ACID MINE DRAINAGE REMEDIATION UTILIZING IRON-OXIDIZING
BACTERIA

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ABSTRACT

Acid mine drainage is pollution that occurs when water trapped in abandoned coal mines leaks out and pollutes the local water systems. One of the most abundant metals found in acid mine drainage is iron. Iron often precipitates out of the system naturally in the form of iron(III) hydroxide, leading to a decrease in fluid pH. Iron oxidizing bacteria can promote this reaction process, assisting in the removal of Fe(II) ions from the acid mine drainage. The increase in acidity can be detrimental to surrounding wildlife. The purpose of this paper is to develop a model that includes the hyrodynamics and reactive transport of ions in the system. The model predictions will be compared to local field data and those found in the literature. In addition the model analyzes the precipitation of the iron(III) hydroxide crust as a function of space and time. Several parameters are varied to observe predictions made by the model with different physical circumstances. Forcing low concentrations of oxygen in the system produces slower the rate of iron(III) hydroxide crust growth. Increasing the angle of inclination while holding the flow rate fixed causes a very small decrease in iron(III) hydroxide crust growth. Decreasing the flow rate of the system while maintaining a fixed angle of inclination to simulate a thinning of the liquid layer produces a slower iron(III) hydroxide crust growth rate. When the angle of inclination
is varied with fixed fluid film thickness, as the angle of inclination increases, iron(III) hydroxide crust growth decreases. When the forward rate for surface reactions and the reverse rate for bulk reactions are increased, both decreased the rate of iron(III) hydroxide crust production. When the reverse rate for surface reactions and the forward rate for bulk reactions are increased, they increase iron(III) hydroxide crust growth rate. An increase in iron oxidizing bacteria can increase the oxidation of Fe(II). Therefore, an increase in the abundance of iron oxidizing bacteria can increase the rate of iron(III) hydroxide crust growth.
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CHAPTER I
INTRODUCTION

Abandoned mines are a source of acid mine drainage (AMD) that can contaminate local environments and pollute water systems. AMD is a liquid waste that contains metals in the form of ions such as $\text{Fe}^{2+}$, $\text{Mn}^{2+}$, $\text{Al}^{3+}$, $\text{Cu}^{2+}$, $\text{Pb}^{2+}$, $\text{Cd}^{2+}$, and $\text{Zn}^{2+}$ [1]. Acidic mine drainage occurs when metal sulfides come into contact with oxygenated water. This, in turn, causes sulfuric acid production, increasing water acidity [2]. When mines are in active use, the water tables within them are controlled by water pumps, keeping the acid mine drainage production to a minimum. However, when mines are abandoned, the water pumps are shut off, causing a rise in the water tables. The water level increase can place a substantial amount of pressure on plugs that seal the mine, allowing for leaks and water eruptions to occur. AMD can then escape the mine and enter surrounding areas [3]. One of the abundant constituents of AMD is iron, which occurs in abandoned coal mines containing pyrite [2].

Because of its adverse effect on the environment, it is important to develop methods to mitigate AMD contamination. There are two major categories of AMD treatment methods in use today: active treatment and passive treatment. The objective for both forms of treatment is to remove unwanted ions and restore pH to neutral levels. Active treatment is a method that has proven to work well. However, the cost
of active treatment systems can be large because it involves the use of chemicals, electricity, and workers [2]. Active methods also present the problem of the disposal of sludge waste material produced from the treatment process [4].

Due to the isolated location of many AMD affected sites, passive treatment is currently the only viable option. Passive treatment methods do not require electrical energy input, but do require a larger land surface area than active treatment methods [5]. Although active treatment systems work well for AMD cleanup, passive treatment methods have recently become more attractive.

Passive treatment methods involve the mitigation of AMD via the introduction of limestone or wetlands. Another possible approach involves iron-removing vegetation or iron-oxidizing bacteria to the site affected by AMD. The process of passive AMD treatment involves the following reactions:

\[
\begin{align*}
\text{Fe}^{2+} + 0.25 \text{O}_2 + \text{H}^+ & \rightarrow \text{Fe}^{3+} + 0.5 \text{H}_2\text{O}, \quad (1.1) \\
\text{Fe}^{3+} + 3 \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 3 \text{H}^+. \quad (1.2)
\end{align*}
\]

Equation (1.1) involves the oxidation of Fe(II), and the reaction rate can be governed by the Fe(II) oxidizing bacteria in low pH systems [6]. Equation (1.2) is the precipitation of iron hydroxide, thus, the removal of iron from the liquid AMD. The objective is to oxidize the iron in Equation (1.1) to promote precipitation and removal of iron in the form of iron-hydroxide in Equation (1.2). This natural method of contaminant removal requires little maintenance by humans, making passive treatment methods much less expensive than active treatment methods.
Because of the price advantages passive treatment methods have over active treatment methods, we will focus on the passive approach. Our AMD system of interest is located in Mahoning County, Ohio and is nicknamed the “Mushroom Farm”. We will create a mathematical model of a passive treatment system relevant to this site. The objective is that this model will not only be applicable to the Mushroom Farm, but also will provide insight to similar systems.

Streams and water systems that experience drastically lowered pH and higher Fe(II) concentrations due to AMD contamination lose much of their naturally occurring wildlife. Likewise, the loss of use of these streams and ponds can negatively affect land-dwelling wildlife that rely on the stream or pond as a source of food or water. Treatment of AMD using an effective passive approach is important because we want to make the cleanup of these sites more manageable. Lower costs and reliable results may increase the number of sites that receive treatment, and decrease the overall negative effects on nature.

Precipitation of iron can occur at high pH ranges as found by Kirby et al. [7]. They found that when pH is greater than 5, it is not necessary to utilize iron-oxidizing bacteria to promote iron oxidation (Equation (1.1)) because it is controlled by abiotic factors. Burke and Banwart [1] created a model for abiotic oxidation of iron using extrapolated literature values to determine abiotic empirical rate laws for iron oxidation. They created a steady state model that would represent a single, completely mixed, reactor in the surface-catalyzed oxidation of iron. Burke and Banwart’s model suggested that Fe(II)_{aq} removal can occur if the AMD is spread
over a sufficiently large surface area. They found in their study that iron removal efficiency decreases with decreasing pH for abiotic systems. This correlation implies that a passive abiotic approach to Fe removal in AMD systems is not appropriate for those with excessively low pH. However, because the modelling was done for a completely mixed system, no considerations for concentration gradients in the tank were taken.

In another study, Kirby et al. [7] developed the first model of passive treatment systems to consider iron oxidation kinetics. In this experiment, Stella II™ software used seven variables to develop a model based on the combination of abiotic and biological rate laws from the literature. The seven variables included in the study were: initial iron concentration, pH (2.8 to 6.8), temperature, concentration of iron-oxidizing bacteria, $O_2$ concentration, flow rate, and pond volume. The research by Kirby et al. found that at a pH range from 2.8 to about 5, the major mechanism for Fe(II) oxidation is biological, because the abiotic oxidation rate is slow within this pH range. When pH ranged from 2.8 to 6.8 the results indicate that abiotic factors control Fe(II) oxidation rates. At pH greater than 6.4, the oxidation rate of Fe(II) appears to be independent of pH. Finally, they developed a model for rate of change in concentration of Fe(II) as a function of biological effects and abiotic effects on overall Fe(II) concentration over time. The model development was achieved by combining reaction rate models from previously developed models by Pesic et al. [8] and Stumm and Morgan [9]. However, the study done by Kirby et al. took no consideration for incomplete mixing. The research done by Kirby et al. is important to
our research because it provides guidelines for when microbial or abiotic factors are controlling oxidation rates of Fe(II). For our study, the Mushroom Farm is an acidic system with pH ranging from 2.8 to 4.2, and microbial impact on oxidation rates are significant [10].

Since microbial communities have an impact at the site of our study, a discussion of the nature of biofilms is necessary. Donlan [11] defined a biofilm as microbial cells that are associated and not removable with gentle rinsing. Bacteria in a biofilm are enclosed in an extracellular polymeric substance which has a varying composition depending on the type of biofilm. These types of bacteria differ from planktonic (free-floating) types in their metabolism, and can be found on a wide variety of surfaces. Donlan also noted that the interface between a solid and a liquid with laminar flow forms the ideal situation for attachment and growth of biofilms. Because the iron hydroxide crust forms a solid-liquid interface, and we know that there are iron-oxidizing bacteria present in the Mushroom Farm iron mound, it is not unreasonable to believe that the bacteria are a part of a matrix much like a biofilm that is located on the top of the iron-hydroxide crust. Furthermore, the system we are modelling is a thin-film laminar flow system, which is ideal for biofilm growth. This justifies our assumption that the iron-oxidizing bacteria are located solely at the solid-liquid interface.

There are two main categories for the study of biofilms. One is a discrete approach, which considers the interactions at a local level, meaning interactions between individual bacteria. The other method is a continuum approach which assumes that the variation and location of individual bacteria average into a continuum body.
Alpkvist et al. [12] derived a biofilm growth model utilizing a hybrid of the continuum and discrete approach. They were able to create a model that retained the benefits of both discrete and continuum approaches and provided realistic descriptions of biofilms in two and three dimensions. The research done by Alpkvist et al. mainly focuses on bacterial behavior and growth in a biofilm. We will be using a continuum approach to account for bacterial location. This allows for ease in mathematical modelling because shape, size, and general location of individual bacteria can be ignored. Because our model deals with a large area, it is not necessary to use the discrete description of bacteria, justifying the use of the continuum approach.

Figure 1.1: A schematic of the proposed geometry with the bacteria-populated portion of the crust treated as part of the AMD fluid domain.

Burgos et al. [13] developed a reaction-based biogeochemical model for the ki-
netics of reductive dissolution of hematite (α-Fe₂O₃) using the bacteria *Shewanella putrefaciens* strain CN32 using a reaction-based software called BIOGEOCHEM. They found that independently-determined reaction-based rate formulations in other experimental systems agreed. This implies that simulation and prediction of complex biogeochemical systems may eventually be performed using reaction-based models. However, reaction-based models are not always easy to develop because reaction networks and mechanisms are sometimes difficult to determine.

Kirby et al. [14] used a continuously-stirred reaction tank to determine Fe(II) oxidation rates in AMD and alkaline mine drainage. Variables such as dissolved O₂, Fe(II) concentration, and pH were controlled, while other factors that may impact Fe(II) oxidation were ignored. The complexities of field settings caused this study to be unable to develop a single rate law to predict field rates based solely on the chosen variables. It was recommended to include additional variables into the model for future work. Development of a composite rate law or combination of rate laws, rather than the single rate law for the entire system was also recommended.

Several studies have evaluated the oxidation rates of different iron oxidizing bacteria using bioreactor experiments. Johnson et al. [3] used a packed-bed bioreactor with porous glass beads as the support matrix for the biofilm that contained iron-oxidizing bacteria. Their study found that native acidophilic bacteria can be utilized in packed-bed bioreactors to oxidize iron, as well as promote other chemical changes in AMD which are necessary for remediation. The study also revealed that the Fe(OH)₃ precipitate used to remove iron from solution tends to form a solid barrier between
the limestone intended to neutralize the AMD, and the hydrogen ions in the mine drainage. This process is called “armoring”. To prevent armoring in our model, we strive to precipitate the maximum quantity of Fe(II) before the placement of a limestone bed to neutralize water.

Ozkaya et al. [15] also modelled iron oxidation, however, they used a fluidized bed reactor (FBR) rather than a packed-bed reactor. Fe(III) concentration in FBR were successfully predicted using the artificial neural network-back-propagation algorithm (ANN-HEAP). Neculita et al. [16] investigated sulfate-reducing passive bioreactors for treatment of AMD. In their study, Neculita et al. observed two different bioreactors that had two different hydraulic retention times (HRT’s) of 10 days and the other 7.3 days. The results indicated that the two bioreactors under study successfully removed sulfate along with metals dissolved in the drainage. The quality of treatment using the 10 HRT bioreactor was greater than the 7.3 HRT bioreactor. However, they also found that the 10 HRT bioreactor reduced the permeability and porosity of the reactive mixture which could cause a lower efficiency of the 10 HRT machine in the long run over the 7.3 HRT bioreactor.

Senko et al. [2] studied two AMD sites, Gum Boot and Fridays-2, located in northern Pennsylvania. They found efficient precipitation of Fe(III) at the Gum Boot site, and little removal of Fe(II) at Fridays-2 without human interference. Sampling of the sites indicated that the greatest abundance of iron-oxidizing bacteria were located along the AMD flow path. These locations demonstrated the greatest Fe(II) removal as well and contained the largest amount of dissolved oxygen. Senko et. al
found evidence for the presence of bacterial lineages capable of iron oxidation at these sites. A few major differences between the Gum Boot and Fridays-2 systems were the greater flow rate and lower abundance of iron-oxidizing bacteria at Fridays-2. These results suggest that the rates of iron oxidation depend on the abundance of iron-oxidizing bacteria. Senko et. al suggest that the availability of dissolved oxygen may act as a control on the population size and activity of iron-oxidizing bacteria in AMD systems. The relationship between the abundance of iron-oxidizing bacteria

![Graph showing the relationship between the abundance of iron-oxidizing bacteria and rate of Fe(II) oxidized.](image)

Figure 1.2: The relationship between the abundance of iron-oxidizing bacteria and rate of Fe(II) oxidized.
and the amount of Fe(II) oxidized for Gum Boot, Fridays-2 and an additional site studied by Senko [10] can be seen in Figure 1.2. Figure 1.2 indicates that there is a positive correlation between the abundance of iron-oxidizing bacteria and the forward reaction rate for Fe(II) oxidation.

Mathematical models of the oxidation of Fe(II) in AMD systems have been studied. Kirby et al. [7] developed a model for the change in Fe(III) as a function of abiotic and biological processes for iron oxidation. Their model sets the time derivative of Fe(III) concentration equal to the rate law for abiotic oxidation of Fe(II) summed with the rate law for Fe(II) oxidation when oxidation is performed by Acidithiobacillus ferrooxidans bacteria. The equation is

\[ \frac{dF_{\text{e}^{3+}}}{dt} = -r_{\text{abiotic}} - r_{\text{biotic}}, \]  

where \( r_{\text{abiotic}} \) is the rate law due to abiotic factors and \( r_{\text{biotic}} \) is the rate law due to biological factors.

Burgos et al. [13] studied empirical rate laws. Changes in concentrations of ionic species were represented by

\[ \frac{dC_i}{dt} = \sum_{k=1}^{n} (\nu_{ik} - \mu_{ik}) R_k, \]  

where \( \nu_{ik} \) is the reaction stoichiometry of the \( i \)th species in the \( k \)th reaction associated with the products, \( \mu_{ik} \) is the reaction stoichiometry of the \( i \)th species in the \( k \)th reaction associated with the products, and \( R_k \) is the rate of the \( k \)th reaction. The advantage to utilizing a reaction based model is that the rate formulas can be applied
to a variety of environmental conditions. While a summation is an efficient way of modelling chemical kinetics of a system, it is not often a practical approach.

Kirby and Cravotta [17] developed a model to calculate the net acidity of an AMD system. Acidity is the ability of a chemical species to react with a strong base and alkalinity is the ability of a chemical species to react with a strong acid. Net acidity is defined as the difference between acidity and alkalinity. The net acidity calculation utilized by Kirby and Cravotta is

$$a_{H^+} = 50 \left[1000(10^{-pH}) + \frac{2}{56}Fe^{II} + \frac{3}{56}Fe^{III} + \frac{2}{55}Mn + \frac{3}{27}Al\right],$$  \hspace{1cm} (1.5)

where $a_{H^+}$ is net acidity and $Fe^{II}$, $Fe^{III}$, $Mn$, and $Al$ are concentrations of iron(II), iron(III), manganese, and aluminum respectively in mg/L. The advantage to using Equation (1.5) is that the modelling of a system does not solely depend on pH. This method for calculating net acidity tends to underestimate the acidity due to hydrogen ions and overestimate the acidity from Fe(III) and Al(III).

In 2009, Kirby et al. [5] expanded upon the model Kirby developed in 1999 and obtained the Fe(II) oxidation rate,

$$\frac{d[Fe^{II}]}{dt} = -\frac{k[Fe^{II}][O_2]}{(a_{H^+})^2},$$  \hspace{1cm} (1.6)

where chemical species encased in [ ] are concentrations in mol · kg$^{-1}$, and $a_{H^+}$ is the net acidity, obtained in the same manner as in Equation (1.5). This equation was created because when dissolved CO$_2$ is degassed toward equilibrium with the atmosphere, the pH of the system increases. This pH increase is important in the
treatment of net-alkaline mine drainage because it causes the oxidation rate of Fe(II) to increase.

Ardejani et al. modelled the effect of oxygen availability on the oxidation of pyrite in areas contaminated by AMD from abandoned coal mines in northeast Iran [18]. Oxygen availability is considered to determine if the oxidation of pyrite takes place. Ardejani et al. consider gaseous diffusion to be the only method of oxygen transport to the surface of pyrite. The only method of oxygen consumption in the model is via pyrite oxidation. The governing equation for oxygen transport in their model is

$$\Phi_a \frac{\partial}{\partial t} (u) = D_e \frac{\partial^2 u}{\partial z^2} - Ku.$$  

Here, $\Phi_a$ is the air-filled porosity of the AMD, $u$ is the oxygen concentration within the pore space, and $D_e$ is the effective diffusion of oxygen within the AMD. The depth of the AMD liquid is $z$ and the first order rate constant for oxygen concentration is $K$. The model developed by Ardenjani et al. found that an increase in the diffusion coefficient for oxygen produced an increase in the concentration of oxygen at low depths of AMD. The increase in oxygen concentration causes an increase in the oxidation of pyrite. The model in this paper includes the transport of oxygen as well as other ions. The model we develop considers the impact of other ions in the system on the concentration of oxygen.

In this paper we create a one-dimensional model of iron(III) hydroxide crust growth as a function of concentration of iron oxidizing bacteria in the system. Only the iron contaminant will be taken into account for removal, ignoring removal of other
ions present. Ultimately, it may be possible to add a vegetated region to remove the other metal ions (Figure (1.3)), however, the main focus will remain on the removal of dissolved iron. In order to remove Fe(II), we will utilize a sheet-flow system, which is simply a thin layer of liquid AMD flowing downhill over relatively smooth land surface. A sheet-flow regime will allow for efficient diffusion of O₂ from the surrounding air to the liquid, which is necessary since aerobic iron-oxidizing bacteria consume it, and oxygen is a reactant in the oxidation of Fe(II) (Equation (1.1)).

![Diagram of AMD treatment system]

Figure 1.3: A schematic diagram of treatment system utilizing sheet-flow, vegetation, and a limestone bed for removal of dissolved metals and neutralization of AMD

The Mushroom Farm AMD layer is only 0.5 - 1 cm thick, covering an area of approximately 45 m² [10]. When the maximum amount of iron is removed, by Equations (1.1) and (1.2), it is clear that there will be an increase in proton concentration in the already acidic mine drainage. To prevent armoring, the [H⁺] will then be neutralized by placing a limestone bed in the path of the AMD flow after all possible Fe(II) is removed. Carbonate-containing rocks, such as limestone, dissolve upon
contact of acidic liquids and CO$_3^{2-}$ neutralizes the acid [2]. A schematic diagram of the proposed treatment system is shown in Figure (1.3).

For our model, we will assume the bacteria to be located only on the surface of the crust and treat it as if it is part of the liquid medium and not a separate porous entity. A diagram of a cross-section of AMD flow is shown in Figure (1.1). In the figure, we define the location of the crust surface, $\hat{z} = \hat{s}(\hat{x}, \hat{t})$, to be located strictly below the bacteria. The location of the top of the air-liquid interface is defined as $\hat{\hat{z}} = \hat{h}(\hat{x}, \hat{t})$. The distance from the top of the crust to the air-liquid interface has a distance that is estimated to be no larger than 2 cm. The solution of the thin liquid film problem and the reactive transport problem are uncoupled by holding iron(III) hydroxide density constant and neglecting buoyancy driven flow due to temperature gradients and concentration gradients.

The approach to our model is similar to previous studies in that we will be modelling the change in concentration of Fe(II) as a function of iron-oxidizing bacteria concentration. Our model differs from others because our study we will be tracking the growth of Fe(OH)$_3$ crust growth as a function of bacteria concentration, with consideration for other variables such as pH, concentration of other ions, pressure, etc. Important limitations of the proposed model include the following:

- Bacteria are located only on the surface of the crust.
- The model is one-dimensional in space.
- Flow is laminar.
- The model is meant to only remove iron, and no other metal ions.
• Density of iron(III) hydroxide crust is constant throughout and the crust is non-porous.

• Thermal effects are not considered in the model.

• The distance over which the AMD flows is far greater than the thickness of crust.

• The rate of iron(III) hydroxide crust growth is slow.

• Temperature effects on bacteria activity are not considered.

The next step in improving the model may involve creating a higher-dimensional problem than the one-dimensional model presented in this study. This will allow for more accurate representation of the system. Also, we may attempt to model the removal of other ions.

The remainder of this document is organized in the following manner. In Section II, the formulation of the mathematical model will be developed. Techniques such as non-dimensionalization and the method of asymptotic expansion will be utilized in the analysis of the governing equations in Section III. The solutions and results to this problem will be presented in Section IV, followed by conclusions and suggestions for future work in Section V.
CHAPTER II
IRON HYDROXIDE CRUST GROWTH MODEL

In this chapter the model for iron hydroxide crust growth is developed and studied. Development of the hydrodynamic system is performed first, followed by the reactive transport system. For the hydrodynamics, equations for fluid mechanics are characterized by a thin-film flow system. The reactive transport of ionic species are described by a series of advection-diffusion equations.

2.1 Hydrodynamic Model

Figure 1.1 is a schematic of the proposed geometry with the bacteria-populated portion of the crust treated as part of the AMD fluid domain. We define all components with hats as dimensional variables. Let the \( \hat{x} \)-axis be the plane inclined at an angle \( \theta \) with respect to the surrounding terrain. The \( \hat{z} \)-axis is normal to the \( \hat{x} \)-axis as shown in Figure 1.1. The air-liquid interface is labeled as \( \hat{z} = \hat{h}(\hat{x}, \hat{t}) \), while the liquid-crust interface is assigned \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \).

There is no evidence that indicates the growth of iron hydroxide covered by deep water [10]. The sheet flow is at most 2 cm deep for the Mushroom Farm, thus, the upper bound for the distance from \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) to \( \hat{z} = \hat{h}(\hat{x}, \hat{t}) \) is between 1 and 2 cm.
Temperature for this model is held constant and its value can be set according
to the time of year under consideration. Therefore, no account is taken for thermal
transport in the model. Density is held constant, which allows us to ignore buoyancy
driven flow. The flow under consideration is two-dimensional because the variations
in the direction transverse to the flow direction are ignored. The liquid in this model
is viscous and incompressible.

The laws of conservation of mass and momentum are necessary to describe
the dynamics of flow. Conservation of mass for the model is characterized by the
continuity equation

$$\hat{u}_{\hat{x}} + \hat{w}_{\hat{z}} = 0, \quad (2.1)$$

where $\hat{u}$ is the velocity component in the $\hat{x}$-direction and $\hat{w}$ is the velocity component
in the $\hat{z}$-direction. Also, all subscripts represent the partial derivative with respect
to the subscripted variable unless otherwise specified. The Navier-Stokes equations
that describe the conservation of linear momentum are

$$\hat{u}_t + \hat{u}\hat{u}_{\hat{x}} + \hat{w}\hat{u}_{\hat{z}} = -\frac{1}{\rho}\hat{p}_{\hat{x}} + \nu(\hat{u}_{\hat{z}\hat{z}} + \hat{u}_{\hat{z}\hat{z}}) + g \sin \theta, \quad (2.2)$$

$$\hat{w}_t + \hat{u}\hat{w}_{\hat{x}} + \hat{w}\hat{w}_{\hat{z}} = -\frac{1}{\rho}\hat{p}_{\hat{z}} + \nu(\hat{w}_{\hat{z}\hat{z}} + \hat{w}_{\hat{z}\hat{z}}) - g \cos \theta, \quad (2.3)$$

where $\rho$ is the density of the AMD liquid, $g$ is gravity, $\hat{p}$ is fluid pressure, and $\nu$ is
the kinematic viscosity of the AMD liquid.

The surface $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ is a fixed solid. For this reason, a no-slip condition is
applied at the crust-liquid interface,

$$\hat{u} = \hat{w} = 0. \quad (2.4)$$
The air-liquid interface, \( \dot{z} = \dot{h}(\dot{x}, \dot{t}) \), is in motion and is a free boundary. The conditions that determine the motion of the boundary are: a kinematic condition, no shear stress in the tangential direction and a dynamic normal force balance equation. The air-liquid interface surface is described by the equation

\[
G(\dot{x}, \dot{z}, \dot{t}) = \dot{z} - \dot{h}(\dot{x}, \dot{t}) = 0, \tag{2.5}
\]

where the normal vector to this surface is given by

\[
\frac{\nabla G}{\| \nabla G \|} = \left\langle -\dot{h}_x, 1 \right\rangle \sqrt{1 + \dot{h}_x^2}. \tag{2.6}
\]

In Equation (2.5) if we have \( G(\dot{x}, \dot{z}, \dot{t}) = 0 \), then this implies that the derivative of \( G(\dot{x}, \dot{z}, \dot{t}) \) with respect to \( \dot{t} \) leads to

\[
\frac{\partial G(\dot{x}(\dot{t}), \dot{z}(\dot{t}), \dot{t})}{\partial \dot{t}} = -\frac{\partial \dot{h}}{\partial \dot{x}} \ddot{u} + \ddot{w} - \frac{\partial \dot{h}}{\partial \dot{t}} = 0, \tag{2.7}
\]

which simplifies to the kinematic condition,

\[
\dot{h}_t = \ddot{w} - \dot{u} \dot{h}_x. \tag{2.8}
\]

The following equation,

\[
2\dot{h}_x(-\dot{u}_x + \dot{w}_z) + (1 - \dot{h}_x^2)(\dot{u}_z + \dot{w}_x) = 0, \tag{2.9}
\]

provides us with an expression for no shear stress in the direction tangent to the surface \( \dot{z} = \dot{h}(\dot{x}, \dot{t}) \). The force in the direction normal to surface \( \dot{z} = \dot{h}(\dot{x}, \dot{t}) \) is

\[
-p + \frac{\mu \left[ \dot{u}_x \dot{h}_x^2 - \dot{h}_x(\dot{u}_z + \dot{w}_x) \right] + \dot{w}_z}{1 + \dot{h}_x^2} = \sigma \frac{\dot{h}_{xx}}{(1 + \dot{h}_x^2)^2}. \tag{2.10}
\]
where \( \sigma \) is the surface tension of the AMD liquid and \( \hat{p} \) is the atmospheric pressure.

