2]}, Spacer[2]],
  Row[{Dynamic[
        Text["Plot Times " <> "(" <> TimeUnits[[TimeSelector]] <> ")": "],
       Spacer[2]]
}];
Dynamic[
  Column[Table[
    With[{{i = i},
      InputField[
        Dynamic[
          HistPlotTimes[[
            i]], (HistPlotTimes[[i]] =
            Min[Max[Round[#1, timestep], tstart], tau]) &],
          FieldSize -> 2]}, {i, NumPlots}]]]]
  }, Alignment -> Left, Spacings -> 1];

(* Creation of Actual Interface *)
Row[
  Column[{ModelParam, InitParam, GrowthParam, DistParam},
    Spacings -> 3,
    Dividers -> Center],
  Column[{Button[Text[Style["Update Figures", Bold, FontSize -> 16]],
      UpdateFigs[], Method -> "Queued", ImageSize -> {320, 40}],
      Dynamic[APDPlot], Dynamic[MMPDPlot], Dynamic[PMFPlot]},
    Spacings -> 3],
  Spacer[30],
  ImageMargins -> 30
]
]