The dynamics of this system are chemically driven. Next, we develop the reactive transport portion of the model.

2.2 Reactive Transport Model

The AMD fluid is in an open atmosphere and contains ions shown in Reaction 1.1. Other ions are present but are not under consideration for this model. The reaction system is based on the oxidation of Fe(II) followed by its subsequent precipitation in the form of Fe(OH)₃. In this model, the precipitation of Fe(II) to Fe(III) is the rate determining step in the sequence of Reactions 1.1 and 1.2. Hence, the reaction system is based on four chemical species. Reaction 1.1 is treated as a bulk reaction as follows:

\[
\text{Fe}^{2+} + 0.25 \text{O}_2 + \text{H}^+ \xrightleftharpoons[k_{-1}]{k_1} \text{Fe}^{3+} + 0.5 \text{H}_2\text{O}. \tag{2.11}
\]

Here, \( k_1 \) is the forward reaction rate and \( k_{-1} \) is the backward reaction rate, where the forward reaction rate is dependent on the concentration of iron-oxidizing bacteria. Therefore, the rate law for the bulk reaction system is

\[
\hat{I} = -k_1 \hat{C}_{Fe^{2+}} \hat{C}_\text{O}_2 \hat{C}_\text{H}^+ + k_{-1} \hat{C}_{Fe^{3+}}. \tag{2.12}
\]

The following are governing equations for concentration of significant ions for bulk reactions:
\[ \frac{\partial \hat{C}_{H^+}}{\partial t} + \hat{u} \frac{\partial \hat{C}_{H^+}}{\partial \hat{x}} + \hat{w} \frac{\partial \hat{C}_{H^+}}{\partial \hat{z}} = \nabla \cdot \left( D_{H^+} \nabla \hat{C}_{H^+} \right) + \hat{I}, \]  
(2.13)

\[ \frac{\partial \hat{C}_{O_2}}{\partial t} + \hat{u} \frac{\partial \hat{C}_{O_2}}{\partial \hat{x}} + \hat{w} \frac{\partial \hat{C}_{O_2}}{\partial \hat{z}} = \nabla \cdot \left( D_{O_2} \nabla \hat{C}_{O_2} \right) + \hat{I}, \]  
(2.14)

\[ \frac{\partial \hat{C}_{Fe^{2+}}}{\partial t} + \hat{u} \frac{\partial \hat{C}_{Fe^{2+}}}{\partial \hat{x}} + \hat{w} \frac{\partial \hat{C}_{Fe^{2+}}}{\partial \hat{z}} = \nabla \cdot \left( D_{Fe^{2+}} \nabla \hat{C}_{Fe^{2+}} \right) + \hat{I}, \]  
(2.15)

\[ \frac{\partial \hat{C}_{Fe^{3+}}}{\partial t} + \hat{u} \frac{\partial \hat{C}_{Fe^{3+}}}{\partial \hat{x}} + \hat{w} \frac{\partial \hat{C}_{Fe^{3+}}}{\partial \hat{z}} = \nabla \cdot \left( D_{Fe^{3+}} \nabla \hat{C}_{Fe^{3+}} \right) - \hat{I}. \]  
(2.16)

In these equations, \( D_i \) is the mass diffusivity of the \( i \)th chemical species.

Similarly, \( \hat{C}_i \) represents the concentration of the \( i \)th chemical species.

All of the reaction transport Equations (2.13)-(2.16) require boundary conditions at both interfaces. At the air-liquid interface, \( \hat{z} = \hat{h}(\hat{x}, \hat{t}) \), there are two different types of conditions. The concentration of oxygen, \( \hat{C}_{O_2} \), is a volatile gas. Therefore, oxygen can both leave and enter the system at \( \hat{z} = \hat{h}(\hat{x}, \hat{t}) \), and the boundary condition for \( \hat{C}_{O_2} \) is

\[ D_{O_2} \nabla \hat{C}_{O_2} \cdot \vec{n} = K_{MT} \left[ K_H P_{O_2} - \hat{C}_{O_2} \right]. \]  
(2.17)

Here, \( K_{MT} \) is the mass transfer coefficient for oxygen gas, \( K_H \) is the Henry’s constant provided by Henry’s Law, and \( P_{O_2} \) is the partial pressure of oxygen. The unit normal vector at the \( \hat{z} = \hat{h}(\hat{x}, \hat{t}) \) interface is \( \vec{n} = \frac{(-\hat{h}_{\hat{z}}, 1)}{\sqrt{1 + \hat{h}_{\hat{z}}^2}} \). All of the other species considered in this model are non-volatile ions, satisfying no-flux conditions at the \( \hat{z} = \hat{h}(\hat{x}, \hat{t}) \) interface,

\[ \nabla C_i \cdot \vec{n} = 0. \]  
(2.18)

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At the crust-fluid interface, \( \hat{z} = (\hat{x}, \hat{t}) \), it is possible for chemical species to leave the fluid via surface reactions. Specifically, Fe(III) in the liquid may precipitate and become a part of the iron-hydroxide crust via Reaction (1.2). The reaction that governs the precipitation and dissolution of the iron-hydroxide crust at the \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) interface is

\[
\text{Fe}^{3+} + 3 \text{H}_2\text{O} \xrightleftharpoons[\kappa_{-1}]{\kappa_1} \text{Fe(OH)}_3 + 3 \text{H}^+, \tag{2.19}
\]

where \( \kappa_1 \) and \( \kappa_{-1} \) are the forward and backward reaction rate coefficients respectively. Therefore, the rate law is given by \( J \) in the equation

\[
J = -\kappa_1 \hat{C}_{\text{H}^+}^3 + \kappa_{-1} \hat{C}_{\text{Fe}^{3+}}. \tag{2.20}
\]

Here, \( J \) is the rate law for Reaction 1.2, the surface reaction that occurs at \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \).

If the value of \( J \) is negative, by Equation (2.20), \( \kappa_1 \hat{C}_{\text{H}^+}^3 \) must be greater in magnitude than \( \kappa_{-1} \hat{C}_{\text{Fe}^{3+}} \). By Le Châtelier’s Principle, equilibrium of Reaction 1.2 shifts to the left-hand side of the reaction, causing the dissolution of \( \text{Fe(OH)}_3 \). Conversely, if \( J \) is positive, \( \kappa_1 \hat{C}_{\text{H}^+}^3 \) must be less in magnitude than \( \kappa_{-1} \hat{C}_{\text{Fe}^{3+}} \). Then the equilibrium in Reaction 1.2 shifts to the right-hand side of the reaction, causing the precipitation of \( \text{Fe(OH)}_3 \). Applying this reaction rate formula as the forcing term for flux conditions to the iron hydroxide crust, the following two boundary conditions are obtained:

\[
D_{\text{H}^+} \nabla \hat{C}_{\text{H}^+} \cdot \hat{n}_s = \kappa_1 \hat{C}_{\text{H}^+}^3 - \kappa_{-1} \hat{C}_{\text{Fe}^{3+}}, \tag{2.21}
\]

\[
D_{\text{Fe}^{3+}} \nabla \hat{C}_{\text{Fe}^{3+}} \cdot \hat{n}_s = -\kappa_1 \hat{C}_{\text{H}^+}^3 + \kappa_{-1} \hat{C}_{\text{Fe}^{3+}}, \tag{2.22}
\]

where \( D_i \) are the mass diffusivities of the \( i \)th chemical component and \( \hat{n}_s = \left( -\hat{s}_x, \frac{1}{\sqrt{1 + \hat{s}_x^2}} \right) \).

Note that \( \hat{n}_s \) is the vector normal to the crust-liquid interface.
Oxygen can leave and enter the surface \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) via absorption by the soil or the roots of plants. For this reason, the net flux of oxygen traveling from the liquid into the crust must be considered. We assume

\[
D_{O_2} \nabla \hat{C}_{O_2} \cdot \vec{n}_s = F_c. \tag{2.23}
\]

Here, \( D_{O_2} \) is the mass diffusivity of oxygen, and \( F_c \) is the net flux of oxygen into the iron-hydroxide crust. Since Fe(II) does not participate in Reaction 1.2, the precipitation reaction, there is no flux of Fe(II) ions into the crust at interface \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \). Thus, we have the boundary condition,

\[
D_{Fe^{2+}} \nabla \hat{C}_{Fe^{2+}} \cdot \vec{n}_s = 0. \tag{2.24}
\]

Now the boundary condition defining the location of the crust-liquid interface can be determined. Utilizing that the normal velocity of the iron-hydroxide crust is driven by surface reactions, followed by deposition, we write

\[
\rho_{\text{Fe(OH)$_3$}} \frac{\partial \hat{s}}{\partial \hat{t}} \sqrt{1 + \hat{s}^2} = \left( -\kappa_1 \hat{C}_{H^+} + \kappa_{-1} \hat{C}_{Fe^{3+}} \right), \tag{2.25}
\]

where \( \rho_{\text{Fe(OH)$_3$}} \) is the density of the iron hydroxide crust. This equation is a mass balance equation which states that the rate of increase of iron hydroxide crust is equal to the rate of loss of species from the liquid due to surface reactions.

The previous discussion for hydrodynamic thin liquid film flow and reactive transport of chemical components encompasses a theoretical model for the physical behavior of the system. This model considers the hydrodynamics, chemical changes, as well as the impact of surface reactions to produce iron hydroxide precipitate at the \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) interface.
CHAPTER III

SOLUTION PROCEDURE

This chapter contains the development and solution to the governing equations for the model described in Chapter 2. First, the solution to the dynamics of the fluid flow in the system is considered. This is followed by the analysis of reactive transport equations. Once the solution to these systems are obtained, the iron hydroxide crust evolution, Equation (2.25), can be determined.

3.1 Hydrodynamics Solution Procedure

The fluid-flow equations for this model are solved using asymptotic expansions. With this approach, Equations (2.1), (2.2), (2.3), (2.4), (2.9), and (2.10) are utilized to define solutions for $\hat{p}$, $\hat{u}$, and $\hat{w}$, which will depend upon $\hat{s}$ and $\hat{h}$, the unknown free boundaries. The kinematic condition from Equation (2.8) along with the solutions obtained for $\hat{p}$, $\hat{u}$, and $\hat{w}$ are used to determine the flow rate of the system in terms of the boundaries $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ and $\hat{z} = \hat{h}(\hat{x}, \hat{t})$. Furthermore, a relationship between the location of $\hat{s}$ and $\hat{h}$ is obtained.

The basic assumption for this model is that the length of the distance over which the fluid is flowing is much larger in magnitude than the depth of the liquid. Let $d$ be the characteristic depth of the liquid and $L$ be the characteristic distance
over which the liquid travels. Since \( d \) is on the order of a few centimeters, while \( L \) is on the order of meters at our location of interest, this assumption is justified. Therefore, we define the aspect ratio, \( \epsilon = \frac{d}{L} \), where \( \epsilon << 1 \). Table 3.1 summarizes the non-dimensional variables employed.

Table 3.1: Non-dimensional variables

<table>
<thead>
<tr>
<th>Dimensional Variable</th>
<th>Scaling</th>
<th>Non-Dimensional Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal Dimension: ( \hat{x} )</td>
<td>( L )</td>
<td>( \hat{x} )</td>
</tr>
<tr>
<td>Transverse Dimension: ( \hat{z} )</td>
<td>( d )</td>
<td>( \hat{z} )</td>
</tr>
<tr>
<td>Longitudinal Velocity: ( \hat{u} )</td>
<td>( U )</td>
<td>( \hat{u} )</td>
</tr>
<tr>
<td>Transverse Velocity: ( \hat{w} )</td>
<td>( W = \frac{ud}{L} )</td>
<td>( \hat{w}L ) ( \frac{U}{d} )</td>
</tr>
<tr>
<td>Pressure: ( \hat{p} )</td>
<td>( P = \frac{\nu UL}{d^2} )</td>
<td>( \frac{\hat{p}}{\frac{\nu U}{d^2}} )</td>
</tr>
<tr>
<td>Air-liquid interface: ( \hat{h} )</td>
<td>( d )</td>
<td>( \hat{h} )</td>
</tr>
<tr>
<td>Crust-liquid interface: ( \hat{s} )</td>
<td>( d )</td>
<td>( \hat{s} )</td>
</tr>
<tr>
<td>Time: ( \hat{t} )</td>
<td>( T = d^2 \frac{1}{\epsilon D_{Fe^{3+}}} )</td>
<td>( \hat{t} ) ( d^2 )</td>
</tr>
</tbody>
</table>

Concentration Hydrogen: \( \hat{C}_{H^+} \) | \( C_{H^+} \) | \( \hat{C}_{H^+} \) \( C_{H^+} \) |
Concentration Oxygen: \( \hat{C}_{O_2} \)  | \( C_{O_2} \) | \( \hat{C}_{O_2} \) \( C_{O_2} \) |
Concentration Fe(II): \( \hat{C}_{Fe^{2+}} \) | \( C_{Fe^{2+}} \) | \( \hat{C}_{Fe^{2+}} \) \( C_{Fe^{2+}} \) |
Concentration Fe(III): \( \hat{C}_{Fe^{3+}} \) | \( C_{Fe^{3+}} \) | \( \hat{C}_{Fe^{3+}} \) \( C_{Fe^{3+}} \) |

In Table 3.1 \( U \), \( P \), and \( T \) are the characteristic velocity, pressure, and time scales respectively. The time scale, \( T = \frac{d^2}{\epsilon D_{Fe^{3+}}} \), is determined utilizing the non-
dimensionalized version of Equation (2.25), which is Equation (3.66). \( T \) is chosen to force the governing equation for iron(III) hydroxide crust growth to be part of the leading order solution. For this reason, \( T \gg 1 \). This is consistent with experimental data which indicate that the growth of the iron-hydroxide crust is on the order of about 1 cm per year. Since the unit of measurement for time is seconds, the magnitude of \( T \) is quite large.

Applying this non-dimensional scheme to the hydrodynamic governing equations, we find that the equation for conservation of mass, Equation (2.1), is

\[
 u_x + w_z = 0. 
\]  

(3.1)

The Navier Stokes equations (2.2) and (2.3) in the \( x \) and \( z \) directions, respectively are

\[
 \epsilon \frac{1}{Sc} u_t + \epsilon Re [u u_x + w u_z] = -p_x + \epsilon^2 u_{xx} + u_{zz} + \sin \theta, 
\]  

(3.2)

and

\[
 \epsilon^3 \frac{1}{Sc} w_t + \epsilon^3 Re [u w_x + w w_z] = -p_z + \epsilon^4 w_{xx} + \epsilon^2 w_{zz} - \epsilon \cos \theta. 
\]  

(3.3)

Here, \( Re = \frac{U d}{\nu} \) is a representation of the inertial forces divided by viscous forces, which is called the Reynold’s number. Furthermore, \( Sc = \frac{\nu}{D_{Fe^{3+}}} \) is called the Schmidt number; it represents mass transport by convection relative to transport by diffusion. These constants and others are included in Table 3.2.

At the crust-liquid interface, \( z = s(x, t) \), the no-slip boundary condition (2.4) becomes

\[
 u = w = 0. 
\]  

(3.4)
Table 3.2: Nondimensional Groups

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Scaling</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reynolds number: $Re$</td>
<td>$\frac{U_d}{\nu}$</td>
<td>Inertial forces divided by viscous forces</td>
</tr>
<tr>
<td>Schmidt number: $Sc$</td>
<td>$\frac{\nu}{D_{Fe^{3+}}}$</td>
<td>Mass transport by convection relative to transport by diffusion</td>
</tr>
<tr>
<td>Capillary number: $Ca$</td>
<td>$\frac{\sigma}{\mu U}$</td>
<td>Surface tension force of the liquid divided by the viscous force</td>
</tr>
<tr>
<td>Peclet number: $Pe$</td>
<td>$\frac{U_d}{D_i}$</td>
<td>The ratio between transport of concentration via convection and transport of concentration via diffusion</td>
</tr>
<tr>
<td>Damköhler number: $Da_{(1)}$</td>
<td>$\frac{\kappa_{1d}}{D_{Fe^{3+}}}$</td>
<td>Ratio between the forward chemical reaction rate and the diffusive transport</td>
</tr>
<tr>
<td>Damköhler number: $Da_{(-1)}$</td>
<td>$\frac{\kappa_{-1d}}{D_{Fe^{3+}}}$</td>
<td>Ratio between the backward chemical reaction rate and the diffusive transport</td>
</tr>
</tbody>
</table>

At the air-liquid interface, $z = h(x,t)$, the non-dimensional representation of the kinematic condition, Equation (2.8), is

$$\frac{D_{Fe^{3+}}}{U_d} h_t = w - uh_x. \quad (3.5)$$

Shear stress in Equation (2.9) is

$$-2\epsilon^2 h_x u_x + 2\epsilon^2 w_z h_x + u_z + \epsilon^2 w_x - \epsilon^2 h_x^2 u_z - \epsilon^4 h_x^2 w_x = 0. \quad (3.6)$$
The normal force balance, Equation (2.10), is given by

$$-p + \epsilon^2 \left[ \epsilon^2 u_x h_x^2 - u_x h_x - \epsilon^2 w_x h_x + w_z \right] = \frac{\epsilon \bar{C}a h_{xx}}{(1 + \epsilon^2 h_x^2)^{3/2}}, \quad (3.7)$$

where $Ca = \frac{\sigma}{\mu U}$ is the capillary number. The capillary number is the surface tension force of the liquid divided by the viscous force. Due to large surface tension, we take $Ca$ to be large, $Ca = \bar{C}a$, where $\bar{C}a$ is an $O(1)$ constant. This completes the non-dimensionalization of the hydrodynamic equations.

Now we assume the following asymptotic expansions, where $\epsilon$ is very small:

$$p = p_0 + \epsilon p_1 + \epsilon^2 p_2 + \cdots, \quad (3.8)$$

$$u = u_0 + \epsilon u_1 + \epsilon^2 u_2 + \cdots,$$

$$w = w_0 + \epsilon w_1 + \epsilon^2 w_2 + \cdots.$$

In addition, we consider the boundary perturbations,

$$s(x, t) = s_0(x, t) + \epsilon s_1(x, t) + \epsilon^2 s_2(x, t) + \cdots \quad (3.9)$$

$$h(x, t) = h_0(x, t) + \epsilon h_1(x, t) + \epsilon^2 h_2(x, t) + \cdots \quad (3.10)$$

Evaluating the equations at the perturbed boundaries gives

$$m_0(x, (z = s_0 + \epsilon s_1 + \cdots), t) + \epsilon m_1(x, (z = s_0 + \epsilon s_1 + \cdots), t) + \cdots,$$

$$m_0(x, (z = h_0 + \epsilon h_1 + \cdots), t) + \epsilon m_1(x, (z = h_0 + \epsilon h_1 + \cdots), t) + \cdots,$$
where $m$ represents the $p$, $u$, or $w$. Performing a Taylor expansion we have

\[
[m_0(x, s_0, t) + m_0z(x, s_0, t)(\epsilon s_1) + \cdots] + \epsilon [m_1(x, s_0, t) + m_1z(x, s_0, t)(\epsilon s_1) + \cdots] + \cdots
\]

\[
[m_0(x, h_0, t) + m_0z(x, h_0, t)(\epsilon h_1) + \cdots] + \epsilon [m_1(x, h_0, t) + m_1z(x, h_0, t)(\epsilon h_1) + \cdots] + \cdots
\]

Equation (3.7) contains fractional powers and powers in denominators, requiring binomial expansions:

\[
\epsilon^2 \left[ \epsilon^2 u_x h_x^2 - u_z h_x - \epsilon^2 w_x h_x + w_z \right] \frac{1}{(1 + \epsilon^2 h_x^2)} =
\]

\[
\epsilon^2 \left( \epsilon^2 u_x h_x^2 - u_z h_x - \epsilon^2 w_x h_x + w_z \right) \left[ 1 - \epsilon^2 h_x^2 + \cdots \right],
\]

\[
\frac{\epsilon \bar{C}ah_{xx}}{(1 + \epsilon^2 h_x^2)^{3/2}} = (\epsilon \bar{C}ah_{xx}) \left[ 1 - \frac{3}{2} \epsilon^2 h_x^2 + \cdots \right].
\]

Placing these expansions in Equations (3.1), (3.2), and (3.3), we obtain the leading order problem

\[
\begin{align*}
    u_0x + w_0z &= 0, \\
    -p_0x + u_0zz &= -\sin \theta, \quad (3.11) \\
    -p_0z &= 0,
\end{align*}
\]

subject to the conditions

\[
    u_0 = w_0 = 0, \quad (3.12)
\]
at $z = s_0(x,t)$, and
\[ p_0 = 0, \quad u_0 = 0, \quad (3.13) \]
at $z = h_0(x,t)$. The details of the solution to this system are provided in Appendix A. The solution to this leading order system is
\[ p_0 = 0, \]
\[ u_0 = \sin \theta \left[ -\frac{z^2}{2} + h_0 z + \frac{s_0^2}{2} - s_0 h_0 \right], \quad (3.14) \]
\[ w_0 = \sin \theta \left[ -\frac{h_0 x z^2}{2} - s_0 s_0 x z + s_0 h_0 x z + s_0 h_0 z z - \frac{s_0^2 h_0}{2} + s_0^2 s_0 x - s_0 s_0 x h_0 \right]. \]

Now, to find the flow rate of the system we take the integral of $u_0$ from $s_0$ to $h_0$ and we find
\[ \int_{s_0}^{h_0} u_0 dz = \frac{\sin \theta}{3} (h_0 - s_0)^3. \quad (3.15) \]
We now denote $Q$ as the flow rate. Thus, we have
\[ Q = \frac{\sin \theta}{3} (h_0 - s_0)^3. \quad (3.16) \]

Now we utilize the leading order kinematic condition to make further conclusions about the system. The leading order kinematic condition is
\[ \frac{D_{Fe^{3+}}}{U_d} h_0 t = w_0 - u_0 h_0 x. \quad (3.17) \]

Table 3.3 lists the approximate values of mass diffusivity estimated from data [10]. From Table 3.3, the magnitude of $D_{Fe^{3+}}$ is very small, thus forcing $\frac{D_{Fe^{3+}}}{U_d}$ to also have a small magnitude. Because $\frac{D_{Fe^{3+}}}{U_d}$ has a small magnitude, we approximate the
left-hand side of the equation by zero, and have

\[ 0 = w_0 - u_0 h_{0x}. \]  

(3.18)

The solution of Equation (3.18) gives the result

\[ -\frac{1}{3} \sin \theta \left[ (h_0 - s_0)^3 \right]_x = 0. \]  

(3.19)

When considering Equations (3.16) and (3.19) together, we conclude that because the derivative of the flow rate \( Q \) with respect to \( x \) is zero, then flow rate must be solely a function of time. Furthermore, this provides a relationship between \( s_0 \) and \( h_0 \), and we have,

\[ h_0 = \left( \frac{3Q}{\sin \theta} \right)^{\frac{1}{3}} + s_0. \]  

(3.20)

This indicates that the position of the liquid-air interface can be determined once the position of the crust-liquid interface is determined. The location of \( h_0 \) is simply a positive vertical shift of the location of \( s_0 \).
3.2 Reactive Transport Solution Procedure

The crust surface, \( z = s(x, t) \) is chemically driven. We now solve the reactive transport system of equations, a set of four nonlinear, coupled, partial differential equations, which are very difficult to solve. We also make a few justifiable assumptions in order to make the system solvable.

First, recall that we consider temperature as a constant at any given season of the year. Additionally, each of the chemical species has a mass diffusivity associated with it. Since we consider temperature to be held constant, the values of mass diffusivity are fairly predictable. The approximate values for diffusivities of significant ions in our model can be viewed in Table 3.3.

Applying the same non-dimensional scheme utilized in the hydrodynamic governing equations, and the non-dimensional variables in Table 3.1, the reactive transport governing equations become,

\[
\epsilon \frac{D_{Fe^{3+}}}{D_{H^+}} C_{H^+} + \epsilon Pe [u C_{H^+} + w C_{H^+}] = \epsilon^2 C_{H^+xx} + C_{H^+zz} + \frac{\epsilon \bar{I} d^2}{D_{H^+} C^*_{H^+}}, \tag{3.21}
\]

\[
\epsilon \frac{D_{Fe^{3+}}}{D_{O_2}} C_{O_2} + \epsilon Pe [u C_{O_2} + w C_{O_2}] = \epsilon^2 C_{O_2xx} + C_{O_2zz} + \frac{\epsilon \bar{I} d^2}{D_{O_2} C^*_{O_2}}, \tag{3.22}
\]

\[
\epsilon \frac{D_{Fe^{3+}}}{D_{Fe^{2+}}} C_{Fe^{2+}} + \epsilon Pe [u C_{Fe^{2+}} + w C_{Fe^{2+}}] = \epsilon^2 C_{Fe^{2+}xx} + C_{Fe^{2+}zz} + \frac{\epsilon \bar{I} d^2}{D_{Fe^{2+}} C^*_{Fe^{2+}}}, \tag{3.23}
\]

\[
\epsilon C_{Fe^{3+}} + \epsilon Pe [u C_{Fe^{3+}} + w C_{Fe^{3+}}] = \epsilon^2 C_{Fe^{3+}xx} + C_{Fe^{3+}zz} - \frac{\epsilon \bar{I} d^2}{D_{Fe^{3+}} C^*_{Fe^{3+}}}. \tag{3.24}
\]

where \( Pe = \frac{U d}{D_i} \) is the Peclet number, which is the transport of concentration due to convection relative to transport of concentration due to diffusion. Also,
\[ I = \left[ -k_1 C_{Fe^{2+}}^{4+} + C_{Fe^{3+}}^{4+} C_{O_2}^{*} C_{O_2}^{4+} C_{H^+}^{4+} + k_{-1} C_{Fe^{3+}}^{4+} + C_{Fe^{3+}}^{4+} \right] \] and \( \epsilon \bar{I} \) is the scaling factor for the approximate size of \( \hat{I} \). This scaling for \( I \) is chosen because the bulk reactions are approximately at equilibrium, making the magnitude of \( I \) near zero.

The nondimensional representation of the \( z = h(x,t) \) boundary condition from Equation (2.17) is

\[
\frac{-\epsilon^2 C_{O_2 x} h_x + C_{O_2 z}}{\sqrt{1 + \epsilon^2 h_x^2}} = \epsilon K_{MT} \left[ K_{PO_2} - C_{O_2}^{*} C_{O_2} \right],
\]

(3.25)

where \( \frac{d}{D_{O_2}} K_{MT} = \epsilon \bar{K}_{MT} \). The scale for the mass transfer coefficient of oxygen is chosen to be small to insure that the flux of oxygen at the air-liquid interface is accounted for in the first correction for the system. Because the bulk reactions in the system are small, the mass transfer coefficient must also be small. For Equations (2.18) we have

\[
\frac{-\epsilon^2 C_{H^+ x} h_x + C_{H^+ z}}{\sqrt{1 + \epsilon^2 h_x^2}} = 0,
\]

\[
\frac{-\epsilon^2 C_{Fe^{2+} x} h_x + C_{Fe^{2+} z}}{\sqrt{1 + \epsilon^2 h_x^2}} = 0,
\]

(3.26)

\[
\frac{-\epsilon^2 C_{Fe^{3+} x} h_x + C_{Fe^{3+} z}}{\sqrt{1 + \epsilon^2 h_x^2}} = 0.
\]

Non-dimensionalization of flux conditions to the iron hydroxide crust provide us with the equations,

\[
\frac{-\epsilon^2 C_{H^+ x} s_x + C_{H^+ z}}{\sqrt{1 + \epsilon^2 s_x^2}} = \left( \epsilon \frac{\bar{D} a_1 D_{Fe^{3+}} C_{H^+}^{*}}{D_{H^+}} \right) C_{H^+}^{3} - \left( \epsilon \frac{\bar{D} a_{-1} D_{Fe^{3+}} C_{Fe^{3+}}^{*}}{C_{H^+}^{*} D_{H^+}} \right) C_{Fe^{3+}},
\]

(3.27)

\[
\frac{-\epsilon^2 C_{Fe^{3+} x} s_x + C_{Fe^{3+} z}}{\sqrt{1 + \epsilon^2 s_x^2}} = - \left( \epsilon \frac{\bar{D} a_1 C_{H^+}^{*}}{C_{Fe^{3+}}^{*}} \right) C_{H^+}^{3} + (\epsilon \bar{D} a_{-1}) C_{Fe^{3+}},
\]

(3.28)
where \( Da_{(1)} = \epsilon \tilde{D} a_{(1)} \) and \( Da_{(-1)} = \epsilon \tilde{D} a_{(-1)} \). \( Da_{(1)} \) and \( Da_{(-1)} \) are Damköhler numbers where \( Da_{(1)} = \frac{\kappa_1 d}{D_{Fe^{3+}}} \) and likewise \( Da_{(-1)} = \frac{\kappa_{-1} d}{D_{Fe^{3+}}} \). Damköhler numbers represent the ratio between the chemical reaction rate and the diffusive transport of ionic species. The scaling for Damköhler numbers are chosen to account for the small magnitude of crust growth in Equation (3.66).

The oxygen transport condition across the surface \( z = s(x, t) \) is

\[
-\epsilon^2 C_{O_2 x} s_x + C_{O_2 z} \sqrt{1 + \epsilon^2 s_x^2} = \epsilon \tilde{F},
\]

where \( \epsilon \tilde{F} = \left( \frac{d}{C^* D_{O_2}} \right) F_c \). The scale for the net flux of oxygen through the iron(III) hydroxide crust is chosen to be small to insure that the flux of oxygen at the liquid-solid interface is accounted for in the first correction for the system. The net flux of oxygen through the crust is assumed to be limited by the non-porous crust.

The no flux condition of Fe(II) at the crust-liquid interface \( (z = s(x, t)) \) is

\[
-\epsilon^2 C_{Fe^{2+} x} s_x + C_{Fe^{2+} z} \sqrt{1 + \epsilon^2 s_x^2} = 0.
\]

This completes the non-dimensionalization of the reactive transport equations. Now we assume the following asymptotic expansions where \( \epsilon \) is small:

\[
C_{H^+} = C_{H^+}^0 + \epsilon C_{H^+}^1 + \epsilon^2 C_{H^+}^2 + \cdots
\]

\[
C_{Fe^{2+}} = C_{Fe^{2+}}^0 + \epsilon C_{Fe^{2+}}^1 + \epsilon^2 C_{Fe^{2+}}^2 + \cdots
\]

\[
C_{Fe^{3+}} = C_{Fe^{3+}}^0 + \epsilon C_{Fe^{3+}}^1 + \epsilon^2 C_{Fe^{3+}}^2 + \cdots
\]

\[
C_{O_2} = C_{O_2}^0 + \epsilon C_{O_2}^1 + \epsilon^2 C_{O_2}^2 + \cdots
\]
In addition, we consider the boundary perturbations,

\[ s(x, t) = s_0(x, t) + \varepsilon s_1(x, t) + \varepsilon^2 s_2(x, t) + \cdots \] (3.32)

\[ h(x, t) = h_0(x, t) + \varepsilon h_1(x, t) + \varepsilon^2 h_2(x, t) + \cdots \] (3.33)

Evaluating the concentrations at the perturbed boundaries gives

\[ C_i(0, z = s_0 + \varepsilon s_1 + \cdots, t) + \varepsilon C_i(0, (z = s_0 + \varepsilon s_1 + \cdots), t) + \cdots, \]

\[ C_i(0, z = h_0 + \varepsilon h_1 + \cdots, t) + \varepsilon C_i(0, (z = h_0 + \varepsilon h_1 + \cdots), t) + \cdots, \]

where \( C_i \) is the \( i \)th chemical species. Performing a Taylor expansion we have

\[
\left[ C_{i_0}(x, s_0, t) + C_{i_0z}(x, s_0, t)(\varepsilon s_1) + \cdots \right] + \varepsilon \left[ C_{i_1}(x, s_0, t) + C_{i_1z}(x, s_0, t)(\varepsilon s_1) + \cdots \right] + \cdots
\]

\[
\left[ C_{i_0}(x, h_0, t) + C_{i_0z}(x, h_0, t)(\varepsilon h_1) + \cdots \right] + \varepsilon \left[ C_{i_1}(x, h_0, t) + C_{i_1z}(x, h_0, t)(\varepsilon h_1) + \cdots \right] + \cdots
\]

For Equations (3.26), a binomial expansion is used to evaluate the fractional power in the denominator. Thus, we note the following:

\[
\frac{-\varepsilon^2 C_{ix}h_x + C_{iz}}{\sqrt{1 + \varepsilon^2 h_x^2}} = \left( -\varepsilon^2 C_{ix}h_x + C_{iz} \right) \left[ 1 - \varepsilon^2 h_x^2 + \cdots \right],
\]

where \( C_i \) is the \( i \)th chemical species. There are similar fractional powers in Equations (3.27)-(3.30). Therefore, we also utilize the binomial expansion,

\[
\frac{-\varepsilon^2 C_{ix}s_x + C_{iz}}{\sqrt{1 + \varepsilon^2 s_x^2}} = \left( -\varepsilon^2 C_{ix}s_x + C_{iz} \right) \left[ 1 - \varepsilon^2 s_x^2 + \cdots \right],
\]
for each chemical species. Placing these expansions into Equations (3.21)-(3.24), we obtain the leading order reactive transport governing equations

\[
C_{H_0^{+}z} = 0, \quad (3.34)
\]
\[
C_{O_{20}z} = 0 \quad (3.35)
\]
\[
C_{Fe^{2+}_{0}z} = 0, \quad (3.36)
\]
\[
C_{Fe^{3+}_{0}z} = 0, \quad (3.37)
\]

subject to

\[
C_{H_0^{+}z} = 0, \quad (3.38)
\]
\[
C_{O_{20}z} = 0, \quad (3.39)
\]
\[
C_{Fe^{2+}_{0}z} = 0, \quad (3.40)
\]
\[
C_{Fe^{3+}_{0}z} = 0, \quad (3.41)
\]

at the \( z = s_0(x,t) \) interface, and

\[
C_{H_0^{+}z} = 0, \quad (3.42)
\]
\[
C_{O_{20}z} = 0, \quad (3.43)
\]
\[
C_{Fe^{2+}_{0}z} = 0, \quad (3.44)
\]
\[
C_{Fe^{3+}_{0}z} = 0, \quad (3.45)
\]

at the \( z = h_0(x,t) \) interface. The governing equation for each ion is integrated twice with respect to \( z \) to solve for the concentration of each ion. This integral is evaluated from \( z = s_0(x,t) \) to \( z = h_0(x,t) \) and the boundary conditions are applied. Detailed
solutions to the above system may be found in Appendices B -E. Solution of these
equations indicates that $C_{H^+}$, $C_{O_2}$, $C_{Fe^{2+}}$, and $C_{Fe^{3+}}$ are all solely functions of $x$.
More detail on the behavior of these ions is necessary for this model. Thus, we find
and solve the first correction to the system of equations. The first correction for the
reactive transport governing equations are

\[
C_{H^+} \frac{d^2}{D_{H^+} C_{H^+}^{*}} - \bar{I} = \frac{D_{Fe^{3+}}}{D_{H^+}} C_{H^+}^{*} + P_e \left[ u_0 C_{H^+0x} + w_0 C_{H^+0z} \right], \tag{3.46}
\]

\[
C_{O_2} \frac{d^2}{D_{O_2} C_{O_2}^{*}} - \bar{I} = \frac{D_{Fe^{3+}}}{D_{O_2}} C_{O_20x} + P_e \left[ u_0 C_{O_20x} + w_0 C_{O_20z} \right], \tag{3.47}
\]

\[
C_{Fe^{2+}} \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}^{*}} - \bar{I} = \frac{D_{Fe^{3+}}}{D_{Fe^{2+}}} C_{Fe^{2+}}^{*} + P_e \left[ u_0 C_{Fe^{2+0x}} + w_0 C_{Fe^{2+0z}} \right], \tag{3.48}
\]

\[
C_{Fe^{3+}} \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}^{*}} - \bar{I} = C_{Fe^{3+0t}} + P_e \left[ u_0 C_{Fe^{3+0x}} + w_0 C_{Fe^{3+0z}} \right], \tag{3.49}
\]

where $\bar{I} = \left[ -k_1 C_{Fe^{2+}}^{*} C_{Fe^{2+0}} C_{O_2}^{*} C_{O_20} C_{H^+}^{*} C_{H^+0}^{*} + k_{-1} C_{Fe^{3+}}^{*} C_{Fe^{3+0}}^{*} \right]$. From the solution
of the leading order system of governing equations for reactive transport, it is seen
that all concentrations are solely functions of $x$. Thus, we know that $C_{i0x} = 0$ as well
as $C_{i0z} = 0$. Therefore, the governing equations for this system reduce to

\[
C_{H^+} \frac{d^2}{D_{H^+} C_{H^+}^{*}} - \bar{I} = P_e \left[ u_0 C_{H^+0x} \right], \tag{3.50}
\]

\[
C_{O_2} \frac{d^2}{D_{O_2} C_{O_2}^{*}} - \bar{I} = P_e \left[ u_0 C_{O_20x} \right], \tag{3.51}
\]

\[
C_{Fe^{2+}} \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}^{*}} - \bar{I} = P_e \left[ u_0 C_{Fe^{2+0x}} \right], \tag{3.52}
\]

\[
C_{Fe^{3+}} \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}^{*}} - \bar{I} = P_e \left[ u_0 C_{Fe^{3+0x}} \right], \tag{3.53}
\]
subject to

\[ C_{H_1^+} s_1 + C_{H_1^+} = \left( \frac{D_{a1}D_{Fe^{3+}}}{D_{H^+}} \right) C_{H_0^+}^{3} - \left( \frac{D_{a1}D_{Fe^{3+}}C_{Fe^{3+}}^{*}}{C_{H^+}^{*}D_{H^+}} \right) C_{Fe^{3+}}, \]

\[ C_{O2^0_z} s_1 + C_{O2^1_z} = F, \]

\[ C_{Fe^{2+}_{0z}} s_1 + C_{Fe^{2+}_{1z}} = 0, \]

\[ C_{Fe^{3+}_{0z}} s_1 + C_{Fe^{3+}_{1z}} = -\frac{D_{a1}C_{H^+}^{*}C_{Fe^{3+}}^{*}}{C_{Fe^{3+}}^{*}C_{H_0^+}^{*}} \]

\[ at \ the \ z = s_0(x, t) \ interface. \ Using \ the \ x \ dependence \ of \ the \ leading \ order \ solutions, \ we \ have \]

\[ C_{H_1^+} = \left( \frac{D_{a1}D_{Fe^{3+}}}{D_{H^+}} \right) C_{H_0^+}^{3} - \left( \frac{D_{a1}D_{Fe^{3+}}C_{Fe^{3+}}^{*}}{C_{H^+}^{*}D_{H^+}} \right) C_{Fe^{3+}}, \] (3.54)

\[ C_{O2^1_z} = F, \] (3.55)

\[ C_{Fe^{2+}_{1z}} = 0, \] (3.56)

\[ C_{Fe^{3+}_{1z}} = -\frac{D_{a1}C_{H^+}^{*}C_{Fe^{3+}}^{*}}{C_{Fe^{3+}}^{*}C_{H_0^+}^{*}} + D_{a1}C_{Fe^{3+}}, \] (3.57)

At the \( z = h_0(x, t) \) interface we have,

\[ C_{H_1^+} = 0, \] (3.58)

\[ C_{O2^1_z} = \frac{K_{MT} [K_{H^+}P_{O2} - C_{O2}^{*}C_{O20}]}{C_{O2}^{*}}, \] (3.59)

\[ C_{Fe^{2+}_{1z}} = 0, \] (3.60)

\[ C_{Fe^{3+}_{1z}} = 0. \] (3.61)

To solve Equations (3.46)-(3.49), each is integrated once with respect to \( z \) from \( z = s(x, t) \) to \( z = h(x, t) \), followed by applying the respective boundary conditions. For ease in later numerical analysis, the equations are re-dimensionalized.
Detailed solution procedures are provided in Appendices B-E. When this is performed on the leading order reactive transport system we have,

\[ \hat{Q} \hat{C}_{H_o^+} = -\kappa_1 \hat{C}_{H_o^+}^3 + \kappa_{-1} \hat{C}_{Fe_0^{3+}} \]

\[ + \left( \frac{3 \hat{Q} \mu}{\rho g \sin \theta} \right)^{1/3} \left[ k_{-1} \hat{C}_{Fe_0^{4+}}^4 - k_{1} \hat{C}_{Fe_0^{2+}}^4 \hat{C}_{H_o^+}^4 \hat{C}_{O_{20}} \right], \]  

(3.62)

\[ \hat{Q} \hat{C}_{O_{20}} = K_{MT} (K_H P_{O_2} - C_{O_{20}}) - F_c \]

\[ + \left( \frac{3 \hat{Q} \mu}{\rho g \sin \theta} \right)^{1/3} \left[ k_{-1} \hat{C}_{Fe_0^{4+}}^4 - k_{1} \hat{C}_{Fe_0^{2+}}^4 \hat{C}_{H_o^+}^4 \hat{C}_{O_{20}} \right], \]  

(3.63)

\[ \hat{Q} \hat{C}_{Fe_0^{2+}} = \left( \frac{3 \hat{Q} \mu}{\rho g \sin \theta} \right)^{1/3} \left[ k_{-1} \hat{C}_{Fe_0^{4+}}^4 - k_{1} \hat{C}_{Fe_0^{2+}}^4 \hat{C}_{H_o^+}^4 \hat{C}_{O_{20}} \right], \]  

(3.64)

\[ \hat{Q} \hat{C}_{Fe_0^{3+}} = \kappa_1 \hat{C}_{H_o^+}^3 - \kappa_{-1} \hat{C}_{Fe_0^{3+}} \]

\[ + \left( \frac{3 \hat{Q} \mu}{\rho g \sin \theta} \right)^{1/3} \left[ -k_{-1} \hat{C}_{Fe_0^{4+}}^4 + k_{1} \hat{C}_{Fe_0^{2+}}^4 \hat{C}_{H_o^+}^4 \hat{C}_{O_{20}} \right]. \]  

(3.65)

From Equations (2.12) and (2.20), we may write Equations (3.62)-(3.65) as follows:

\[ \hat{Q} \hat{C}_{H_o^+} = J + \left( \frac{3 \hat{Q} \mu}{\rho g \sin \theta} \right)^{1/3} \hat{I}, \]  

\[ \hat{Q} \hat{C}_{O_{20}} = K_{MT} (K_H P_{O_2} - C_{O_{20}}) - F_c + \left( \frac{3 \hat{Q} \mu}{\rho g \sin \theta} \right)^{1/3} \hat{I}, \]  

\[ \hat{Q} \hat{C}_{Fe_0^{2+}} = \left( \frac{3 \hat{Q} \mu}{\rho g \sin \theta} \right)^{1/3} \hat{I}, \]  

\[ \hat{Q} \hat{C}_{Fe_0^{3+}} = -J - \left( \frac{3 \hat{Q} \mu}{\rho g \sin \theta} \right)^{1/3} \hat{I}. \]  

Here, the left-hand side is the convective transport of each respective ion. For oxygen, we see \( K_{MT} (K_H P_{O_2} - C_{O_{20}}) \), which represents the surface flux through the gas-liquid
interface and $F_c$, the flux through the solid-liquid interface. All other chemical species only involve sources due to reactions. $J$ is the source due to surface reactions. $\dot{I}$ is the source due to bulk reactions, and is multiplied by $\left(\frac{3\dot{Q} \mu}{\rho g \sin \theta}\right)^{1/3}$, the thickness of the liquid. From Equations (2.12) and (2.20), precipitation of iron(III) hydroxide crust occurs when $J$ is positive and $\dot{I}$ is negative.

The reactive transport system consists of four coupled ordinary differential equations. Because these equations are coupled, they are too difficult to be solved analytically. Therefore, it is necessary to solve these using numerical methods. We utilize the parameter values in Table 3.4 to create a matlab code to solve this system.

Next, we non-dimensionalize Equation (2.25), the iron-hydroxide crust growth equation, using Table 3.1 and find

$$\frac{s_t}{\sqrt{1 + \epsilon^2 s^2 x}} = - \frac{\dot{D} a_{(1)} C_{H+}^{*3} C_{H_0}^3}{\rho_{Fe(OH)_3}} + \frac{\dot{D} a_{(-1)} C_{Fe^{3+}}^{*}}{\rho_{Fe(OH)_3}} C_{Fe^{3+}_0}. \quad (3.66)$$

Performing an asymptotic expansion on Equation (3.66), the iron-hydroxide crust growth equation, we must use a binomial expansion to evaluate the fractional power in the denominator. Thus, we note that

$$\frac{s_t}{\sqrt{1 + \epsilon^2 s^2 x}} = s_t \left[ 1 - \frac{1}{2} \epsilon^2 s^2 x + \cdots \right].$$

Now, we have the leading order problem,

$$s_{0t} = - \left( \frac{\dot{D} a_{(1)} C_{H+}^{*3}}{\rho_{Fe(OH)_3}} \right) C_{H_0}^3 + \left( \frac{\dot{D} a_{(-1)} C_{Fe^{3+}}^{*}}{\rho_{Fe(OH)_3}} \right) C_{Fe^{3+}_0}. \quad (3.67)$$

We note that the crust growth rate in Equation (3.67) is a function of $C_{H_0}^3$ and $C_{Fe^{3+}_0}$. Since the system of concentration equations must be solved numerically,
because $s_0$, is a function of concentration, it must also be solved numerically. To match the form of Equations (3.62)-(3.65), we re-dimensionalize Equation (3.67) utilizing Table 3.1 and find,

$$s_0 = \left(\frac{\kappa_1}{\rho_{Fe(OH)_3}}\right) C_{H_0}^3 + \left(\frac{\kappa_{-1}}{\rho_{Fe(OH)_3}}\right) C_{Fe^{3+}_0}. \quad (3.68)$$

In order to solve this system, we use a standard matlab ordinary differential equation solver. The solver we utilize is ode15s, and implements multistep numerical differentiation. The ode15s solver is stable for all systems of first or second order. Because the system for the model is first order, utilizing ode15s will produce a stable solution.

A grid study for resolution in $x$ is conducted by comparing the data on the domain $1 < x < 4000$, for increments $dx = 1$cm and $dx = 10$cm. Results indicate that there is no noticeable difference in the concentration graphs or graphs of interface growth for the two increments. For this reason, we allow the change in $x$ at each step to be $10$cm. Similarly, a grid study for $t$ is performed on a domain $0 < t < 3.1536 \cdot 10^7$. This indicates that a one year period can be discretized into $10,000$ time steps.

A sensitivity analysis on the parameters of the system is conducted by making small variations in the magnitude of parameters, such as $\hat{Q}$, $K_{MT}$, $\theta$ and all reaction rates. This will determine whether small variations in the magnitude of each of these parameters causes drastic differences in the output of the program. The numerical solution procedure can be viewed in more detail in Appendix F.

Table 3.4 is a list of parameters utilized in the model, and their values. In
Table 3.4, the forward reaction rate for surface reactions $k_1$ is derived from work done by Kirby et al. [17]. The remaining reaction rates: $k_{-1}$, $\kappa_1$, and $\kappa_{-1}$ and the mass transfer coefficient, $K_{MT}$, are chosen to fit data obtained from the Mushroom Farm [10].
Table 3.4: Non-dimensional variables

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forward Reaction rate for Surface Reaction: $\kappa_1$</td>
<td>$1 , \text{cm} \cdot \text{L}^2 \text{sec}^{-1} \cdot \text{mg}^{-2}$</td>
</tr>
<tr>
<td>Backward Reaction Rate for Surface Reaction: $\kappa_{-1}$</td>
<td>$0.17 , \text{cm} \cdot \text{L}^2 \text{sec}^{-1} \cdot \text{mg}^{-2}$</td>
</tr>
<tr>
<td>Forward Reaction Rate for Bulk Reaction: $k_1$</td>
<td>$2.5 \cdot 10^{-7} , \text{sec} \cdot \text{mg}^8 \cdot \text{L}^{-8}$</td>
</tr>
<tr>
<td>Backward Reaction Rate for Bulk Reaction: $k_{-1}$</td>
<td>$2.5 \cdot 10^{-3} , \text{sec} \cdot \text{mg}^3 \cdot \text{L}^{-3}$</td>
</tr>
<tr>
<td>Dynamic Viscosity: $\mu$</td>
<td>$0.01 , \text{g} \cdot \text{sec}^{-1} \cdot \text{cm}^{-1}$</td>
</tr>
<tr>
<td>Density of water: $\rho$</td>
<td>$1 , \text{g} \cdot \text{cm}^{-3}$</td>
</tr>
<tr>
<td>Gravity: $g$</td>
<td>$980 , \text{cm} \cdot \text{sec}^{-2}$</td>
</tr>
<tr>
<td>Net Flux of Oxygen to the Crust: $F_c$</td>
<td>$1 \cdot 10^{-7} , \text{cm} \cdot \text{mg} \cdot \text{sec}^{-1} \cdot \text{L}^{-1}$</td>
</tr>
<tr>
<td>Henry’s Constant for Oxygen : $K_H$</td>
<td>$41.6 , \text{mg} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$</td>
</tr>
<tr>
<td>Partial Pressure of Oxygen: $P_{O_2}$</td>
<td>$0.2 , \text{atm}$</td>
</tr>
<tr>
<td>Angle of Inclination: $\theta$</td>
<td>$\frac{0.03\pi}{180}$</td>
</tr>
<tr>
<td>Density of Iron-Hydroxide Crust : $\rho_{Fe(OH)_3}$</td>
<td>$3.3 \cdot 10^{-6} , \text{mg} \cdot \text{L}^{-1}$</td>
</tr>
<tr>
<td>Mass Transfer Coefficient for Oxygen: $K_{MT}$</td>
<td>$0.37 , \text{cm} \cdot \text{sec}^{-1}$</td>
</tr>
</tbody>
</table>
CHAPTER IV
SOLUTIONS AND RESULTS

This chapter utilizes the mathematical model and the solution to describe the growth of the iron-hydroxide crust. Behavior of significant chemical species is also interpreted. Exploration of the chemical kinetics at the iron-hydroxide surface provide insight into the impact of chemical species on the precipitation and dissolution of the iron-hydroxide crust.

4.1 Analysis of Significant Chemical Species

The transport of important chemical species in this model are expressed in Equations (3.62)-(3.65). Each of these concentrations is considered over the entire length of flow away from the AMD emergence site.

Figure 4.1 is the pH profile for the AMD liquid. In Figure 4.1 we see that the pH decreases from 4.2 to about 2.9 over a 35 meter distance. The decrease in pH is consistent with the trend in experimental data [10]. From Equation (3.62), the concentration of hydrogen ions is a function of the sink due to bulk reactions multiplied by the thickness of the liquid AMD added to the source due to surface reactions. Because the pH of the system is decreasing, hydrogen ion concentration is increasing. The model is developed to promote iron(III) hydroxide crust growth to
simulate the Mushroom Farm system. Because of this, in Equation (3.62) we must have $J > 0$ and $\hat{I} < 0$. An increase in hydrogen ion concentration indicates that the surface reactions are dominating in the control of pH. After 35 meters, the pH becomes constant, and from Equation (3.62), $J = \hat{I} = 0$, because net change in ion concentration is no longer apparent. This indicates that the minimum pH occurs about 35 meters away from the source.

Figure 4.2 is the concentration profile for dissolved oxygen in the AMD liquid. The model approximation closely fits data collected from the Mushroom Farm. In Figure 4.2 we see that dissolved oxygen concentration increases rapidly from 3
mg/L to about 5.8 mg/L in the first few centimeters from the emergence site. This rapid rise in oxygen concentration occurs because when the AMD is in the mine it is oxygen-starved. Upon entering the open atmosphere, immediately the amount of oxygen entering the AMD increases. The mass transfer across the air-liquid interface in Equation (3.63) controls the behavior of the dissolved oxygen concentration for the first few centimeters from the emergence site. After the initial jump in oxygen concentration, in Figure 4.2 the dissolved oxygen concentration remains a constant value of 5.8 mg/L until about 30 meters from the emergence site. The constant concentration occurs because of the balance between the net flux of oxygen into the AMD, net flux of oxygen from the liquid to the crust, and the sink due to bulk reactions.
Because the model simulates crust growth, the source due to bulk reactions must be negative, \( \dot{I} < 0 \). The net flux of oxygen from the air into the liquid must balance with the removal of oxygen due to bulk reactions and the loss of oxygen to the iron(III) hydroxide crust. From 30 meters to 34 meters from the AMD emergence site there is a linear increase in oxygen concentration to 8.2 mg/L. As shown in Figure 4.3, all possible Fe(II) under the conditions imposed by the model has been removed from the AMD 30 meters from the emergence site. Equation (3.63) indicates that having no net change in concentration of Fe(II) implies \( \dot{I} = 0 \). Thus mass transfer across the air-liquid interface controls the concentration of oxygen until 34 meters from the AMD emergence site. At 35 meters from the emergence site the net flux of oxygen at the air-liquid interface equilibrates with the atmosphere.

Figure 4.3 is the concentration profile for Fe(II) ions in the AMD liquid. In Figure 4.3 we see that concentration of Fe(II) decreases linearly from 600 mg/L to about 50 mg/L over a 30 meter distance. The linear behavior of the decrease in Fe(II) concentration is also consistent with experimental data [10]. From Equation (3.64), the concentration of Fe(II) is a function of the sink due to bulk reactions multiplied by the thickness of the liquid AMD. The linear decreasing behavior in Figure 4.3 indicates that the bulk reactions in the system have a constant negative slope and therefore the bulk reaction rates are constant and \( \dot{I} \), the sink due to bulk reactions, has a negative value. Recall that \( \dot{I} < 0 \) promotes iron(III) hydroxide crust growth. After 30 meters, the concentration levels of Fe(II) become constant, and from Equa-
Figure 4.3: The change in Fe(II) concentration in the AMD as it flows away from the mine.

From integrated reaction (3.64), the bulk reactions have reduced to zero. This indicates that the maximum Fe(II) removal occurs about 30 meters away from the source.

Figure 4.4 is the concentration profile for Fe(III) ions in the AMD liquid. From Figure 4.4, the concentration of Fe(III) decreases slowly from 5.6 mg/L to about 5.4 mg/L for the first 25 meters from the mine. A rapid decrease in Fe(III) concentration occurs 25 meters to 35 meters from the emergence site, where the concentration of Fe(III) has the constant value of a little over 4.7 mg/L. From Equation (3.65) when \( \dot{I} < 0 \) and \( J > 0 \) iron(III) hydroxide crust is formed. The decrease in Fe(III) concentration implies that the magnitude of \( J \) is less than \( \dot{I} \) multiplied by
Figure 4.4: The change in Fe(III) concentration in the AMD as it flows away from the mine.

the thickness of the liquid from the emergence site until 35 meters from the emergence site, where they become balanced. Because the thickness of the AMD liquid is constant, the cause for the rapid decrease in Fe(III) concentration at 25 meters from the emergence site must be that the disparity in magnitude between $\dot{I}$ and $J$ increased.

Figure 4.5(a) shows the crust growth that occurs at 91.25, 182.5, 273.75, and 365 days from the AMD emergence site to 40 meters away from the mine. We see that there is fairly constant growth of crust throughout the year from the emergence of the mine to about 30 meters away. From Equation (3.68), growth at the $\dot{z} = \dot{s}(\dot{x}, \dot{t})$ interface is a function of hydrogen ion and Fe(III) concentration. The forward and
backward rate of bulk reactions, and density of the iron(III) hydroxide crust are constant for the model. The concentrations of hydrogen ions and Fe(III) balance in such a way that the rate of Fe(OH)_3 growth is constant from the AMD emergence site to about 25 meters from the mine over the course of a year. Then, the value of $J$ in Equation (3.68) is constant from the AMD emergence site to about 25 meters from the mine. From Figure 4.5(a), at about 35 meters from the mine, the iron(III)-hydroxide crust shows little growth over the course of a year due to depletion of reactants downstream as shown in Figure 4.3. This is consistent with data from the Mushroom Farm [10], yet the growth rate of the model does exceed that observed from data.

Figure 4.5(b) shows the seasonal changes for interface growth in a year, built into the model. In Appendix F, the flow rate, $\dot{Q}$, is defined as a sine function where
two periods occur over the course of a year. This simulates the alternating dry and rainy seasons that occur at the Mushroom Farm. During seasons that are near the crest of the waves, the crust is growing at a slightly greater rate. Seasons represented by the troughs of the sine waves have a slightly slower crust growth rate.

Figure 4.6: The growth in $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ and $\hat{z} = \hat{h}(\hat{x}, \hat{t})$ interfaces located 1 meter from the emergence site over time.

Figures 4.6-4.8 depict the growth of iron(III) hydroxide crust during the course of a year. Figure 4.6 represents the growth at the location 1 meter away from the AMD emergence site, and Figure 4.7 represents the growth at the location 13.5 meters away from the AMD emergence site. Interface growth for distances 1
Figure 4.7: The growth in $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ and $\hat{z} = \hat{h}(\hat{x}, \hat{t})$ interfaces located 13.5 meters from the emergence site over time.

and 13.5 meters from the emergence site are almost linearly increasing at a relatively constant rate throughout the year. The deviations from linearity are caused by the modelling of seasonal changes as seen in Figure 4.5(b). From Equation (3.68), we have $J > 0$. Because the density of the iron(III) hydroxide crust is held constant, $J$ must also be near constant at locations 1 and 13.5 meters from the AMD emergence site. Interface growth 27 meters from emergence is not constantly increasing as seen in Figure 4.8. The interface growth is always increasing at the distance 27 meters, so by Equation (3.68) we may still assume $J > 0$. The deviation from linearity occurs because of the seasonal changes imposed upon the model as seen in Figure 4.5(b).

Now we vary several parameters in the system to see how their changes affect
concentrations of chemical species and iron(III) hydroxide crust growth. The mass transfer coefficient of oxygen is varied to simulate an oxygen starved and an oxygen rich system. Then, the flow rate varies with angle of inclination followed by variation in the angle of inclination with fixed flow rates. This is followed by variation in the angle of inclination with fixed fluid film thickness. Finally, reaction rates are varied to analyze their impact on the system.

4.2 Varying Mass Transfer Coefficient

We vary the value of the mass transfer coefficient, $K_{MT}$, to observe the impact the presence of oxygen has in the AMD. Low values for $K_{MT}$ simulate an oxygen starved
system, while larger values of $K_{MT}$ simulate an oxygen rich system. The greater the concentration of oxygen in the AMD, the larger the negative value of $\hat{I}$. This implies lower concentrations for Fe(II), and hydrogen ions, and a higher concentration for Fe(III). From Equation (3.68), with lower concentrations of hydrogen ions and greater concentrations of Fe(III), the rate of iron(III) hydroxide crust growth increases. With greater values of $K_{MT}$, the rate of iron(III) hydroxide crust growth increases.

Figure 4.9(a)  

Figure 4.9(b)

Figure 4.9: (a) The change in hydrogen ion concentration in the AMD as it flows away from the mine with varying mass transfer coefficient for oxygen, $K_{MT}$ having units $\text{cm sec}^{-1}$. (b) The change in oxygen concentration in the AMD as it flows away from the mine with varying mass transfer coefficient for oxygen, $K_{MT}$ having units $\text{cm sec}^{-1}$.

In Figure 4.9(a) $K_{MT}$ values are varied to be 0.17, 0.27, and 0.37 $\text{cm sec}^{-1}$. When $K_{MT}$ is 0.17, 0.27, and 0.37 $\text{cm sec}^{-1}$ the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.64 mg/L at 30 meters from the mine. The concentration of hydrogen ions over the 30 meter distance was greater for lower $K_{MT}$ values.
Figure 4.10(a)  
Figure 4.10(b)  

Figure 4.10: (a) The change in Fe(II) concentration in the AMD as it flows away from the mine with varying mass transfer coefficient for oxygen, $K_{MT}$ having units $\text{cm} \text{sec}^{-1}$. (b) The change in Fe(III) concentration in the AMD as it flows away from the mine with varying mass transfer coefficient for oxygen, $K_{MT}$ having units $\text{cm} \text{sec}^{-1}$.

Figure 4.11(a)  
Figure 4.11(b)  

Figure 4.11: (a) The growth of the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 13.5 meters from the AMD emergence site with varying mass transfer coefficient for oxygen, $K_{MT}$ having units $\text{cm} \text{sec}^{-1}$. (b) The growth of the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 27 meters from the AMD emergence site with varying mass transfer coefficient for oxygen, $K_{MT}$ having units $\text{cm} \text{sec}^{-1}$.

The larger negative values of $\hat{I}$, by Equation (3.63), the lower the concentration of hydrogen ions.
Figure 4.9(b) displays change in oxygen concentration when the mass transfer coefficient, $K_{MT}$, varies. When $K_{MT}$ is $0.17 \text{ cm/sec}$ the oxygen concentration increases from 3 mg/L at the emergence site to 4.2 mg/L at 30 meters from the mine. At a $K_{MT}$ value of $0.27 \text{ cm/sec}$ the oxygen concentration increases from 3 mg/L at the emergence site to 5.7 mg/L 30 meters from the mine. When $K_{MT}$ is $0.37 \text{ cm/sec}$ the oxygen concentration increases from 3 mg/L at the emergence site to 6.4 mg/L at 30 meters from the mine. Figure 4.9(b) indicates that the larger the value of $K_{MT}$, the greater the net increase in oxygen concentration. This is consistent with Equation (3.63), where $K_{MT}$ is a source term for oxygen.

Figure 4.10(a) displays change in Fe(II) concentration when the mass transfer coefficient, $K_{MT}$, varies. When $K_{MT}$ is $0.17 \text{ cm/sec}$ the Fe(II) concentration decreases 600 mg/L at the emergence site to slightly more than 125 mg/L at 30 meters from the mine. At a $K_{MT}$ value of 0.27 and 0.37 $\text{ cm/sec}$ the Fe(II) concentration decreases from 600 mg/L at the emergence site to 125 mg/L 30 meters from the mine. Figure 4.10(a) indicates that the larger the value of $K_{MT}$, the greater the net decrease in Fe(II) concentration. From Equation (3.63) larger values of $K_{MT}$ lead to greater oxygen concentration. Greater oxygen concentration leads to larger negative values for $\hat{I}$. Equation (3.64) indicates that Fe(II) concentration is lower for larger negative values of $\hat{I}$.

Figure 4.10(b) displays change in Fe(III) concentration when the mass transfer coefficient for oxygen, $K_{MT}$, varies. When $K_{MT}$ is $0.17 \text{ cm/sec}$ the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to slightly less than 5.05 mg/L at
30 meters from the mine. At a $K_M T$ value of 0.27 and 0.37 cm/sec the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5.05 mg/L 30 meters from the mine. Figure 4.10(b) indicates that the smaller the value of $K_M T$, the lower the net decrease in Fe(III) concentration. From Equation (3.63) larger values of $K_M T$ lead to greater oxygen concentration. Greater oxygen concentration leads to larger negative values for $\hat{I}$. From Equation (3.65), the concentration of Fe(III) is larger for greater negative values of $\hat{I}$.

For larger values of $K_M T$, $\hat{I}$ becomes a larger negative value. Larger negative values for $\hat{I}$ produce smaller concentrations of hydrogen ions and higher concentration of Fe(III) from Equations (3.62) and (3.65). Equation (3.68) indicates that lower hydrogen ion concentrations and higher concentrations of Fe(III) provide a faster iron(III) hydroxide crust growth rate. This trend appears in Figures 4.11(a) and 4.11(b). Figure 4.11(a) is the growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 13.5 meters from the AMD emergence site with varying mass transfer coefficients. Figure 4.11(b) is the growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 27 meters from the AMD emergence site with varying mass transfer coefficients. The iron(III) hydroxide crust growth increases as $K_M T$ increases. We conclude that larger values of $K_M T$ produce an increase in Fe(OH)$_3$ crust growth.

4.3 Varying Flow Rate with a Fixed Angle of Inclination

Varying the flow rate of the system while maintaining a fixed angle of inclination imposes changes in the thickness of the fluid film layer. In Equations (3.62)-(3.65),
\[ \left( \frac{3Q \mu}{\rho g \sin \theta} \right)^{1/3} \] is the thickness of the liquid layer. Increasing \( \dot{Q} \) while maintaining a fixed angle of inclination simulates increasing the amount of bulk solution. Increasing the fluid film thickness increases the impact of \( \dot{I} \) on Equations (3.62)-(3.65). This decreases the concentrations of hydrogen ions, oxygen, and Fe(II) with increasing \( \dot{Q} \). Increasing \( \dot{Q} \) increases the concentration of Fe(III) by increasing the fluid film thickness. By Equation (3.68), lower concentrations of hydrogen ions and higher concentrations of Fe(III) induce faster growth at the \( \dot{s} = (\dot{x}, \dot{t}) \) interface. Hence, a large flow rate, \( \dot{Q} \), indicates a greater rate of iron(III) hydroxide crust growth.

Figure 4.12(a) \hspace{1cm} Figure 4.12(b)

Figure 4.12: (a) The change in hydrogen ion concentration in the AMD as it flows away from the mine, with varying flow rate, \( \dot{Q} \) with units \( \text{cm}^2\text{sec}^{-1} \). (b) The change in oxygen concentration in the AMD as it flows away from the mine, with varying flow rate, \( \dot{Q} \) with units \( \text{cm}^2\text{sec}^{-1} \).

In Figure 4.12(a) \( \dot{Q} \) values are varied to be 3, 5, and 7 \( \text{cm}^2\text{sec}^{-1} \), with a fixed angle of inclination. When \( \dot{Q} \) is 3 \( \text{cm}^2\text{sec}^{-1} \) the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.95 mg/L at 30 meters from the mine. At a
Figure 4.13: (a) The change in Fe(II) concentration in the AMD as it flows away from the mine, with varying flow rate, $\hat{Q}$ with units $\text{cm}^2/\text{sec}$. (b) The change Fe(III) concentration in the AMD as it flows away from the mine, with varying flow rate, $\hat{Q}$ with units $\text{cm}^2/\text{sec}$.

Figure 4.14: (a) The growth in the $\hat{e} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 13.5 meters from the AMD emergence site with varying flow rate, $\hat{Q}$ in $\text{cm}^2/\text{sec}$ with a fixed angle of inclination. (b) The growth in the $\hat{e} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 27 meters from the AMD emergence site with varying flow rate, $\hat{Q}$ in $\text{cm}^2/\text{sec}$ with a fixed angle of inclination.

$\hat{Q}$ value of 5 $\text{cm}^2/\text{sec}$ the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.65 mg/L 30 meters from the mine. When $\hat{Q}$ is 7 $\text{cm}^2/\text{sec}$ the hydrogen
ion concentration increases from 0.063 mg/L at the emergence site to 0.2 mg/L at 30 meters from the mine. Figure 4.12(a) indicates that the larger the value of $\hat{Q}$, the slower the increase in hydrogen ion concentration. From Equation (3.62), smaller values of $\hat{Q}$ imply smaller fluid thickness. Fluid thickness multiplies $\hat{I}$ in Equation (3.62), and $\hat{I}$ has a negative value. A larger fluid thickness induced by an increase in $\hat{Q}$ causes a decrease in hydrogen ion concentration. Then, the greater the value of $\hat{Q}$, the lower the concentration of hydrogen ions.

Figure 4.12(b) displays change in oxygen concentration when the flow rate, $\hat{Q}$, varies with a fixed angle of inclination. When $\hat{Q}$ is $3 \text{ cm}^2\text{ sec}^{-1}$ the oxygen concentration increases from 3 mg/L at the emergence site to 8.4 mg/L at 30 meters from the mine. At a $\hat{Q}$ value of $5 \text{ cm}^2\text{ sec}^{-1}$ the oxygen concentration increases from 3 mg/L at the emergence site to 6.5 mg/L 30 meters from the mine. When $\hat{Q}$ is $7 \text{ cm}^2\text{ sec}^{-1}$ the oxygen concentration increases from 3 mg/L at the emergence site to 5.5 mg/L at 30 meters from the mine. Figure 4.12(b) indicates that the larger the value of $\hat{Q}$, the faster the increase in oxygen concentration. In Equation (3.63), larger values of $\hat{Q}$ imply larger fluid thickness. Fluid thickness multiplies $\hat{I}$ in Equation (3.63), and $\hat{I}$ has a negative value. A larger fluid thickness induced by an increase in $\hat{Q}$ with a fixed flow rate causes a decrease in oxygen concentration.

Figure 4.13(a) displays change in Fe(II) concentration when the flow rate, $\hat{Q}$, varies with a fixed angle of inclination. When $\hat{Q}$ is $3 \text{ cm}^2\text{ sec}^{-1}$ the Fe(II) concentration decreases from 600 mg/L at the emergence site to 30 mg/L at 30 meters from the mine. At a $\hat{Q}$ value of $5 \text{ cm}^2\text{ sec}^{-1}$ the Fe(II) concentration decreases from 600 mg/L at
the emergence site to 50 mg/L 30 meters from the mine. When \( \dot{Q} \) is 7 cm\(^2\) sec\(^{-1}\) the Fe(II) concentration decreases from 600 mg/L at the emergence site to 200 mg/L at 30 meters from the mine. Figure 4.13(a) indicates that the larger the value of \( \dot{Q} \), the slower the decrease in Fe(II) concentration. In Equation (3.64), larger values of \( \dot{Q} \) imply larger fluid thickness. Fluid thickness multiplies \( \dot{I} \) in Equation (3.64), and \( \dot{I} \) has a negative value. A larger fluid thickness induced by an increase in \( \dot{Q} \) with a fixed flow rate causes a decrease in Fe(II) concentration.

Figure 4.13(b) displays change in Fe(III) concentration when the flow rate, \( \dot{Q} \), varies. When \( \dot{Q} \) is 3 cm\(^2\) sec\(^{-1}\) the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 4.75 mg/L at 30 meters from the mine. At a \( \dot{Q} \) value of 5 cm\(^2\) sec\(^{-1}\) the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5.05 mg/L 30 meters from the mine. When \( \dot{Q} \) is 7 cm\(^2\) sec\(^{-1}\) the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5 mg/L at 30 meters from the mine. Figure 4.13(b) indicates that the greater the value of \( \dot{Q} \), the higher the Fe(III) concentration. In Equation (3.65), larger values of \( \dot{Q} \) imply larger fluid film thickness. Fluid thickness multiplies \( \dot{I} \) in Equation (3.65), and \( \dot{I} \) has a negative value. A larger fluid thickness induced by an increase in \( \dot{Q} \) with a fixed flow rate causes an increase in Fe(III) concentration.

From Equation (3.68) the smaller the value of \( \dot{Q} \), the smaller the concentration of Fe(III) and the higher the concentration of hydrogen ion concentration. Equation (3.68) highe hydrogen ion concentrations and low Fe(III) concentrations imply a lower iron(III) hydroxide crust growth rate. This trend appears in Figures
4.14(a) and 4.14(b). Figure 4.14(a) shows the growth in the \( \dot{z} = \dot{s}(\dot{x}, \dot{t}) \) interface over time at a location 13.5 meters from the AMD emergence site with varying flow rate, \( \dot{Q} \) with a fixed angle of inclination. Figure 4.14(b) is the growth in the \( \dot{z} = \dot{s}(\dot{x}, \dot{t}) \) interface over time at a location 27 meters from the AMD emergence site with varying flow rate, \( \dot{Q} \) with a fixed angle of inclination. The greater the value of \( \dot{Q} \) the greater the rate of crust growth due to an increase of bulk solution.

4.4 Varying Angle of Inclination with a Fixed Flow Rate

We vary the angle of inclination with fixed flow rates. By Equations (3.62)-(3.65), changing values for \( \theta \) with fixed \( \dot{Q} \) forces the fluid film thickness to change. As the angle of inclination increases, the fluid film thickness decreases by Equations (3.62)-(3.65). Then the volume of bulk solution decreases. By Equations (3.62)-(3.65), as the fluid film thickness decreases, the fluid flow velocity increases. With increasing fluid flow velocity, there is less time for ions in the system to react and form Fe(OH)\(_3\). Then, with increasing \( \theta \), the rate of formation of iron(III) hydroxide crust decreases.

In Figure 4.15(a) \( \theta \) values are varied to be 0.03°, 1.5°, and 5°, with a fixed flow rate. When \( \theta \) is 0.03°, the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.65 mg/L at 30 meters from the mine. At a \( \theta \) value of 1.5° the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.66 mg/L 30 meters from the mine. When \( \theta \) is 5°, the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.68 mg/L at 30 meters from the
Figure 4.15: (a) The change in hydrogen ion concentration in the AMD as it flows away from the mine, with varying angle of inclination, $\theta$ with a fixed flow rate 13.5 meters from the mine. (b) The change in oxygen concentration in the AMD as it flows away from the mine, with varying angle of inclination, $\theta$ with a fixed flow rate 27 meters from the mine.

Figure 4.16: (a) The change in Fe(II) concentration in the AMD as it flows away from the mine, with varying angle of inclination, $\theta$. (b) The change in Fe(III) concentration in the AMD as it flows away from the mine, with varying angle of inclination, $\theta$.

mine. Figure 4.15(a) indicates that the larger the value of $\theta$, the slower the increase in hydrogen ion concentration. From Equation (3.62), larger values of $\theta$ imply smaller fluid thickness. Fluid thickness multiplies $\hat{I}$ in Equation (3.62), and $\hat{I}$ has a negative
Figure 4.17: (a) The growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 13.5 meters from the AMD emergence site while varying angle of inclination, $\theta$ with a fixed flow rate. (b) The growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 27 meters from the AMD emergence site while varying angle of inclination, $\theta$ with a fixed flow rate.

value. A smaller fluid thickness induced by an increase in $\theta$ causes an increase in hydrogen ion concentration.

Figure 4.15(b) displays change in oxygen concentration when the angle of inclination, $\theta$, varies. When $\theta$ is $0.03^\circ$, the oxygen concentration increases from 3 mg/L at the emergence site to 5.03 mg/L at 30 meters from the mine. At a $\theta$ value of $1.5^\circ$ the oxygen concentration increases from 3 mg/L at the emergence site to 5.02 mg/L 30 meters from the mine. When $\theta$ is $5^\circ$, the oxygen concentration increases from 3 mg/L at the emergence site to 5 mg/L at 30 meters from the mine. Figure 4.15(b) indicates that the larger the value of $\theta$, the faster the increase in oxygen concentration. In Equation (3.63), larger values of $\theta$ imply smaller fluid thickness. Fluid thickness multiplies $\hat{I}$ in Equation (3.63), and $\hat{I}$ has a negative value. A smaller fluid thickness induced by an increase in $\theta$ with a fixed flow rate causes an increase
in oxygen concentration.

Figure 4.16(a) displays change in Fe(II) concentration when the angle of inclination, $\theta$, varies with fixed flow rates. When $\theta$ is 0.03°, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 70 mg/L at 30 meters from the mine. At a $\theta$ value of 1.5° the Fe(II) concentration decreases from 600 mg/L at the emergence site to 80 mg/L 30 meters from the mine. When $\theta$ is 5°, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 80 mg/L at 30 meters from the mine. Figure 4.16(a) indicates that the larger the value of $\theta$, the slower the decrease in Fe(II) concentration. In Equation (3.64), larger values of $\theta$ imply smaller fluid thickness. Fluid thickness multiplies $\hat{I}$ in Equation (3.64), and $\hat{I}$ has a negative value. A smaller fluid thickness induced by an increase in $\theta$ with a fixed flow rate causes an increase in Fe(II) concentration.

Figure 4.16(b) displays change in Fe(III) concentration when the angle of inclination, $\theta$, varies with fixed flow rates. When $\theta$ is 0.03°, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5.03 mg/L at 30 meters from the mine. At a $\theta$ value of 1.5° the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5.02 mg/L 30 meters from the mine. When $\theta$ is 5°, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5 mg/L at 30 meters from the mine. Figure 4.16(b) indicates that the greater the value of $\theta$, the smaller the Fe(III) concentration. In Equation (3.65), larger values of $\theta$ imply smaller fluid thickness. Fluid thickness multiplies $\hat{I}$ in Equation (3.65), and $\hat{I}$ has a negative value. A smaller fluid thickness induced by an increase in $\theta$ with a fixed flow rate causes a
decrease in Fe(II) concentration.

From Equation (3.68) the smaller the value of $\theta$, the higher the concentration of Fe(III) and lower the concentration of hydrogen ion concentration. Equation (3.68) shows low hydrogen ion concentrations and high Fe(III) concentrations imply a greater iron(III) hydroxide crust growth rate. This trend appears in Figures 4.17(a) and 4.17(b). Figure 4.17(a) is the growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 13.5 meters from the AMD emergence site with varying angle of inclination, $\theta$ with a fixed flow rate. Figure 4.17(b) is the growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 27 meters from the AMD emergence site with varying angle of inclination, $\theta$ with a fixed flow rate.

4.5 Varying Angle of Inclination with a Fixed Fluid Film Thickness

Now we vary the angle of inclination with fixed values for the fluid film thickness. By Equations (3.62)-(3.65), changing values for $\theta$ with fixed fluid film thickness forces $\hat{Q}$ to change. As the angle of inclination increases the flow rate increases by Equations (3.62)-(3.65). Then the fluid velocity increases. With increasing fluid flow velocity, there is less time for ions in the system to react and form Fe(OH)$_3$. With increasing $\theta$, the flow rate increases and the fluid velocity increases. Then, with increasing $\theta$, the rate of formation of iron(III) hydroxide crust decreases.

In Figure 4.18(a) $\theta$ values are varied to be 0.03°, 3°, and 6° with a fixed fluid film thickness. When $\theta$ is 0.03°, the hydrogen ion concentration increases from 0.063
Figure 4.18: (a) The change in hydrogen ion concentration in the AMD as it flows away from the mine, with varying angle of inclination, $\theta$ with a fixed fluid film thickness. (b) The change in oxygen concentration in the AMD as it flows away from the mine, with varying angle of inclination, $\theta$ with a fixed fluid film thickness.

Figure 4.19: (a) The change in Fe(II) concentration in the AMD as it flows away from the mine, with varying angle of inclination, $\theta$ with a fixed fluid film thickness. (b) The change in Fe(III) concentration in the AMD as it flows away from the mine, with varying angle of inclination, $\theta$ with a fixed fluid film thickness.

mg/L at the emergence site to 0.68 mg/L at 30 meters from the mine. At a $\theta$ value of $3^\circ$ the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.7 mg/L 30 meters from the mine. When $\theta$ is $6^\circ$, the hydrogen ion concentration
increases from 0.063 mg/L at the emergence site to 0.7 mg/L at 30 meters from the mine. Figure 4.18(a) indicates that the larger the value of $\theta$, the greater the net increase in hydrogen ion concentration. From Equation (3.62), larger values of $\theta$ with fixed fluid thickness implies an increase in the flow rate of the system. The increase in flow rate causes some of the ions to move through the sheet flow system without having the opportunity to react.

Figure 4.18(b) displays change in oxygen concentration when the angle of inclination, $\theta$, varies with a fixed fluid film thickness. When $\theta$ is 0.03° the oxygen concentration increases from 3 mg/L at the emergence site to 6.5 mg/L at 30 meters from the mine. At a $\theta$ value of 3°, the oxygen concentration increases from 3 mg/L at the emergence site to 6.8 mg/L 30 meters from the mine. When $\theta$ is 6°, the oxygen concentration increases from 3 mg/L at the emergence site to 6.8 mg/L at 30 meters
from the mine. Figure 4.18(b) indicates that the larger the value of $\theta$, the greater the net increase in oxygen concentration. In Equation (3.63), larger values of $\theta$ with fixed fluid thickness implies an increase in the flow rate of the system. The increase in flow rate causes some of the ions to move through the sheet flow system without having the opportunity to react.

Figure 4.19(a) displays change in Fe(II) concentration when the forward rate for surface reactions, $\theta$, varies with a fixed fluid film thickness. When $\theta$ is 0.03°, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 60 mg/L at 30 meters from the mine. At a $\theta$ value of 3°, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 70 mg/L 30 meters from the mine. When $\theta$ is 6°, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 70 mg/L at 30 meters from the mine. Figure 4.19(a) indicates that the larger the value of $\theta$, the smaller the net decrease in Fe(II) concentration. In Equation (3.64), larger values of $\theta$ with fixed fluid thickness implies an increase in the flow rate of the system. The increase in flow rate causes some of the ions to move through the sheet flow system without having the opportunity to react, causing less reduction of Fe(II).

Figure 4.19(b) displays change in Fe(III) concentration when the forward rate for surface reactions, $\theta$, varies with a fixed fluid film thickness. When $\theta$ is 0.03°, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5.03 mg/L at 30 meters from the mine. At a $\theta$ value of 3°, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5.02 mg/L 30 meters from the mine. When $\theta$ is 5°, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to
5 mg/L at 30 meters from the mine. Figure 4.19(b) indicates that the greater the value of $\theta$, the smaller the Fe(III) concentration. Larger values of $\theta$ with fixed fluid thickness implies an increase in the flow rate of the system. The increase in flow rate causes some of the ions to move through the sheet flow system without having the opportunity to react, causing less formation of Fe(III).

From Equation (3.68) the larger the value of $\theta$, the lower the concentration of Fe(III) and higher the concentration of hydrogen ion concentration. Equation (3.68) high hydrogen ion concentrations and low Fe(III) concentrations imply a slower iron(III) hydroxide crust growth rate. This trend appears in Figures 4.20(a) and 4.20(b). Figure 4.20(a) is the growth in the $z = \hat{s}(\hat{x}, \hat{t})$ interface located 27 meters from the emergence site over time with varying angle of inclination with a fixed fluid film thickness. Figure 4.20(b) is the growth in the $z = \hat{s}(\hat{x}, \hat{t})$ interface located 32 meters from the emergence site over time with varying angle of inclination with a fixed fluid film thickness. Figure 4.20(a) shows that as the angle of inclination increases at a fixed fluid film thickness, the rate of crust growth decreases. Figure 4.20(b) indicates that as the angle of inclination increases at a fixed fluid film thickness, the rate of crust growth increases. The rate of crust growth appears to increase as the angle of inclination increases in Figure 4.20(b) because a greater value for $\theta$ implies a greater fluid velocity. At lower angles of inclination, oxidation and precipitation reactions can occur at locations close to the mine and are not carried as far downstream as those with faster fluid velocities. At greater angles of inclination, chemical species are washed further downstream because of the faster fluid velocity. Then there are more
reactive chemical species available downstream with a greater angle of inclination.

4.6 Varying Surface Reaction Rates

Next, the backward surface reaction rate, $\kappa_{-1}$ and forward surface reaction rate, $\kappa_{1}$ are varied. Increasing $\kappa_{-1}$ promotes the dissolution of Fe(OH)$_3$. By Reaction 1.2, as $\kappa_{-1}$ increases, the concentration of Fe(OH)$_3$ decreases and the concentration of Fe(III) increases. Increasing $\kappa_{-1}$ causes slower iron(III) hydroxide crust growth. By Reaction 1.2, increasing $\kappa_{1}$ promotes the precipitation of Fe(OH)$_3$. Increasing $\kappa_{1}$ promotes a faster iron(III) hydroxide crust growth.

![Figure 4.21(a)](image1)
![Figure 4.21(b)](image2)

Figure 4.21: (a) The change in hydrogen ion concentration in the AMD as it flows away from the mine, when varying $\kappa_{-1}$ with units $\frac{cm-L}{sec-mg}$. (b) The change in oxygen concentration in the AMD as it flows away from the mine, when varying $\kappa_{-1}$ with units $\frac{cm-L}{sec-mg}$.

In Figure 4.21(a) $\kappa_{-1}$ values are varied to be 0.085, 0.17, and 0.34 $\frac{cm-L}{sec-mg}$. When $\kappa_{-1}$ is 0.085 $\frac{cm-L}{sec-mg}$, the hydrogen ion concentration increases from 0.063 mg/L.
Figure 4.22: (a) The change in Fe(II) concentration in the AMD as it flows away from the mine, when varying $\kappa_{-1}$ with units $\text{cm}^{-1} \cdot \text{L sec}^{-1} \cdot \text{mg}$. (b) The change in Fe(III) concentration in the AMD as it flows away from the mine, when varying $\kappa_{-1}$ with units $\text{cm}^{-1} \cdot \text{L sec}^{-1} \cdot \text{mg}$.

Figure 4.23: (a) The growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 13.5 meters from the AMD emergence site with varying $\kappa_{-1}$ with units $\text{cm}^{-1} \cdot \text{L sec}^{-1} \cdot \text{mg}$. (b) The growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 27 meters from the AMD emergence site with varying $\kappa_{-1}$ with units $\text{cm}^{-1} \cdot \text{L sec}^{-1} \cdot \text{mg}$.

at the emergence site to .13 mg/L at 30 meters from the mine. At a $\kappa_{-1}$ value of 0.17 $\text{cm}^{-1} \cdot \text{L sec}^{-1} \cdot \text{mg}$, the hydrogen ion concentration increases from 0.63 mg/L at the emergence site to 0.7 mg/L 30 meters from the mine. When $\kappa_{-1}$ is 0.34 $\text{cm}^{-1} \cdot \text{L sec}^{-1} \cdot \text{mg}$, the hydrogen ion
concentration increases from 0.063 mg/L at the emergence site to 1.2 mg/L at 30 meters from the mine. Figure 4.21(a) indicates that the smaller the value of $\kappa_{-1}$, the lower the hydrogen ion concentration. From Equation (2.20) smaller values of $\kappa_{-1}$ lead to smaller values for $J$. From Equation (3.62), the concentration of hydrogen ions decreases with smaller values of $J$.

Figure 4.21(b) displays change in oxygen concentration when the forward rate for surface reactions, $\kappa_{-1}$, varies. When $\kappa_{-1}$ is 0.085 \( \frac{\text{cm} \cdot \text{L}}{\text{sec} \cdot \text{mg}} \), the oxygen concentration increases from 3 mg/L at the emergence site to 6.1 mg/L at 30 meters from the mine. At a $\kappa_{-1}$ value of 0.17 \( \frac{\text{cm} \cdot \text{L}}{\text{sec} \cdot \text{mg}} \) the oxygen concentration increases from 3 mg/L at the emergence site to 6.8 mg/L 30 meters from the mine. When $\kappa_{-1}$ is 0.34 \( \frac{\text{cm} \cdot \text{L}}{\text{sec} \cdot \text{mg}} \), the oxygen concentration increases from 3 mg/L at the emergence site to 7.6 mg/L at 30 meters from the mine. Figure 4.21(b) indicates that the smaller the value of $\kappa_{-1}$, the greater the oxygen concentration up to about 35 meters from the mine. After this point, the oxygen concentration for $\kappa_{-1}$ at 0.34 \( \frac{\text{cm} \cdot \text{L}}{\text{sec} \cdot \text{mg}} \) becomes greater than the concentration of oxygen at $\kappa_{-1}$ at 0.085 and 0.17 \( \frac{\text{cm} \cdot \text{L}}{\text{sec} \cdot \text{mg}} \). At a location about 31 meters from the AMD emergence site, it becomes the case that the lower the value of $\kappa_{-1}$ the lower the oxygen concentration.

Figure 4.22(a) displays change in Fe(II) concentration when the backward rate for surface reactions, $\kappa_{-1}$, varies. When $\kappa_{-1}$ is 0.085 \( \frac{\text{cm} \cdot \text{L}}{\text{sec} \cdot \text{mg}} \), the Fe(II) concentration decreases from 600 mg/L at the emergence site to 340 mg/L at 30 meters from the mine. At a $\kappa_{-1}$ value of 0.17 \( \frac{\text{cm} \cdot \text{L}}{\text{sec} \cdot \text{mg}} \), the Fe(II) concentration decreases from 600 mg/L at the emergence site to 70 mg/L 30 meters from the mine. When $\kappa_{-1}$ is 0.34
the Fe(II) concentration decreases from 600 mg/L at the emergence site to 25 mg/L at 30 meters from the mine. Figure 4.22(a) indicates that the smaller the value of $\kappa_{-1}$, the greater the Fe(II) concentration. Increases in hydrogen ion concentration and increases in Fe(III) concentration with decreasing $\kappa_{-1}$ cause larger negative values for $\hat{I}$. Equation (3.64) indicates that Fe(II) concentration is lower for larger negative values of $\hat{I}$.

Figure 4.22(b) displays change in Fe(III) concentration when the backward rate for surface reactions, $\kappa_{-1}$, varies. When $\kappa_{-1}$ is 0.085 cm·L/sec·mg, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5.55 mg/L at 30 meters from the mine. At a $\kappa_{-1}$ value of 0.17 cm·L/sec·mg the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5 mg/L 30 meters from the mine. When $\kappa_{-1}$ is 0.34 cm·L/sec·mg, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to nearly 0 mg/L at 30 meters from the mine. Figure 4.22(b) indicates that the smaller the value of $\kappa_{-1}$, the greater the Fe(III) concentration. From Equation (2.20) smaller values of $\kappa_{-1}$ lead to smaller values for $J$. From Equation (3.65), the concentration of Fe(III) increases with larger values of $J$.

From Equation (2.20) the smaller the value of $\kappa_{-1}$, the smaller the value of $J$. Smaller values of $J$ imply slower iron(III) hydroxide crust growth. Equation (3.68) indicates that smaller values of $J$ provide a slower iron(III) hydroxide crust growth rate. This trend appears in Figures 4.23(a). In Figure 4.23(a) the growth of the iron(III) hydroxide crust is greatest for when $\kappa_{-1}$ is the greatest. In Figure 4.23(b), we see that the iron(III) hydroxide crust growth is greatest for the lowest value of
κ_{-1}. This occurs because most of the ions have reacted before the AMD reaches 27 meters away from the mine. Then in Figure 4.23(b) because most of the reactions occur closer to the AMD emergence there are very few reactions occurring further away from the mine. The iron(III) hydroxide crust growth decreases as κ_{-1} decreases near the AMD emergence site and increases at greater distances away from the mine.

In Figure 4.24(a) κ_{1} values are varied to be 0.001, 1, and 100 \( \text{cm}^{-1} \text{L}^2 \text{sec}^{-1} \text{mg}^{-2} \). When κ_{1} is 0.001 \( \text{cm}^{-1} \text{L}^2 \text{sec}^{-1} \text{mg}^{-2} \), the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.3 mg/L at 30 meters from the mine. At a κ_{1} value of 1 \( \text{cm}^{-1} \text{L}^2 \text{sec}^{-1} \text{mg}^{-2} \), the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.7 mg/L 30 meters from the mine. When κ_{1} is 100 \( \text{cm}^{-1} \text{L}^2 \text{sec}^{-1} \text{mg}^{-2} \), the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 1 mg/L at 30
Figure 4.25(a)  
Figure 4.25(b)

Figure 4.25: (a) The change in Fe(II) concentration in the AMD as it flows away from the mine, with varying forward rates for surface reactions, $\kappa_1$, with units $\text{cm} \cdot \text{L}^2 \cdot \text{sec} \cdot \text{mg}^2$. (b) The change Fe(III) concentration in the AMD as it flows away from the mine, with varying forward rates for surface reactions, $\kappa_1$, with units $\text{cm} \cdot \text{L}^2 \cdot \text{sec} \cdot \text{mg}^2$.

Figure 4.26(a)  
Figure 4.26(b)

Figure 4.26: (a) The growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 13.5 meters from the AMD emergence site with varying forward rate for surface reactions. (b) The growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 27 meters from the AMD emergence site with varying forward rate for surface reactions.

meters from the mine. Figure 4.24(a) indicates that the smaller the value of $\kappa_1$, the greater the increase in hydrogen ion concentration over the 30 meter distance. From
Equation (2.20) smaller values of $\kappa_1$ lead to larger the values for $J$. From Equation (3.62), the concentration of hydrogen ions increases with larger values of $J$.

Figure 4.24(b) displays change in oxygen concentration when the forward rate for surface reactions, $\kappa_1$, varies. When $\kappa_1$ is $0.001 \frac{cm\cdot L^2}{sec\cdot mg^2}$, the oxygen concentration increases from 3 mg/L at the emergence site to 6.1 mg/L at 30 meters from the mine. At a $\kappa_1$ value of $1 \frac{cm\cdot L^2}{sec\cdot mg^2}$, the oxygen concentration increases from 3 mg/L at the emergence site to 6.8 mg/L 30 meters from the mine. When $\kappa_1$ is $100 \frac{cm\cdot L^2}{sec\cdot mg^2}$, the oxygen concentration increases from 3 mg/L at the emergence site to 7.6 mg/L at 30 meters from the mine. Figure 4.24(b) indicates that the smaller the value of $\kappa_1$, the smaller the net increase in oxygen concentration over the 30 meter distance. Increases in hydrogen ion concentration and decreases in Fe(III) concentration with decreasing $\kappa_1$ cause larger negative values for $\hat{I}$. Equation (3.63) indicates that oxygen concentration is lower for larger negative values of $\hat{I}$.

Figure 4.25(a) displays change in Fe(II) concentration when the forward rate for surface reactions, $\kappa_1$, varies. When $\kappa_1$ is $0.001 \frac{cm\cdot L^2}{sec\cdot mg^2}$, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 50 mg/L at 30 meters from the mine. At a $\kappa_1$ value of $1 \frac{cm\cdot L^2}{sec\cdot mg^2}$, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 60 mg/L 30 meters from the mine. When $\kappa_1$ is $100 \frac{cm\cdot L^2}{sec\cdot mg^2}$, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 180 mg/L at 30 meters from the mine. Figure 4.25(a) indicates that the smaller the value of $\kappa_1$, the greater the net decrease in Fe(II) concentration. Increases in hydrogen ion concentration and decreases in Fe(III) concentration with decreasing $\kappa_1$ cause larger
negative values for $\hat{I}$. Equation (3.64) indicates that Fe(II) concentration is lower for larger negative values of $\hat{I}$.

Figure 4.25(b) displays change in Fe(III) concentration when the forward rate for surface reactions, $\kappa_1$, varies. When $\kappa_1$ is $0.001 \frac{cm \cdot L^2}{sec \cdot mg^2}$, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 4.6 mg/L at 30 meters from the mine. At a $\kappa_1$ value of $1 \frac{cm \cdot L^2}{sec \cdot mg^2}$ the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5 mg/L 30 meters from the mine. When $\kappa_1$ is $100 \frac{cm \cdot L^2}{sec \cdot mg^2}$, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5.5 mg/L at 30 meters from the mine. Figure 4.25(b) indicates that the smaller the value of $\kappa_1$, the faster the decrease in Fe(III) concentration. From Equation (2.20) smaller values of $\kappa_1$ lead to larger values for $J$. In Equation (3.65), the concentration of Fe(III) decreases with larger values of $J$.

From Equation (2.20) the smaller the value of $\kappa_1$, the larger the value of $J$. Larger values of $J$ imply faster iron(III) hydroxide crust growth. Similarly, larger values of $J$ imply higher concentrations of hydrogen ions and lower concentration of Fe(III) from Equations (3.62) and (3.65). Equation (3.68) indicates that higher hydrogen ion concentrations and lower concentrations of Fe(III) imply a slower crust growth rate. The lower concentration of Fe(III) and higher hydrogen ion concentrations are not the dominating factor in Equation (3.68). The controlling parameter in Equation (3.68) is $\kappa_1$ which is associated with the negative component of iron(III) hydroxide crust growth rate. When $\kappa_1$ is small, the negative component in crust growth rate is smaller and the rate of Fe(OH)$_3$ crust growth increases. This trend
appears in Figures 4.26(a) and 4.26(b). Figure 4.26(a) is the growth in the \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) interface over time at a location 13.5 meters from the AMD emergence site with varying backward rate for bulk reactions. Figure 4.26(b) is the growth in the \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) interface over time at a location 27 meters from the AMD emergence site with varying backward rate for bulk reactions.

4.7 Varying Bulk Reaction Rates

Next, the backward bulk reaction rate, \( k_{-1} \) and forward reaction rate, \( k_1 \) are varied. Increasing \( k_{-1} \) promotes the reduction of Fe(III). By Reaction 1.1, as \( k_{-1} \) increases, the concentration of Fe(III) decreases and the concentrations of Fe(II), oxygen, and hydrogen ions increase. The lower concentration of Fe(III) hinders Reaction 1.2, forcing a slower iron(III) hydroxide crust growth with increasing \( k_{-1} \). Increasing \( k_1 \) promotes the oxidation of Fe(II). By Reaction 1.1, as \( k_1 \) increases, the concentrations of Fe(II), oxygen, and hydrogen ions decrease while the concentration of Fe(III) increases. The higher concentration of Fe(III) promotes the precipitation in Reaction 1.2, implying a faster iron(III) hydroxide crust growth with increasing \( k_1 \).

In Figure 4.27(a) \( k_{-1} \) values are varied to be 0.000025, 0.0025, and 0.25 \( \frac{sec \cdot mg^3}{L^2} \). When \( k_{-1} \) is 0.000025 \( \frac{cm \cdot L^2}{sec \cdot mg^2} \) the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to .6 mg/L at 30 meters from the mine. At a \( k_{-1} \) value of 0.0025 \( \frac{sec \cdot mg^3}{L^2} \) the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.65 mg/L 30 meters from the mine. When \( k_{-1} \) is 0.25 \( \frac{sec \cdot mg^3}{L^3} \)
Figure 4.27: (a) The change in hydrogen ion concentration in the AMD as it flows away from the mine, with varying reverse reaction rates for bulk solution, \( k_{-1} \), in \( \text{sec} \cdot \text{mg}^3 \text{L}^{-3} \). (b) The change in oxygen concentration in the AMD as it flows away from the mine, with varying reverse reaction rates for bulk solution, \( k_{-1} \), in \( \text{sec} \cdot \text{mg}^3 \text{L}^{-3} \).

Figure 4.28: (a) The change in Fe(II) concentration in the AMD as it flows away from the mine, with varying reverse reaction rates for bulk solution, \( k_{-1} \), having units \( \text{sec} \cdot \text{mg}^3 \text{L}^{-3} \). (b) The change in Fe(III) concentration in the AMD as it flows away from the mine, with varying reverse reaction rates for bulk solution, \( k_{-1} \), having units \( \text{sec} \cdot \text{mg}^3 \text{L}^{-3} \).

The hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.8 mg/L at 30 meters from the mine. Figure 4.27(a) indicates that the smaller the
Figure 4.29: (a) The growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 13.5 meters from the AMD emergence site with varying backward rate for bulk reactions. (b) The growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 27 meters from the AMD emergence site with varying backward rate for bulk reactions.

value of $k_{-1}$, the lower the net increase in hydrogen ion concentration. From Equation (2.12) smaller values of $k_{-1}$ lead to larger negative values for $\hat{I}$. From Equation (3.62), the concentration of hydrogen ions decreases with larger negative values of $\hat{I}$.

Figure 4.27(b) displays change in oxygen concentration when the forward rate for surface reactions, $k_{-1}$, varies. When $k_{-1}$ is 0.000025 $\frac{sec \cdot mg}{L^3}$, the oxygen concentration increases from 3 mg/L at the emergence site to 6.4 mg/L at 30 meters from the mine. At a $k_{-1}$ value of 0.0025 $\frac{sec \cdot mg}{L^3}$ the oxygen concentration increases from 3 mg/L at the emergence site to 6.5 mg/L 30 meters from the mine. When $k_{-1}$ is 0.25 $\frac{sec \cdot mg}{L^3}$, the oxygen concentration increases from 3 mg/L at the emergence site to 7.4 mg/L at 30 meters from the mine. Figure 4.27(b) indicates that the smaller the value of $k_{-1}$, the lower the net increase in oxygen concentration. Equation (3.63) indicates that oxygen concentration is lower for larger negative values of $\hat{I}$.
Figure 4.28(a) displays change in Fe(II) concentration when the forward rate for surface reactions, $k_{-1}$, varies. When $k_{-1}$ is $0.000025 \frac{sec \cdot mg^3}{L^3}$, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 50 mg/L at 30 meters from the mine. At a $k_{-1}$ value of $0.0025 \frac{sec \cdot mg^3}{L^3}$ the Fe(II) concentration decreases from 600 mg/L at the emergence site to 55 mg/L 30 meters from the mine. When $k_{-1}$ is $0.25 \frac{sec \cdot mg^3}{L^3}$, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 120 mg/L at 30 meters from the mine. Figure 4.28(a) indicates that the smaller the value of $k_{-1}$, the larger the net decrease in Fe(II) concentration. Decreasing $k_{-1}$ causes larger negative values for $\dot{I}$, as shown in Equation (2.12). Equation (3.64) indicates that Fe(II) concentration is lower for larger negative values of $\dot{I}$.

Figure 4.28(b) displays change in Fe(III) concentration when the forward rate for surface reactions, $k_{-1}$, varies. When $k_{-1}$ is $0.000025 \frac{sec \cdot mg^3}{L^3}$, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5.1 mg/L at 30 meters from the mine. At a $k_{-1}$ value of $0.0025 \frac{sec \cdot mg^3}{L^3}$ the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5.15 mg/L 30 meters from the mine. When $k_{-1}$ is $0.25 \frac{sec \cdot mg^3}{L^3}$, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 4.9 mg/L at 30 meters from the mine. Figure 4.28(b) indicates that the smaller the value of $k_{-1}$, the lower the net decrease in Fe(III) concentration. From Equation (2.20) smaller values of $k_{-1}$ lead to larger negative values for $\dot{I}$. From Equation (3.65), the concentration of Fe(III) is larger for greater negative values of $\dot{I}$.

For smaller values of $k_{-1}$, $\dot{I}$ becomes a larger negative value. Larger negative
values for \( \hat{I} \) produce smaller concentrations of hydrogen ions and higher concentration of Fe(III) from Equations (3.62) and (3.65). Equation (3.68) indicates that lower hydrogen ion concentrations and higher concentrations of Fe(III) provide a faster iron(III) hydroxide crust growth rate. This trend appears in Figures 4.29(a) and 4.29(b). Figure 4.29(a) is The growth in the \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) interface over time at a location 13.5 meters from the AMD emergence site with varying backward rate for bulk reactions. Figure 4.29(b) is the growth in the \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) interface over time at a location 27 meters from the AMD emergence site with varying backward rate for bulk reactions. The iron(III) hydroxide crust growth increases as \( k_{-1} \) decreases. Therefore, we conclude that smaller values of \( k_{-1} \) produce an increase in Fe(OH)\(_3\)

Figure 4.30(a) and Figure 4.30(b)

Figure 4.30: (a) The change in hydrogen ion concentration in the AMD as it flows away from the mine, with varying forward reaction rates for bulk solution, \( k_1 \), in \( \frac{sec \cdot mg}{L^8} \). (b) The change in oxygen concentration in the AMD as it flows away from the mine, with varying forward reaction rates for bulk solution, \( k_1 \), in \( \frac{sec \cdot mg}{L^8} \).

In Figure 4.30(a) \( k_1 \) values are varied to be \( 2.5 \times 10^{-9}, 2.5 \times 10^{-8} \) and \( 2.5 \times 10^{-7} \).
Figure 4.31: (a) The change in Fe(II) concentration in the AMD as it flows away from the mine, with varying forward reaction rates for bulk solution, $k_1$, having units $\frac{sec \cdot mg}{L^8}$. (b) The change in Fe(III) concentration in the AMD as it flows away from the mine, with varying forward reaction rates for bulk solution, $k_1$, having units $\frac{sec \cdot mg}{L^8}$.

Figure 4.32: (a) The growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 13.5 meters from the AMD emergence site with varying forward rate for bulk reactions. (b) The growth in the $\hat{z} = \hat{s}(\hat{x}, \hat{t})$ interface over time at a location 27 meters from the AMD emergence site with varying forward rate for bulk reactions.

$10^{-7} \frac{sec \cdot mg}{L^8}$. When $k_1$ is $2.5 \times 10^{-9} \frac{cm \cdot L^2}{sec \cdot mg^2}$, the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to .76 mg/L at 30 meters from the mine.
At a $k_1$ value of $2.5 \times 10^{-8} \frac{sec-mg^8}{L^8}$ the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.74 mg/L 30 meters from the mine. When $k_1$ is $2.5 \times 10^{-7} \frac{sec-mg^8}{L^8}$, the hydrogen ion concentration increases from 0.063 mg/L at the emergence site to 0.66 mg/L at 30 meters from the mine. Figure 4.30(a) indicates that the smaller the value of $k_1$, the larger the net hydrogen ion concentration. From Equation (2.12) smaller values of $k_1$ lead to smaller negative values for $\hat{I}$. From Equation (3.62), the concentration of hydrogen ions increases with smaller negative values of $\hat{I}$.

Figure 4.30(b) displays change in oxygen concentration when the forward rate for surface reactions, $k_1$, varies. When $k_1$ is $2.5 \times 10^{-9} \frac{sec-mg^8}{L^8}$, the oxygen concentration increases from 3 mg/L at the emergence site to 7.3 mg/L at 30 meters from the mine. At a $k_1$ value of $2.5 \times 10^{-8} \frac{sec-mg^8}{L^8}$ the oxygen concentration increases from 3 mg/L at the emergence site to 6.9 mg/L 30 meters from the mine. When $k_1$ is $2.5 \times 10^{-7} \frac{sec-mg^8}{L^8}$, the oxygen concentration increases from 3 mg/L at the emergence site to 6.7 mg/L at 30 meters from the mine. Figure 4.30(b)) indicates that the smaller the value of $k_1$, the greater the oxygen concentration. Equation (3.63) indicates that oxygen concentration is larger for smaller negative values of $\hat{I}$.

Figure 4.31(a) displays change in Fe(II) concentration when the forward rate for surface reactions, $k_1$, varies. When $k_1$ is $2.5 \times 10^{-9} \frac{sec-mg^8}{L^8}$, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 150 mg/L at 30 meters from the mine. At a $k_1$ value of $2.5 \times 10^{-8} \frac{sec-mg^8}{L^8}$ the Fe(II) concentration decreases from 600 mg/L at the emergence site to 100 mg/L 30 meters from the mine. When $k_1$ is $2.5 \times
10^{-7} \frac{\text{sec-mg}^8}{\text{L}^8}$, the Fe(II) concentration decreases from 600 mg/L at the emergence site to 70 mg/L at 30 meters from the mine. Figure 4.31(a) indicates that the smaller the value of $k_1$, the lower the net decrease in Fe(II) concentration. Decreasing $k_1$ causes smaller negative values for $\hat{I}$, as shown in Equation (2.12). Equation (3.64) indicates that Fe(II) concentration is larger for smaller negative values of $\hat{I}$. Therefore, the larger the value for $k_1$, the faster the oxidation of Fe(II), and the faster the removal of Fe(II).

Figure 4.31(b) displays change in Fe(III) concentration when the forward rate for surface reactions, $k_1$, varies. When $k_1$ is $2.5 \times 10^{-9} \frac{\text{sec-mg}^8}{\text{L}^8}$, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 4.9 mg/L at 30 meters from the mine. At a $k_1$ value of $2.5 \times 10^{-8} \frac{\text{sec-mg}^8}{\text{L}^8}$ the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 4.95 mg/L 30 meters from the mine. When $k_1$ is $2.5 \times 10^{-7} \frac{\text{sec-mg}^8}{\text{L}^8}$, the Fe(III) concentration decreases from 5.6 mg/L at the emergence site to 5 mg/L at 30 meters from the mine. Figure 4.31(b) indicates that the smaller the value of $k_1$, the greater the overall net decrease in Fe(III) concentration. From Equation (2.20) smaller values of $k_1$ lead to smaller negative values for $\hat{I}$. From Equation (3.65), the concentration of Fe(III) is lower for smaller negative values of $\hat{I}$.

For larger values of $k_1$, the hydrogen ion concentration is smaller and Fe(III) concentration is larger. Similarly, larger negative values of $\hat{I}$ produce lower concentrations of hydrogen ions and higher concentration of Fe(III) from Equations (3.62) and (3.65). Equation (3.68) indicates that lower hydrogen ion concentrations and higher
concentrations of Fe(III) provide a faster iron(III) hydroxide crust growth rate. Figure 4.32(a) is the growth in the \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) interface over time at a location 13.5 meters from the AMD emergence site with varying forward rate for bulk reactions. Figure 4.32(b) is the growth in the \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) interface over time at a location 27 meters from the AMD emergence site with varying forward rate for bulk reactions. From Figures 4.32(a) and 4.32(b), the greater the value of \( k_1 \), the greater the rate of crust growth. The abundance of Fe(II) oxidizing bacteria are one of the factors that induce a faster oxidation rate for Fe(II), or higher \( k_1 \) value. An increased \( k_1 \) can be obtained with an increased abundance of iron-oxidizing bacteria [2].
CHAPTER V
CONCLUSIONS

We develop a mathematical model for an AMD system that includes hydrodynamic and reactive transport. Model predictions are consistent with experimental results and results observed from literature. A thin-film fluid flow approximation is applied to the equations of fluid mechanics. Chemical kinetics are utilized to describe the reactive transport of chemical species in the bulk solution. To describe surface reactions, surface controlled kinetics driven by reactive transport to the liquid-crust interface are adopted. The hydrodynamic and reactive transport components are coupled via the free boundaries defining the crust-liquid and liquid-air interfaces. The major components that control the formation of iron(III) hydroxide crust such as: concentrations of Fe(II) and Fe(III), dissolved oxygen, pH, flow rate, angle of inclination, and reaction rates are described by the model.

Model predictions are plotted over data collected from the Mushroom Farm. These concentration profiles include Fe(II) concentration, amount of dissolved oxygen, and pH. The pH predicted by the model followed the same general trend as measured data. The amount of dissolved oxygen closely fits the data collected from the Mushroom Farm because the mass transfer coefficient for oxygen, $K_{MT}$, is chosen to fit the data. The linear decreasing profile for the change in Fe(II) concentration in
the $x$-direction closely fit the data points. Because the maximum amount of Fe(II) removal occurs approximately 30 meters from the AMD emergence site, this would be the optimal location for the placement of a limestone bed to prevent armoring and raise pH levels.

There is no available measurement of Fe(III) concentration from the Mushroom Farm, yet when plotted, we find a decrease in Fe(III) consistent with the growth in iron(III) hydroxide crust growth. The concentration is reduced to nearly zero in the bulk because it is being removed via precipitation. The growth of iron(III) hydroxide crust growth is also plotted at locations 1, 13.7, and 27 meters from the mine. Each indicates a crust growth rate of approximately 10 cm/yr. This is a slow rate of growth, similar to that of the Mushroom Farm, yet larger than the growth rate from measured data at approximately 1 cm/yr.

Several parameters were varied to observe predictions made by the model with different physical circumstances. Forcing low concentrations of dissolved oxygen in the model hindered the oxidation of Fe(II), subsequently slowing the rate of iron(III) hydroxide crust growth significantly. Increasing the angle of inclination while holding the flow rate fixed caused a slight decrease in the oxidation of Fe(II) due to flow through a thinner fluid film. It also caused a very small decrease in iron(III) hydroxide crust growth. Decreasing the flow rate of the system while maintaining a fixed angle of inclination simulated a thinning of the liquid layer of bulk solution. When flow rate was reduced, the model predicts less oxidation of Fe(II) and a slower iron(III) hydroxide crust growth rate. Because less bulk solution is available, less
iron was oxidized, providing lower concentrations of Fe(III), one of the reactants for precipitation of Fe(OH)$_3$. When the angle of inclination was increased with fixed fluid film thickness, the flow rate increased. This caused a decrease iron(III) hydroxide crust growth.

Reaction rates for the oxidation of Fe(II) as well as those for the precipitation of Fe(OH)$_3$ were varied to observe the model prediction for their impact on the system. When the forward rate for surface reactions, $\kappa_1$, and the reverse rate for bulk reactions, $k_{-1}$, were increased, they both decreased the quantity of Fe(II) oxidized and decreased the rate of iron(III) hydroxide crust production. When the reverse rate for surface reactions, $\kappa_{-1}$, and the forward rate for bulk reactions, $k_1$, were increased, they promoted an increase in Fe(II) oxidation and an increase in Fe(OH)$_3$ crust growth rate. An increase in iron oxidizing bacteria can increase the oxidation of Fe(II), due to an increased value of $k_1$. Therefore, an increase in the abundance of iron oxidizing bacteria can increase the rate of iron(III) hydroxide crust growth.

The limitations for the model are:

- Bacteria are located only on the surface of the crust.
- The model is one-dimensional in space.
- Flow is laminar.
- The model is meant to only remove iron, and no other metal ions.
- Density of iron(III) hydroxide crust is constant throughout and the crust is non-porous.
- Thermal effects are not considered in the model.
• The distance over which the AMD flows is far greater than the thickness of crust.
• The rate of iron(III) hydroxide crust growth is slow.
• Temperature effects on bacteria activity are not considered.

Future work for the model may include:

• The collection of field data from other site locations can provide insight about the usefulness of the model for systems other than the Mushroom Farm.
• A model may be developed that is more than one-dimensional in space.
• The impact of the addition of a limestone bed at the end of the maximum removal of Fe(II) may be included.
• The consequences of adding vegetation to the system and the removal of metal ions other than just Fe(II) might be considered.
• The inclusion of the impact of thermal transport terms into the model could be examined.
• Generalizing the flow rate and the angle of inclination to functions of $x$ will provide a more accurate model.

The progression and analysis of the model describes the significant characteristics of the precipitation of iron(III) hydroxide. The model exhibits the dependence of reactive transport on hydrodynamics in the process of precipitation. The various concentration representations predicted by the model are consistent with field measurements.
APPENDICES
APPENDIX A

HYDRODYNAMIC CALCULATIONS

We solve the leading order problem:

\[ u_{0x} + w_{0z} = 0, \]
\[ -p_{0x} + u_{0zz} = -\sin \theta, \]
\[ -p_{0z} = 0, \]

subject to the conditions

\[ u_0 = w_0 = 0, \]

at \( z = s_0(x,t) \) and

\[ p_0 = 0, \quad u_{0z} = 0, \]

at \( z = h(x,t) \). First, we integrate,

\[ p_{0z} = 0 \]

once with respect to \( z \). This allows us to conclude that the solution for \( p_0 \) is

\[ p_0 = \alpha(x), \]

where \( \alpha \) is some unknown function of \( x \). However, when we apply the boundary condition at \( z = h_0(x,t) \),

\[ p_0 = 0, \]
so the solution to $p_0$ is

$$p_0 \equiv 0.$$ 

This concludes the solution procedure for $p_0$. Next we solve for $u_0$. First we notice that in the governing equation,

$$-p_0 x + u_{0zz} = -\sin \theta,$$

$p_0 \equiv 0$ implies that the derivative of $p_0$ with respect to $x$ is also zero. Thus, we have the equation

$$u_{0zz} = -\sin \theta.$$ 

To solve this equation, we integrate twice with respect to $z$ to obtain $u_0$. The first integration with respect to $z$ yields

$$u_{0z} + (\sin \theta)z + \beta(x) = 0,$$

where $\beta$ is some unknown function of $x$. Applying the boundary condition at $z = h_0(x, t)$,

$$u_{0z} = 0,$$

we find

$$u_{0z} + (\sin \theta)z - h_0 \sin \theta = 0.$$ 

The second integration of this equation with respect to $z$ gives

$$u_0 + \frac{(\sin \theta)z^2}{2} - h_0(\sin \theta)z + \gamma(x) = 0,$$
where $\gamma$ is some unknown function of $x$. Solving for $u_0$ and applying the condition at $z = s_0(x, t)$,

$$u_0 = 0,$$

we have

$$u_0 = -\frac{(\sin \theta)z^2}{2} + h_0(\sin \theta)z + \frac{s_0^2 \sin \theta}{2} - s_0h_0 \sin \theta.$$

This concludes the solution procedure for $u_0$. Now, we solve for $w_0$, utilizing the governing equation

$$u_{0x} + w_{0z} = 0.$$

Since $u_0$ is now known, we can take its derivative with respect to $x$ and place it in the governing equation. This derivative is

$$u_{0x} = zh_{0x} \sin \theta + s_0s_{0x} \sin \theta - s_{0x}h_0 \sin \theta - s_0h_{0x} \sin \theta.$$

Placing this into the governing equation, we have

$$zh_{0x} \sin \theta + s_0s_{0x} \sin \theta - s_{0x}h_0 \sin \theta - s_0h_{0x} \sin \theta + w_{0z} = 0.$$

Integrating once with respect to $z$, and solving for $w_0$ we find

$$w_0 = -\sin \theta \left[ \frac{h_{0x}z^2}{2} + s_0s_{0x}z - s_{0x}h_0z - s_0h_{0x}z \right] + \xi(x),$$

where $\xi(x)$ is some unknown function of $x$. Applying the condition at $z = s_0(x, t)$,

$$w_0 = 0,$$

we have

$$\xi(x) = \sin \theta \left[ \frac{s_0^2 h_0}{2} + s_0^2 s_{0x} - s_0s_{0x}h_0 - s_0^2 h_{0x} \right].$$
Substituting for $\xi(x)$ we have

\[
w_0 = -\sin \theta \left[ \frac{h_{0x} z^2}{2} + s_0 s_{0x} z - s_{0x} h_0 z - s_0 h_{0x} z \right] \\
+ \sin \theta \left[ \frac{s_0^2 h_0}{2} + s_0^2 s_{0x} - s_0 s_{0x} h_0 - s_0^2 h_{0x} \right].
\]

A few simplifications give

\[
w_0 = \sin \theta \left[ -\frac{h_{0x} z^2}{2} - s_0 s_{0x} z + s_{0x} h_0 z + s_0 h_{0x} z - \frac{s_0^2 h_0}{2} + s_0^2 s_{0x} - s_0 s_{0x} h_0 \right].
\]

This concludes the solution to the leading order system to find $p_0$, $u_0$, and $w_0$. Next, we take the integral of $u_0$ from $s_0(x, t)$ to $h_0(x, t)$ with respect to $z$ to obtain an expression for $h_0$. This integration gives

\[
\int_s^h u_0 dz = \left[ -\sin \frac{\theta z^3}{6} + \sin \theta h_0 z^2 + \frac{s_0^2 z}{2} - \sin \theta s_0 z \right]_{s_0}^{h_0},
\]

which is equal to

\[
\int_s^{h_0} u_0 dz = -\sin \frac{\theta}{6} (h_0^3 - s_0^3) + \sin \theta h_0 \frac{1}{2} (h_0^2 - s_0^2) + \sin \frac{s_0^2}{2} (h_0 - s_0) \\
- \sin \theta h_0 s_0 (h_0 - s_0),
\]

Making simplifications, we have

\[
\int_s^{h_0} u_0 dz = \frac{\sin \theta}{3} (h_0^3 - s_0^3 - 3h_0^2 s_0 + 3h_0 s_0^2).
\]

This can also be further simplified into

\[
\int_s^{h_0} u_0 dz = \frac{\sin \theta}{3} (h_0 - s_0)^3.
\]

This integral is equal to the flow rate, which we call $Q$. Thus we have

\[
Q = \frac{\sin \theta}{3} (h_0 - s_0)^3.
\]
Now we utilize the leading order kinematic condition to make further conclusions about the system. The leading order kinematic condition is
\[
\frac{D_{Fe^{3+}}}{Ud} h_{0t} = w_0 - u_0 h_{0x}.
\]
Because \(\frac{D_{Fe^{3+}}}{Ud}\) has a small magnitude, we approximate the left-hand side of the equation by zero,
\[
0 = w_0 - u_0 h_{0x}.
\]
Since we have solutions for \(u_0\) and \(w_0\), we place them in the kinematic condition equation,
\[
\sin \theta \left[ -\frac{h_{0x} z^2}{2} - s_0 s_{0x} z + s_{0x} h_0 z + s_0 h_{0x} z - \frac{s_0^2 h_0}{2} + s_0^2 s_{0x} - s_0 s_{0x} h_0 \right] \\
- \left[ -\frac{z^2}{2} + h_0 z + \frac{s_0^2}{2} - s_0 h_0 \right] \sin \theta h_{0x} = 0.
\]
Making a few simplifications gives
\[
\sin \theta \left[ -2s_0 s_{0x} h_0 + 2s_0 h_0 h_{0x} + h_0^2 (s_{0x} - h_{0x}) + s_0^2 (s_{0x} - h_{0x}) \right] = 0.
\]
Further simplification provides
\[
\sin \theta \left[ - (s_{0x} - h_{0x}) \left( h_0^2 - 2s_0 h_0 + s_0^2 \right) \right] = 0.
\]
Finally, this can be reduced to
\[
-\frac{1}{3} \sin \theta \left[ (h_0 - s_0)^3 \right]_x = 0.
\]
From the integration of \(u_0\), we have that
\[
Q = \frac{1}{3} \sin \theta (h_0 - s_0)^3,
\]
where $Q$ is the flow rate of the system. Then we can conclude that

$$\frac{1}{3} \sin \theta \left[ (h_0 - s_0)^3 \right]_x = 0$$

implies that the flow rate of the system, $Q$, is spatially constant as it flows in the $x$-direction. Thus, $Q$ is solely a function of time. Furthermore, this provides a relationship between $s_0$ and $h_0$, and we have

$$h_0 = \left( \frac{3Q}{\sin \theta} \right)^{\frac{1}{3}} + s_0.$$
APPENDIX B

ANALYTIC HYDROGEN ION CONCENTRATION CALCULATIONS

This Appendix contains the details for the leading order and part of the first correction solutions found in the solution procedure in Chapter 3. This Appendix encompasses complete solutions for the leading order governing equations for hydrogen ions followed by all possible analytical analysis of the first correction. These calculations are utilized in the matlab code in Appendix F.

The leading order system for hydrogen ion concentration is

\[ C_{H_0^+} = 0, \]

subject to

\[ C_{H_0^+}(s_0) = 0, \]
\[ C_{H_0^+}(h_0) = 0. \]

We integrate with respect to \( z \) and have

\[ C_{H_0^+} = g(x)z + j(x), \]

where \( g(x) \) and \( j(x) \) are unknown functions of \( x \). Applying the boundary conditions we find

\[ g(x) \equiv 0. \]
The hydrogen ion concentration is solely a function of $x$ and we have

$$C_{H_0^+} = j(x).$$

To find the leading order solution for $C_{H^+}$ we resort to the first correction problem,

$$C_{H_1^+} + \frac{d^2}{D_{H^+}C_{H_1^+}} I = Pe [u_0 C_{H^+0x}]$$

subject to the conditions

$$C_{H_1^+}(s_0) = \left(\frac{D a_1 D_{Fe^3+} C_{H^+}^{4}}{D_{H^+}}\right) C_{H_0^+}^3 - \left(\frac{D a_1 D_{Fe^3+} C_{H^+}^{4}}{C_{H_1^+}^{4} D_{H^+}}\right) C_{F_e^{3+}},$$

$$C_{H_1^+}(h_0) = 0.$$

Recall that for the first correction problem:

$$I = \left[-k_1 C_{Fe^{4+}}^{4} C_{O_2}^{4} C_{H^+}^{4} C_{Fe^{2+}}^{4} C_{Fe^{3+}}^{4} + k_{-1} C_{Fe^{3+}}^{4} C_{Fe^{3+}}^{4}\right]$$

and we have,

$$C_{H_1^+} + \frac{d^2}{D_{H^+}C_{H_1^+}} \left[-k_1 C_{Fe^{4+}}^{4} C_{O_2}^{4} C_{H^+}^{4} C_{Fe^{2+}}^{4} C_{Fe^{3+}}^{4} + k_{-1} C_{Fe^{3+}}^{4} C_{Fe^{3+}}^{4}\right]$$

$$= Pe [u_0 C_{H^+0x}].$$

Next, we isolate $C_{H_1^+}$ and integrate both sides from $s_0$ to $z$ with respect to $z$ to find $C_{H_1^+}$ as follows

$$\int_{s_0}^{z} C_{H_1^+} dz = - \int_{s_0}^{z} \left(\frac{d^2}{D_{H^+}C_{H_1^+}}\right) \left[-k_1 C_{Fe^{4+}}^{4} C_{O_2}^{4} C_{H^+}^{4} C_{Fe^{2+}}^{4} C_{Fe^{3+}}^{4} + k_{-1} C_{Fe^{3+}}^{4} C_{Fe^{3+}}^{4}\right] dz$$

$$+ \int_{s_0}^{z} \left(\frac{d^2}{D_{H^+}C_{H_1^+}}\right) [k_{-1} C_{Fe^{3+}}^{4} C_{Fe^{3+}}^{4}] + Pe [u_0 C_{H^+0x}] dz.$$
Because $C_{H^+}, C_{O_2}, C_{Fe^{2+}},$ and $C_{Fe^{3+}}$ are only functions of $x$, we write

\[
C_{H^+} = A(x, t) - \left( \frac{d^2}{D_{H^+}C_{H^+}^*} \right) \left[ -k_1 C_{Fe^{2+}}^{*4} C_{H^+}^{*4} C_{Fe^{2+}}^{*4} C_{O_2}^{*4} C_{H^+}^{*4} \right] z
+ \left( \frac{d^2}{D_{H^+}C_{H^+}^*} \right) \left[ -k_1 C_{Fe^{2+}}^{*4} C_{H^+}^{*4} \right] z + P\varepsilon C_{H^+0x} \int_{s_0}^{z} u_0 dz.
\]

The boundary condition $C_{H^+} = (s_0) = \left( \frac{D_{a1} D_{Fe^{3+}} C_{Fe^{3+}}^*}{D_{H^+}} \right) C_{H^+}^{*3} - \left( \frac{D_{a1} D_{Fe^{3+}} C_{Fe^{3+}}^*}{D_{H^+} D_{H^+}} \right) C_{Fe^{3+}} = A(x, t)
\]

gives

\[
\left( \frac{D_{a1} D_{Fe^{3+}} C_{Fe^{3+}}^*/C_{H^+}^{*4}}{D_{H^+}} \right) C_{H^+}^{*3} - \left( \frac{D_{a1} D_{Fe^{3+}} C_{Fe^{3+}}^*}{C_{H^+}^{*3} D_{H^+}} \right) C_{Fe^{3+}} = A(x, t)
\]

\[
- \left( \frac{d^2}{D_{H^+}C_{H^+}^*} \right) \left[ -k_1 C_{Fe^{2+}}^{*4} C_{O_2}^{*4} C_{Fe^{2+}}^{*4} C_{O_2}^{*4} C_{H^+}^{*4} + k_1 C_{Fe^{3+}}^{*4} C_{Fe^{3+}}^{*4} \right] s_0
+ P\varepsilon C_{H^+0x} \int_{s_0}^{z} u_0 dz.
\]

Since $\int_{s_0}^{z} u_0 dz = 0$, solving for $A(x, t)$ gives

\[
A(x, t) = \left( \frac{D_{a1} D_{Fe^{3+}} C_{Fe^{3+}}^*/C_{H^+}^{*4}}{D_{H^+}} \right) C_{H^+}^{*3} - \left( \frac{D_{a1} D_{Fe^{3+}} C_{Fe^{3+}}^*}{C_{H^+}^{*3} D_{H^+}} \right) C_{Fe^{3+}}
+ \left( \frac{d^2}{D_{H^+}C_{H^+}^*} \right) \left[ -k_1 C_{Fe^{2+}}^{*4} C_{O_2}^{*4} C_{Fe^{2+}}^{*4} C_{O_2}^{*4} C_{H^+}^{*4} + k_1 C_{Fe^{3+}}^{*4} C_{Fe^{3+}}^{*4} \right] s_0.
\]

Placing the value for $A(x, t)$ back into the equation we have

\[
C_{H^+} = \left( \frac{D_{a1} D_{Fe^{3+}} C_{Fe^{3+}}^*/C_{H^+}^{*4}}{D_{H^+}} \right) C_{H^+}^{*3} - \left( \frac{D_{a1} D_{Fe^{3+}} C_{Fe^{3+}}^*}{C_{H^+}^{*3} D_{H^+}} \right) C_{Fe^{3+}}
+ \left( \frac{d^2}{D_{H^+}C_{H^+}^*} \right) \left[ -k_1 C_{Fe^{2+}}^{*4} C_{O_2}^{*4} C_{Fe^{2+}}^{*4} C_{O_2}^{*4} C_{H^+}^{*4} + k_1 C_{Fe^{3+}}^{*4} C_{Fe^{3+}}^{*4} \right] s_0
- \left( \frac{d^2}{D_{H^+}C_{H^+}^*} \right) \left[ -k_1 C_{Fe^{2+}}^{*4} C_{O_2}^{*4} C_{Fe^{2+}}^{*4} C_{O_2}^{*4} C_{H^+}^{*4} + k_1 C_{Fe^{3+}}^{*4} C_{Fe^{3+}}^{*4} \right] z
+ P\varepsilon C_{H^+0x} \int_{s_0}^{z} u_0 dz.
\]
Now we apply the condition $C_{H^+}(h_0) = 0$, and find

$$0 = \left( \frac{D a_1 D_{Fe^{3+}} C_{H^+}^{*}}{D_{H^+}^{}} \right)^{2} C_{H^+}^{3} - \left( \frac{D a_{-1} D_{Fe^{3+}} C_{Fe^{3+}}^{*}}{C_{H^+}^{*} D_{H^+}^{}} \right) C_{Fe^{3+}_0}^{3} + \left( \frac{d^2}{D_{H^+}^{*} C_{H^+}^{*}} \right) \left[ -k_1 C_{Fe^{2+}}^{*} C_{O_2}^{*} C_{Fe^{2+}}^{*} + k_{-1} C_{Fe^{3+}}^{*} \right] s_0$$

$$- \left( \frac{d^2}{D_{H^+}^{*} C_{H^+}^{*}} \right) \left[ k_{-1} C_{Fe^{3+}}^{*} + k_{-1} C_{Fe^{3+}}^{*} \right] h_0$$

$$+ Pe C_{H^+0x} \int_{s_0}^{h_0} u_0 d z.$$ 

Now, we isolate $Pe C_{H^+0x} \int_{s_0}^{h_0} u_0 d z$ on one side of the equation and obtain,

$$Pe C_{H^+0x} \int_{s_0}^{h_0} u_0 d z = - \left( \frac{D a_1 D_{Fe^{3+}} C_{H^+}^{*}}{D_{H^+}^{}} \right)^{2} C_{H^+}^{3} - \left( \frac{D a_{-1} D_{Fe^{3+}} C_{Fe^{3+}}^{*}}{C_{H^+}^{*} D_{H^+}^{}} \right) C_{Fe^{3+}_0}^{3}$$

$$- \left( \frac{d^2}{D_{H^+}^{*} C_{H^+}^{*}} \right) \left[ -k_1 C_{Fe^{2+}}^{*} C_{O_2}^{*} C_{Fe^{2+}}^{*} + k_{-1} C_{Fe^{3+}}^{*} \right] s_0$$

$$+ \left( \frac{d^2}{D_{H^+}^{*} C_{H^+}^{*}} \right) \left[ k_{-1} C_{Fe^{3+}}^{*} + k_{-1} C_{Fe^{3+}}^{*} \right] h_0.$$ 

Now we recall that $\int_{s_0}^{h_0} u_0 d z$ is equal to the flow rate $Q$. Making this replacement along with simplifying, we have

$$Pe C_{H^+0x} Q = - \left( \frac{D a_1 D_{Fe^{3+}} C_{H^+}^{*}}{D_{H^+}^{}} \right)^{2} C_{H^+}^{3} - \left( \frac{D a_{-1} D_{Fe^{3+}} C_{Fe^{3+}}^{*}}{C_{H^+}^{*} D_{H^+}^{}} \right) C_{Fe^{3+}_0}^{3}$$

$$+ \left( \frac{d^2}{D_{H^+}^{*} C_{H^+}^{*}} \right) \left[ -k_1 C_{Fe^{2+}}^{*} C_{O_2}^{*} C_{Fe^{2+}}^{*} + k_{-1} C_{Fe^{3+}}^{*} \right] (h_0 - s_0).$$

We know that $(h_0 - s_0) = \left( \frac{3Q}{\sin \theta} \right)^{\frac{1}{3}}$, and this replacement gives

$$Pe C_{H^+0x} Q = - \left( \frac{D a_1 D_{Fe^{3+}} C_{H^+}^{*}}{D_{H^+}^{}} \right)^{2} C_{H^+}^{3} - \left( \frac{D a_{-1} D_{Fe^{3+}} C_{Fe^{3+}}^{*}}{C_{H^+}^{*} D_{H^+}^{}} \right) C_{Fe^{3+}_0}^{3}$$

$$+ \left( \frac{d^2}{D_{H^+}^{*} C_{H^+}^{*}} \right) \left[ -k_1 C_{Fe^{2+}}^{*} C_{O_2}^{*} C_{Fe^{2+}}^{*} + k_{-1} C_{Fe^{3+}}^{*} \right] \left( \frac{3Q}{\sin \theta} \right)^{\frac{1}{3}},$$

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The analytical solution procedure for hydrogen concentration is complete. Now, we re-dimensionalize the solution. First, we recall,

\[ \hat{I} = \epsilon \bar{I}, \]

\[ Q = \frac{\dot{Q}_\mu}{\rho gd^3}. \]

Here, the value \( Q = \frac{\dot{Q}_\mu}{\rho gd^3} \), where the dimensional representation of \( Q, \hat{Q} \), is determined from Table 3.1 and the unit balance relationship in Equation (3.20). Making these substitutions we have

\[
P e C_{H^+0x} \frac{\dot{Q}_\mu}{\rho gd^3} = - \left( \frac{Da_1 D_{Fe^{3+}} C_{H^+}^*}{D_{H^+}} \right)^2 C_{H_0}^3 + \left( \frac{D a_{-1} D_{Fe^{3+}} C_{H^+}^*}{D_{H^+}} \right) C_{Fe^{3+}}^3
\]

\[+ \left( \frac{d^2}{\epsilon D_{H^+} C_{H^+}^*} \right) \left[ -k_1 \dot{C}_{Fe^{2+}} \dot{C}_{O_2} \dot{C}_{H^+} + k_{-1} \dot{C}_{Fe^{3+}} \right] \left( \frac{3 \dot{Q}_\mu}{\rho gd^3} \right)^{\frac{1}{3}}. \]

We also make the replacements,

\[ Da_1 = \frac{\kappa_1 d}{\epsilon D_{Fe^{3+}}}, \]

\[ Da_{-1} = \frac{\kappa_{-1} d}{\epsilon D_{Fe^{3+}}}, \]

\[ Pe = \frac{U d}{D_{H^+}}, \]

\[ U = \frac{\rho gd^2}{\mu}. \]

Then, \( Pe = \frac{\rho gd^3}{\mu D_{H^+}} \), and we have

\[
\frac{\rho gd^3}{\mu D_{H^+}} C_{H^+0x} \frac{\dot{Q}_\mu}{\rho gd^3} = - \left( \frac{\kappa_1 d}{\epsilon D_{Fe^{3+}} D_{Fe^{3+}} C_{H^+}^*}{D_{H^+}} \right)^2 C_{H_0}^3 + \left( \frac{\kappa_{-1} d}{\epsilon D_{Fe^{3+}} C_{H^+}^*}{D_{H^+}} \right) C_{Fe^{3+}}^3
\]

\[+ \left( \frac{d^2}{\epsilon D_{H^+} C_{H^+}^*} \right) \left[ -k_1 \dot{C}_{Fe^{2+}} \dot{C}_{O_2} \dot{C}_{H^+} + k_{-1} \dot{C}_{Fe^{3+}} \right] \left( \frac{3 \dot{Q}_\mu}{\rho gd^3} \right)^{\frac{1}{3}}. \]
Making simplifications, gives

\[
\frac{\hat{Q}}{D_{H^+}^+} C_{H+0_x} = - \left( \frac{\kappa_1 d C_{H+}^{*+}^2}{\epsilon D_{H+}^+} \right) C_{H_0}^{3+} + \left( \frac{\kappa_{-1} d C_{Fe^{3+}}^{*+}}{\epsilon C_{Fe^{3+}}^{*+} D_{H+}^+} \right) C_{Fe^{3+}}^3 \\
+ \left( \frac{d}{\epsilon D_{H+}^+ C_{H+}^{*+}} \right) \left[ -k_1 \hat{C}_{Fe^{2+}} \hat{C}_{O_2} \hat{C}_{H+}^{4+} + k_{-1} \hat{C}_{Fe^{3+}}^{4+} \right] \left( \frac{3\hat{Q}_\mu}{\rho g \sin \theta} \right)^{\frac{1}{3}}.
\]

We make the replacement \( C_{H+0_x} = \frac{L}{C_{H^+}^+} \hat{C}_{H_0}^+ \) and have

\[
\frac{\hat{Q} L}{D_{H^+}^+ C_{H_0}^{*+}} \hat{C}_{H_0}^+ = - \left( \frac{\kappa_1 d C_{H+}^{*+}^2}{\epsilon D_{H+}^+} \right) C_{H_0}^{3+} + \left( \frac{\kappa_{-1} d C_{Fe^{3+}}^{*+}}{\epsilon C_{Fe^{3+}}^{*+} D_{H+}^+} \right) C_{Fe^{3+}}^3 \\
+ \left( \frac{d}{\epsilon D_{H+}^+ C_{H+}^{*+}} \right) \left[ -k_1 \hat{C}_{Fe^{2+}} \hat{C}_{O_2} \hat{C}_{H+}^{4+} + k_{-1} \hat{C}_{Fe^{3+}}^{4+} \right] \left( \frac{3\hat{Q}_\mu}{\rho g \sin \theta} \right)^{\frac{1}{3}}.
\]

Multiplying all components of the equation by \( \frac{D_{H^+}^+ C_{H+}^{*+}}{L} \), we have

\[
\hat{Q} \hat{C}_{H_0}^+ = -\kappa_1 \hat{C}_{H_0}^{3+} + \kappa_{-1} \hat{C}_{Fe^{3+}}^{4+} \\
+ \left[ -k_1 \hat{C}_{Fe^{2+}} \hat{C}_{O_2} \hat{C}_{H+}^{4+} + k_{-1} \hat{C}_{Fe^{3+}}^{4+} \right] \left( \frac{3\hat{Q}_\mu}{\rho g \sin \theta} \right)^{\frac{1}{3}}.
\]
This Appendix contains the details for the leading order and part of the first correction solutions found in the solution procedure in Chapter 3. This Appendix encompasses complete solutions for the leading order governing equations for oxygen followed by all possible analytical analysis of the first correction. These calculations are utilized in the matlab code in Appendix F.

The leading order system for oxygen concentration is

\[ C_{O_2 zz} = 0, \]

subject to

\[ C_{O_2 z}(s_0) = 0, \]
\[ C_{O_2 z}(h_0) = 0. \]

We integrate with respect to \( z \) and have

\[ C_{O_2} = g(x)z + j(x), \]

where \( g(x) \) and \( j(x) \) are unknown functions of \( x \). Applying the boundary conditions we find

\[ g(x) \equiv 0. \]
The hydrogen ion concentration is solely a function of \( x \) and we have

\[
C_{O_20} = j(x).
\]

To find the leading order solution for \( C_{O_2} \) we resort to the first correction problem,

\[
C_{O_21zz} + \frac{d^2}{D_{O_2} C_{O_2}^*} \bar{I} = \frac{D_{Fe^{3+}}}{D_{O_2}} C_{O_20r} + Pe \left[ u_0 C_{O_20z} \right],
\]

subject to the conditions

\[
C_{O_21z} (s_0) = \bar{F},
\]

\[
C_{O_21z} (h_0) = \frac{\bar{K}_{MT} \left[ K_{H^+} P_{O_2} - C_{O_2}^* C_{O_20} \right]}{C_{O_2}^*}.
\]

Recall that for the first correction problem:

\[
\bar{I} = \left[ -k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 C_{Fe^{2+}}^4 C_{O_2} C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] \text{ and we have,}
\]

\[
C_{O_21zz} + \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ -k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 C_{Fe^{2+}}^4 C_{O_2} C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right]
\]

\[= Pe \left[ u_0 C_{O_20z} \right].\]

Next, we isolate \( C_{O_21zz} \) and integrate both sides from \( s_0 \) to \( z \) with respect to \( z \) to find \( C_{O_21z} \) as follows

\[
\int_{s_0}^{z} C_{O_21zz} \, dz = \int_{s_0}^{z} \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ -k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 C_{Fe^{2+}}^4 C_{O_2} C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] + Pe \left[ u_0 C_{O_20z} \right] \, dz.
\]
Because $C_{F_1}, C_{O_2}, C_{Fe^{2+}},$ and $C_{Fe^{3+}}$ are only functions of $x$, we write

$$C_{O_{2z1}} = A(x, t) - \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ -k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 + C_{Fe^{2+}}^4 C_{O_2}^4 C_{H^+}^4 \right] s_0$$

$$+ \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] s_0 + P e C_{O_{20z}} \int_{s_0}^z u_0 dz.$$

Now we apply the boundary condition $C_{O_{2z1}} (s_0) = \bar{F}$ and find,

$$\bar{F} = A(x, t) - \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ -k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 + C_{Fe^{2+}}^4 C_{O_2}^4 C_{H^+}^4 \right] s_0$$

$$+ \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] s_0 + P e C_{O_{20z}} \int_{s_0}^z u_0 dz.$$

Since $\int_{s_0}^z u_0 = 0$, solving for $A(x, t)$ gives

$$A(x, t) = \bar{F} + \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ -k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 + C_{Fe^{2+}}^4 C_{O_2}^4 C_{H^+}^4 \right] s_0$$

$$+ \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] s_0.$$

Placing the value for $A(x, t)$ back into the equation we have

$$C_{O_{2z1}} = \bar{F} + \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ -k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 + C_{Fe^{2+}}^4 C_{O_2}^4 C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] s_0$$

$$- \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ -k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 + C_{Fe^{2+}}^4 C_{O_2}^4 C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] z$$

$$+ P e C_{O_{20z}} \int_{s_0}^z u_0 dz.$$

Now we apply the condition $C_{O_{2z1}} = \frac{K_{MT} [K_H P_{O_2} - C_{O_2}^* C_{O_2}]}{C_{O_2}^*}$, and find

$$\frac{K_{MT} [K_H P_{O_2} - C_{O_2}^* C_{O_2}]}{C_{O_2}^*} = \bar{F}$$

$$+ \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ -k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 + C_{Fe^{2+}}^4 C_{O_2}^4 C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] s_0$$

$$- \left( \frac{d^2}{D_{O_2} C_{O_2}^*} \right) \left[ -k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 + C_{Fe^{2+}}^4 C_{O_2}^4 C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] h_0$$

$$+ P e C_{O_{20z}} \int_{s_0}^{h_0} u_0 dz.$$

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Now, we isolate $PeC_{O_{20}} \int_{s_0}^{h_0} u_0 dz$ on one side of the equation and obtain,

$$PeC_{O_{20}} \int_{s_0}^{h_0} u_0 dz = \frac{K_{MT} [K_H P_{O2} - C_{O_{2}}^{*} C_{O_{20}}]}{C_{O_{2}}^{*}} - \bar{F}$$

$$- \left( \frac{d^2}{D_{O_{2}} C_{O_{2}}^{*}} \right) \left[ -k_1 C_{Fe^{2+}}^{*} C_{O_{2}}^{*} C_{H^{+}}^{4} C_{Fe^{2+}}^{4} C_{O_{2}} C_{H^{+}}^{4} + k_{-1} C_{Fe^{3+}}^{*} C_{Fe^{3+}}^{4} \right] s_0$$

$$+ \left( \frac{d^2}{D_{O_{2}} C_{O_{2}}^{*}} \right) \left[ -k_1 C_{Fe^{2+}}^{*} C_{O_{2}}^{*} C_{H^{+}}^{4} C_{Fe^{2+}}^{4} C_{O_{2}} C_{H^{+}}^{4} + k_{-1} C_{Fe^{3+}}^{*} C_{Fe^{3+}}^{4} \right] h_0.$$

Now we recall that $\int_{s_0}^{h_0} u_0 dz$ is equal to the flow rate $Q$. Making this replacement along with simplifying, we have

$$PeC_{O_{20}} Q = \frac{K_{MT} [K_H P_{O2} - C_{O_{2}}^{*} C_{O_{20}}]}{C_{O_{2}}^{*}} - \bar{F}$$

$$+ \left( \frac{d^2}{D_{O_{2}} C_{O_{2}}^{*}} \right) \left[ -k_1 C_{Fe^{2+}}^{*} C_{O_{2}}^{*} C_{H^{+}}^{4} C_{Fe^{2+}}^{4} C_{O_{2}} C_{H^{+}}^{4} + k_{-1} C_{Fe^{3+}}^{*} C_{Fe^{3+}}^{4} \right] (h_0 - s_0).$$

We know that $(h_0 - s_0) = \left( \frac{3Q}{\sin \theta} \right)^{\frac{1}{3}}$, and this replacement gives

$$PeC_{O_{20}} Q = \frac{K_{MT} [K_H P_{O2} - C_{O_{2}}^{*} C_{O_{20}}]}{C_{O_{2}}^{*}} - \bar{F}$$

$$+ \left( \frac{d^2}{D_{O_{2}} C_{O_{2}}^{*}} \right) \left[ -k_1 C_{Fe^{2+}}^{*} C_{O_{2}}^{*} C_{H^{+}}^{4} C_{Fe^{2+}}^{4} C_{O_{2}} C_{H^{+}}^{4} + k_{-1} C_{Fe^{3+}}^{*} C_{Fe^{3+}}^{4} \right] \left( \frac{3Q}{\sin \theta} \right)^{\frac{1}{3}}.$$

The analytical solution procedure for oxygen concentration is complete. Now, we re-dimensionalize the solution. First, we recall,

$$\hat{I} = \epsilon \bar{I},$$

$$Q = \frac{\hat{Q}_u}{\rho g d^3}.$$
substitutions we have

\[
P e C_{O20} \dot{Q}_\mu \rho gd^3 = \frac{K_{MT} [K_H P_{O2} - C_{O2}^* C_{O20}]}{C_{O2}^*} - \bar{F} \\
+ \left( \frac{d^2}{\epsilon D_O C_{O2}^*} \right) \left[ -k_1 \hat{C}_{Fe^{2+}}^4 \hat{C}_{O2} \hat{C}_{H^+}^4 + k_{-1} \hat{C}_{Fe^{3+}}^4 \right] \left( \frac{3 \dot{Q}_\mu}{\rho gd^3} \right)^{1/3}.
\]

We also make the replacements,

\[
P e = \frac{U d}{D_O}, \\
U = \frac{\rho gd^2}{\mu}.
\]

Then, \( Pe = \frac{\rho gd^3}{\mu D_O} \), and we have

\[
\frac{\rho gd^3}{\mu D_O} C_{O20x} \dot{Q}_\mu \rho gd^3 = \frac{K_{MT} [K_H P_{O2} - C_{O2}^* C_{O20}]}{C_{O2}^*} - \bar{F} \\
+ \left( \frac{d^2}{\epsilon D_O C_{O2}^*} \right) \left[ -k_1 \hat{C}_{Fe^{2+}}^4 \hat{C}_{O2} \hat{C}_{H^+}^4 + k_{-1} \hat{C}_{Fe^{3+}}^4 \right] \left( \frac{3 \dot{Q}_\mu}{\rho gd^3} \right)^{1/3}.
\]

We let \( \bar{F} = \left( \frac{d}{\epsilon C_{O2}^* D_O} \right) F_c \), recall \( C_{O2}^* C_{O20} = \hat{C}_{O20} \), and make simplifications to obtain

\[
\frac{\dot{Q}}{D_O} C_{O20x} = \frac{K_{MT} [K_H P_{O2} - \hat{C}_{O20}]}{C_{O2}^*} - \left( \frac{d}{C_{O2}^* D_O} \right) F_c \\
+ \left( \frac{d}{\epsilon D_O C_{O2}^*} \right) \left[ -k_1 \hat{C}_{Fe^{2+}}^4 \hat{C}_{O2} \hat{C}_{H^+}^4 + k_{-1} \hat{C}_{Fe^{3+}}^4 \right] \left( \frac{3 \dot{Q}_\mu}{\rho gd^3} \right)^{1/3}.
\]

We make the replacement \( C_{O20x} = \frac{L}{C_{O2}} \hat{C}_{O20x} \) and have

\[
\frac{\dot{Q}_L}{D_O C_{O2}^*} \hat{C}_{O20x} = \frac{K_{MT} [K_H P_{O2} - \hat{C}_{O20}]}{C_{O2}^*} - \left( \frac{d}{\epsilon C_{O2}^* D_O} \right) F_c \\
+ \left( \frac{d}{\epsilon D_O C_{O2}^*} \right) \left[ -k_1 \hat{C}_{Fe^{2+}}^4 \hat{C}_{O2} \hat{C}_{H^+}^4 + k_{-1} \hat{C}_{Fe^{3+}}^4 \right] \left( \frac{3 \dot{Q}_\mu}{\rho gd^3} \right)^{1/3}.
\]
We also make the replacement \( \dot{K}_{MT} = \frac{L}{cD_{O2}} K_{MT} \), and have

\[
\frac{\dot{Q} L}{D_{O2} C_{O2}^*} \dot{C}_{O20x} = \frac{K_{MT} L}{\epsilon D_{O2} C_{O2}^*} \left[ K_{HPO2} - \dot{C}_{O20} \right] - \left( \frac{d}{\epsilon C_{O2}^* D_{O2}} \right) F_c \\
+ \left( \frac{d}{\epsilon D_{O2} C_{O2}^*} \right) \left[ -k_1 \dot{C}_{Fe}^{2+} \dot{C}_{O2} \dot{C}_{H^+} + k_{-1} \dot{C}_{Fe}^{3+} \right] \left( \frac{3\dot{Q} \mu}{\rho g \sin \theta} \right)^{\frac{1}{3}}.
\]

Multiplying all components of the equation by \( \frac{D_{O2} C_{O2}^*}{L} \), we have

\[
\dot{Q} \dot{C}_{O20x} = K_{MT} \left[ K_{HPO2} - \dot{C}_{O20} \right] - F_c \\
+ \left[ -k_1 \dot{C}_{Fe}^{2+} \dot{C}_{O2} \dot{C}_{H^+} + k_{-1} \dot{C}_{Fe}^{3+} \right] \left( \frac{3\dot{Q} \mu}{\rho g \sin \theta} \right)^{\frac{1}{3}}.
\]
APPENDIX D

ANALYTIC Fe(II) CONCENTRATION CALCULATIONS

This Appendix contains the details for the leading order and part of the first correction solutions found in the solution procedure in Chapter 3. This Appendix encompasses complete solutions for the leading order governing equations for Fe(II) followed by all possible analytical analysis of the first correction. These calculations are utilized in the matlab code in Appendix F.

The leading order system for oxygen concentration is

\[ C_{Fe^{2+}}^{0} = 0, \]

subject to

\[ C_{Fe^{2+}}^{0} (s_0) = 0, \]
\[ C_{Fe^{2+}}^{0} (h_0) = 0. \]

We integrate with respect to \( z \) and have

\[ C_{Fe^{2+}}^{0} = g(x)z + j(x), \]

where \( g(x) \) and \( j(x) \) are unknown functions of \( x \). Applying the boundary conditions we find

\[ g(x) \equiv 0. \]
The hydrogen ion concentration is solely a function of $x$ and we have

$$C_{Fe^{2+}_{0z}} = j(x).$$

To find the leading order solution for $C_{Fe^{2+}}$ we resort to the first correction problem,

$$C_{Fe^{2+}} + \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}^*} \bar{I} = Pe \left[ u_0 C_{Fe^{2+}_{0z}} \right]$$

subject to the conditions

$$C_{Fe^{2+}_{1z}}(s_0) = 0,$$

$$C_{Fe^{2+}_{1z}}(h_0) = 0.$$  

Recall that for the first correction problem:

$$\bar{I} = \left[-k_1 C_{Fe^{2+}}^{*4} C_{O_2}^{*4} C_{H^+}^{*4} C_{Fe^{2+}}^{*4} C_{O_2} C_{H^+} + k_{-1} C_{Fe^{3+}}^{*4} C_{Fe^{3+}}^{*4}\right]$$

and we have,

$$C_{Fe^{2+}} + \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}^*} \left[-k_1 C_{Fe^{2+}}^{*4} C_{O_2} C_{H^+} C_{Fe^{2+}}^{*4} C_{O_2} C_{H^+} + k_{-1} C_{Fe^{3+}}^{*4} C_{Fe^{3+}}^{*4}\right]$$

$$= Pe \left[ u_0 C_{Fe^{2+}_{0z}} \right].$$

Next, we isolate $C_{Fe^{2+}_{1z}}$ and integrate both sides from $s_0$ to $z$ with respect to $z$ to find $C_{Fe^{2+}_{1z}}$ as follows

$$\int_{s_0}^{z} C_{Fe^{2+}_{1z}} dz = \int_{s_0}^{z} \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}^*} \right) \left[-k_1 C_{Fe^{2+}}^{*4} C_{O_2} C_{H^+} C_{Fe^{2+}}^{*4} C_{O_2} C_{H^+} \right]$$

$$+ \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}^*} \right) \left[k_{-1} C_{Fe^{3+}}^{*4} C_{Fe^{3+}}^{*4}\right] + Pe \left[ u_0 C_{Fe^{2+}_{0z}} \right] dz.$$  

Because $C_{H^+}$, $C_{O_2}$, $C_{Fe^{3+}}$, and $C_{Fe^{3+}}$ are only functions of $x$, we write

$$C_{Fe^{2+}_{1z}} = A(x, t) - \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}^*} \right) \left[-k_1 C_{Fe^{2+}}^{*4} C_{O_2} C_{H^+} C_{Fe^{2+}}^{*4} C_{O_2} C_{H^+} \right] z$$

$$+ \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}^*} \right) \left[k_{-1} C_{Fe^{3+}}^{*4} C_{Fe^{3+}}^{*4}\right] z + Pe C_{Fe^{2+}_{0z}} \int_{s_0}^{z} u_0 dz.$$  

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Now we apply the boundary condition \( C_{Fe^{2+}_{1z}}(s_0) = 0 \) and find,

\[
0 = A(x, t) - \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}} \right) \left[ -k_1 C_{Fe^{2+}_{1z}} C_{O_2} C_{H^+} C_{Fe^{2+}} C_{O_2} C_{H^+} \right] s_0 \\
+ \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}} \right) \left[ k_{-1} C_{Fe^{3+}} C_{Fe^{2+}} \right] s_0 + Pe C_{Fe^{2+}} \int_{s_0}^{s_0} u_0 dz.
\]

Since \( \int_{s_0}^{s_0} u_0 dz = 0 \), solving for \( A(x, t) \) gives

\[
A(x, t) = \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}} \right) \left[ -k_1 C_{Fe^{2+}_{1z}} C_{O_2} C_{H^+} C_{Fe^{2+}} C_{O_2} C_{H^+} \right] s_0 \\
+ \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}} \right) \left[ k_{-1} C_{Fe^{3+}} C_{Fe^{2+}} \right] s_0.
\]

Placing the value for \( A(x, t) \) back into the equation we have

\[
C_{Fe^{2+}_{1z}} = \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}} \right) \left[ -k_1 C_{Fe^{2+}_{1z}} C_{O_2} C_{H^+} C_{Fe^{2+}} C_{O_2} C_{H^+} + k_{-1} C_{Fe^{3+}} C_{Fe^{2+}} \right] s_0 \\
- \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}} \right) \left[ k_{-1} C_{Fe^{3+}} C_{Fe^{2+}} C_{O_2} C_{H^+} + k_{-1} C_{Fe^{3+}} C_{Fe^{2+}} \right] z \\
+ Pe C_{Fe^{2+}} \int_{s_0}^{z} u_0 dz.
\]

Now we apply the condition \( C_{Fe^{2+}_{1z}}(h_0) = 0 \), and find

\[
0 = \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}} \right) \left[ -k_1 C_{Fe^{2+}_{1z}} C_{O_2} C_{H^+} C_{Fe^{2+}} C_{O_2} C_{H^+} + k_{-1} C_{Fe^{3+}} C_{Fe^{2+}} \right] s_0 \\
- \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}} \right) \left[ -k_1 C_{Fe^{3+}} C_{Fe^{2+}} C_{O_2} C_{H^+} + k_{-1} C_{Fe^{3+}} C_{Fe^{2+}} \right] h_0 \\
+ Pe C_{Fe^{2+}} \int_{s_0}^{h_0} u_0 dz.
\]

Now, we isolate \( Pe C_{Fe^{2+}} \int_{s_0}^{h_0} u_0 dz \) on one side of the equation and simplify to obtain,

\[
Pe C_{Fe^{2+}} \int_{s_0}^{h_0} u_0 dz = \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}} \right) \left[ -k_1 C_{Fe^{2+}_{1z}} C_{O_2} C_{H^+} C_{Fe^{2+}} C_{O_2} C_{H^+} \right] \\
+ \left( \frac{d^2}{D_{Fe^{2+}} C_{Fe^{2+}}} \right) \left[ k_{-1} C_{Fe^{3+}} C_{Fe^{2+}} \right] (h_0 - s_0).
\]

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Now we recall that \( \int_{s_0}^{h_0} u_0 dz \) is equal to the flow rate \( Q \) and \( (h_0 - s_0) = (\frac{3Q}{\sin \theta})^{\frac{1}{3}} \).

Making this replacement along with simplifying, we have

\[
PeC_{Fe^{2+}}Q = -\left( \frac{d^2}{D_{Fe^{2+}}C_{Fe^{2+}}^*} \right) k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 + \left( \frac{3Q}{\sin \theta} \right)^{\frac{1}{3}} \frac{1}{3}.
\]

The analytical solution procedure for Fe(II) concentration is complete. Now, we re-dimensionalize the solution. First, we recall,

\[
\hat{I} = \epsilon \hat{I},\]
\[
Q = \frac{\hat{Q} \mu}{\rho g d^3}.
\]

Here, the value \( Q = \frac{\hat{Q} \mu}{\rho g d^3} \), where the dimensional representation of \( Q, \hat{Q} \), is determined from Table 3.1 and the unit balance relationship in Equation (3.20). Making these substitutions we have

\[
PeC_{Fe^{2+}} \frac{\hat{Q} \mu}{\rho g d^3} = -\left( \frac{d^2}{\epsilon D_{Fe^{2+}}C_{Fe^{2+}}^*} \right) k_1 C_{Fe^{2+}}^* C_{O_2}^* C_{H^+}^4 \left( \frac{3 \frac{\hat{Q} \mu}{\rho g d^3}}{\sin \theta} \right)^{\frac{1}{3}}
\]

\[
+ \left( \frac{d^2}{\epsilon D_{Fe^{2+}}C_{Fe^{2+}}^*} \right) k_{-1} C_{Fe^{3+}}^* \left( \frac{3 \frac{\hat{Q} \mu}{\rho g d^3}}{\sin \theta} \right)^{\frac{1}{3}}.
\]

We also make the replacements,

\[
Pe = \frac{U d}{D_{Fe^{2+}}},
\]
\[
U = \frac{\rho g d^2}{\mu}.
\]
Then, $Pe = \frac{\rho gd^3}{\mu D_{Fe^{2+}}}$, and we have

$$\frac{\rho gd^3}{\mu D_{Fe^{2+}} C_{Fe^{2+}_0x}} \frac{\hat{Q} \mu}{\rho gd^3} = -\left( \frac{d^2}{\epsilon D_{Fe^{2+}} C^*_{Fe^{2+}} \epsilon D_{Fe^{2+}} C^*_{Fe^{2+}}} \right) k_1 \hat{C}^4_{Fe^{2+}} \hat{C}_{O_2} \hat{C}^4_{H+} \left( \frac{3 \hat{Q} \mu}{\rho gd^3} \right)^{\frac{1}{3}}$$

$$\text{+} \left( \frac{d^2}{\epsilon D_{Fe^{2+}} C^*_{Fe^{2+}}} \right) k_{-1} \hat{C}^4_{Fe^{3+}} \left( \frac{3 \hat{Q} \mu}{\rho gd^3} \right)^{\frac{1}{3}}.$$

Making simplifications gives

$$\frac{\hat{Q} \mu}{D_{Fe^{2+}} C_{Fe^{2+}_0x}} = -\left( \frac{d}{\epsilon D_{Fe^{2+}} C^*_{Fe^{2+}}} \right) k_1 \hat{C}^4_{Fe^{2+}} \hat{C}_{O_2} \hat{C}^4_{H+} \left( \frac{3 \hat{Q} \mu}{\rho gd^3} \right)^{\frac{1}{3}}$$

$$\text{+} \left( \frac{d}{\epsilon D_{Fe^{2+}} C^*_{Fe^{2+}}} \right) k_{-1} \hat{C}^4_{Fe^{3+}} \left( \frac{3 \hat{Q} \mu}{\rho gd^3} \right)^{\frac{1}{3}}.$$

We make the replacement $C_{Fe^{2+}_0x} = \frac{L}{C_{Fe^{2+}_0x}} \hat{C}_{Fe^{2+}}$ and have

$$\frac{\hat{Q} \mu}{D_{Fe^{2+}} C^*_{Fe^{2+}} C_{Fe^{2+}_0x}} = -\left( \frac{d}{\epsilon D_{Fe^{2+}} C^*_{Fe^{2+}}} \right) k_1 \hat{C}^4_{Fe^{2+}} \hat{C}_{O_2} \hat{C}^4_{H+} \left( \frac{3 \hat{Q} \mu}{\rho gd^3} \right)^{\frac{1}{3}}$$

$$\text{+} \left( \frac{d}{\epsilon D_{Fe^{2+}} C^*_{Fe^{2+}}} \right) k_{-1} \hat{C}^4_{Fe^{3+}} \left( \frac{3 \hat{Q} \mu}{\rho gd^3} \right)^{\frac{1}{3}}.$$

Multiplying all components of the equation by $\frac{D_{Fe^{3+}} C^*_{Fe^{3+}}}{L}$, we have

$$\hat{Q} \hat{C}_{Fe^{2+}} = -k_1 \hat{C}^4_{Fe^{2+}} \hat{C}_{O_2} \hat{C}^4_{H+} \left( \frac{3 \hat{Q} \mu}{\rho gd^3} \right)^{\frac{1}{3}}$$

$$\text{+} k_{-1} \hat{C}^4_{Fe^{3+}} \left( \frac{3 \hat{Q} \mu}{\rho gd^3} \right)^{\frac{1}{3}}.$$
APPENDIX E

ANALYTIC Fe(III) CALCULATIONS

This Appendix contains the details for the leading order and part of the first correction solutions found in the solution procedure in Chapter 3. This Appendix encompasses complete solutions for the leading order governing equations for Fe(III) followed by all possible analytical analysis of the first correction. These calculations are utilized in the matlab code in Appendix F.

The leading order system for oxygen concentration is

\[ C_{Fe^{3+}} = 0, \]

subject to

\[ C_{Fe^{3+}}(s_0) = 0, \]
\[ C_{Fe^{3+}}(h_0) = 0. \]

We integrate with respect to \( z \) and have

\[ C_{Fe^{3+}} = g(x)z + j(x), \]

where \( g(x) \) and \( j(x) \) are unknown functions of \( x \). Applying the boundary conditions we find

\[ g(x) \equiv 0. \]
The hydrogen ion concentration is solely a function of $x$ and we have

$$C_{Fe^{3+}_{0z}} = j(x).$$

To find the leading order solution for $C_{Fe^{3+}}$ we resort to the first correction problem,

$$C_{Fe^{3+}_{1zz}} - \frac{d^2}{D_{Fe^{3+}}C_{Fe^{3+}}} \bar{I} = Pe \left[ u_0 C_{Fe^{3+}_{0z}} \right]$$

subject to the conditions

$$C_{Fe^{3+}_{1z}}(s_0) = -\frac{D a_1 C_{H^+}^{*3}}{C_{Fe^{3+}}^*} C_{H_0^+}^3 + Da_1 C_{Fe^{3+}}^*,$$

$$C_{Fe^{3+}_{1z}}(h_0) = 0.$$

Recall that for the first correction problem:

$$\bar{I} = \left[ -k_1 C_{Fe^{2+}+}^*C_{O_2}^{*4}C_{H^+}^{*3} C_{Fe^{3+}}^* + k_{-1} C_{Fe^{3+}}^* C_{Fe^{3+}}^* \right]$$

and we have,

$$C_{Fe^{3+}_{1zz}} = \frac{d^2}{D_{Fe^{3+}}C_{Fe^{3+}}} \left[ -k_1 C_{Fe^{2+}+}^*C_{O_2}^{*4}C_{H^+}^{*3} C_{Fe^{3+}}^* + k_{-1} C_{Fe^{3+}}^* C_{Fe^{3+}}^* \right]$$

$$= Pe \left[ u_0 C_{Fe^{3+}_{0z}} \right].$$

Next, we isolate $C_{Fe^{3+}_{1zz}}$ and integrate both sides from $s_0$ to $z$ with respect to $z$ to find $C_{Fe^{3+}_{1z}}$ as follows

$$\int_{s_0}^{z} C_{Fe^{3+}_{1zz}} dz = \int_{s_0}^{z} \left( \frac{d^2}{D_{Fe^{3+}}C_{Fe^{3+}}} \right) \left[ -k_1 C_{Fe^{2+}+}^*C_{O_2}^{*4}C_{H^+}^{*3} C_{Fe^{3+}}^* + k_{-1} C_{Fe^{3+}}^* C_{Fe^{3+}}^* \right]$$

$$+ \left( \frac{d^2}{D_{Fe^{3+}}C_{Fe^{3+}}} \right) \left[ k_{-1} C_{Fe^{3+}}^* C_{Fe^{3+}}^* \right] + Pe \left[ u_0 C_{Fe^{3+}_{0z}} \right] dz.$$
Because \( C_{H^+}, C_{O_2}, C_{Fe^{2+}}, \) and \( C_{Fe^{3+}} \) are only functions of \( x \), we write

\[
C_{Fe^{3+}} = A(x, t) + \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}} \right) \left[ -k_1 C_{Fe^{2+}}^s C_{O_2}^s C_{H^+}^4 C_{Fe^{2+}}^4 C_{O_2} C_{H^+}^4 \right] z
\]

\[
+ \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}} \right) \left[ k_{-1} C_{Fe^{4+}}^s C_{Fe^{3+}}^4 \right] z + PeC_{Fe^{3+}} \int_{s_0}^{z} u_0 dz.
\]

Now we apply the boundary condition \( C_{Fe^{3+}}(s_0) = -\frac{Da_1 C_{H^+}^3}{C_{Fe^{3+}} H_0^3} + Da_{-1} C_{Fe^{3+}} \) and find,

\[
- \frac{Da_1 C_{H^+}^3}{C_{Fe^{3+}} H_0^3} C_{Fe^{3+}}^3 + D a_{-1} C_{Fe^{3+}} = A(x, t)
\]

\[
+ \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}} \right) \left[ -k_1 C_{Fe^{2+}}^s C_{O_2}^s C_{H^+}^4 C_{Fe^{2+}}^4 C_{O_2} C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^s C_{Fe^{3+}}^4 \right] s_0
\]

\[
+ PeC_{Fe^{3+}} \int_{s_0}^{z} u_0 dz.
\]

Since \( \int_{s_0}^{z} u_0 dz = 0 \), solving for \( A(x, t) \) gives

\[
A(x, t) = - \frac{Da_1 C_{H^+}^3}{C_{Fe^{3+}} H_0^3} C_{Fe^{3+}}^3 + D a_{-1} C_{Fe^{3+}}
\]

\[- \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}} \right) \left[ -k_1 C_{Fe^{2+}}^s C_{O_2}^s C_{H^+}^4 C_{Fe^{2+}}^4 C_{O_2} C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^s C_{Fe^{3+}}^4 \right] s_0.
\]

Placing the value for \( A(x, t) \) back into the equation we have

\[
C_{Fe^{3+}} = - \frac{Da_1 C_{H^+}^3}{C_{Fe^{3+}} H_0^3} C_{Fe^{3+}}^3 + D a_{-1} C_{Fe^{3+}}
\]

\[- \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}} \right) \left[ -k_1 C_{Fe^{2+}}^s C_{O_2}^s C_{H^+}^4 C_{Fe^{2+}}^4 C_{O_2} C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^s C_{Fe^{3+}}^4 \right] s_0
\]

\[+ \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}} \right) \left[ -k_1 C_{Fe^{2+}}^s C_{O_2}^s C_{H^+}^4 C_{Fe^{2+}}^4 C_{O_2} C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^s C_{Fe^{3+}}^4 \right] z
\]

\[+ PeC_{Fe^{3+}} \int_{s_0}^{z} u_0 dz.
\]
Now we apply the condition $C_{Fe^{3+}}(h_0) = 0$, and find

$$0 = -\frac{D\alpha_1 C_{Fe^{3+}}^3}{C_{Fe^{3+}}^3} \frac{C_{Fe^{3+}}^3}{C_{H^0}^3} + D\alpha_1 C_{Fe^{3+}}^3$$

$$- \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}^3} \right) \left[ -k_1 C_{Fe^{2+}}^4 C_{O_2} C_{H^0} C_{Fe^{2+}} C_{O_2} C_{H^0} + k_1 C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] s_0$$

$$+ \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}^3} \right) \left[ -k_1 C_{Fe^{2+}}^4 C_{O_2} C_{H^0} C_{Fe^{2+}} C_{O_2} C_{H^0} + k_1 C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] h_0$$

$$+ PeC_{Fe^{3+}} \int_{s_0}^{h_0} u_0 dz.$$

Now, we isolate $PeC_{O_{2+}} \int_{s_0}^{h_0} u_0 dz$ on one side of the equation and obtain,

$$PeC_{Fe^{3+}} \int_{s_0}^{h_0} u_0 dz = \frac{D\alpha_1 C_{Fe^{3+}}^3}{C_{Fe^{3+}}^3} \frac{C_{Fe^{3+}}^3}{C_{H^0}^3} - D\alpha_1 C_{Fe^{3+}}^3$$

$$+ \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}^3} \right) \left[ -k_1 C_{Fe^{2+}}^4 C_{O_2} C_{H^0} C_{Fe^{2+}} C_{O_2} C_{H^0} + k_1 C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] s_0$$

$$- \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}^3} \right) \left[ -k_1 C_{Fe^{2+}}^4 C_{O_2} C_{H^0} C_{Fe^{2+}} C_{O_2} C_{H^0} + k_1 C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] h_0.$$

Now we recall that $\int_{s_0}^{h_0} u_0 dz$ is equal to the flow rate $Q$. Making this replacement along with simplifying, we have

$$PeC_{Fe^{3+}} Q = \frac{D\alpha_1 C_{Fe^{3+}}^3}{C_{Fe^{3+}}^3} \frac{C_{Fe^{3+}}^3}{C_{H^0}^3} - D\alpha_1 C_{Fe^{3+}}^3$$

$$- \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}^3} \right) \left[ -k_1 C_{Fe^{2+}}^4 C_{O_2} C_{H^0} C_{Fe^{2+}} C_{O_2} C_{H^0} + k_1 C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] (h_0 - s_0).$$

We know that $(h_0 - s_0) = \left( \frac{3Q}{\sin \theta} \right)^{\frac{1}{3}}$, and this replacement gives

$$PeC_{Fe^{3+}} Q = \frac{D\alpha_1 C_{Fe^{3+}}^3}{C_{Fe^{3+}}^3} \frac{C_{Fe^{3+}}^3}{C_{H^0}^3} - D\alpha_1 C_{Fe^{3+}}^3$$

$$- \left( \frac{d^2}{D_{Fe^{3+}} C_{Fe^{3+}}^3} \right) \left[ -k_1 C_{Fe^{2+}}^4 C_{O_2} C_{H^0} C_{Fe^{2+}} C_{O_2} C_{H^0} + k_1 C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 \right] \left( \frac{3Q}{\sin \theta} \right)^{\frac{1}{3}}.$$
The analytical solution procedure for Fe(III) concentration is complete. Now, we re-dimensionalize the solution. First, we recall,

\[ \hat{I} = \epsilon \bar{I}, \]
\[ Q = \frac{\hat{Q} \mu}{\rho g d^3}. \]

Here, the value \( Q = \frac{\hat{Q} \mu}{\rho g d^3} \), where the dimensional representation of \( Q, \hat{Q} \), is determined from Table 3.1 and the unit balance relationship in Equation (3.20). Making these substitutions we have

\[ Pe C_{Fe^{3+}} \frac{\hat{Q} \mu}{\rho g d^3} = \frac{\hat{D} a_1 C^*_H C^3}{C^*_F e^{3+} C^3 H^*_0} - \hat{D} a_{-1} C^*_F e^{3+} \]
\[ - \left( \frac{d}{\epsilon D_{Fe^{3+}} C^*_F e^{3+}} \right) \left[ -k_1 \hat{C}^4_{Fe^{3+}} \hat{C} \hat{O}_2 \hat{C}^4_{H^+} + k_{-1} \hat{C}^4_{Fe^{3+}} \right] \left( \frac{3 \hat{Q} \mu}{\rho g d^3} \right)^{\frac{1}{3}} \frac{\sin \theta}{\sin \theta}. \]

We also make the replacements,

\[ \hat{D} a_1 = \frac{\kappa_1 d}{\epsilon D_{Fe^{3+}}}, \]
\[ \hat{D} a_{-1} = \frac{\kappa_{-1} d}{\epsilon D_{Fe^{3+}}}, \]
\[ P e = \frac{U d}{D_{Fe^{3+}}}, \]
\[ U = \frac{\rho g d^2}{\mu}. \]
Then, \( P_e = \frac{\rho gd^3}{\mu D_{Fe}^3} \), and we have

\[
\frac{\rho gd^3}{\mu D_{Fe}^3} C_{Fe_{0x}} \frac{\dot{Q} \mu}{\rho g \rho d^3} = \frac{\kappa_1 d C_{H_0}^3}{\epsilon D_{Fe}^3 C_{Fe_{0x}}^3} \frac{\dot{C}_{H_0}^3}{\rho g \rho d^3} - \frac{\kappa_{-1} d}{\epsilon D_{Fe}^3} C_{Fe_{0x}}^3
\]

\[
- \left( \frac{d^2}{\epsilon D_{Fe_{0x}}^3 C_{Fe_{0x}}^3} \right) \left[ -k_1 \dot{C}_{Fe_2}^4 \dot{C}_{Fe_2}^4 \dot{C}_{H_0}^4 + k_{-1} \dot{C}_{Fe_3}^4 \right] \left( \frac{3 \dot{Q} \mu}{\rho g \rho d^3} \sin \theta \right)^\frac{1}{3}.
\]

Recalling that \( \dot{C}_{H_0}^3 = C_{H_0}^3 C_{H_0}^3 \) and making simplifications, gives

\[
\frac{\dot{Q}}{D_{Fe}^3} C_{Fe_{0x}}^3 = \frac{\kappa_1 d}{\epsilon D_{Fe}^3 C_{Fe_{0x}}^3} \dot{C}_{H_0}^3 - \frac{\kappa_{-1} d}{\epsilon D_{Fe}^3} C_{Fe_{0x}}^3
\]

\[
- \left( \frac{d}{\epsilon D_{Fe}^3 C_{Fe_{0x}}^3} \right) \left[ -k_1 \dot{C}_{Fe_2}^4 \dot{C}_{Fe_2}^4 \dot{C}_{H_0}^4 + k_{-1} \dot{C}_{Fe_3}^4 \right] \left( \frac{3 \dot{Q} \mu}{\rho g \rho d^3} \sin \theta \right)^\frac{1}{3}.
\]

We make the replacement \( C_{Fe_{0x}}^3 = \frac{L}{C_{Fe_{0x}}^3} \dot{C}_{Fe_{0x}}^3 \) and have

\[
\frac{\dot{Q} L}{D_{Fe}^3 C_{Fe_{0x}}^3} \dot{C}_{Fe_{0x}}^3 = \frac{\kappa_1 d}{\epsilon D_{Fe}^3 C_{Fe_{0x}}^3} \dot{C}_{H_0}^3 - \frac{\kappa_{-1} d}{\epsilon D_{Fe}^3} C_{Fe_{0x}}^3
\]

\[
- \left( \frac{d}{\epsilon D_{Fe}^3 C_{Fe_{0x}}^3} \right) \left[ -k_1 \dot{C}_{Fe_2}^4 \dot{C}_{Fe_2}^4 \dot{C}_{H_0}^4 + k_{-1} \dot{C}_{Fe_3}^4 \right] \left( \frac{3 \dot{Q} \mu}{\rho g \rho d^3} \sin \theta \right)^\frac{1}{3}.
\]

Multiplying all components of the equation by \( \frac{D_{Fe_{0x}}^3}{L} \), we have

\[
\dot{Q} \dot{C}_{Fe_{0x}}^3 = \kappa_1 \dot{C}_{H_0}^3 - \kappa_{-1} C_{Fe_{0x}}^3
\]

\[
- \left[ -k_1 \dot{C}_{Fe_2}^4 \dot{C}_{Fe_2}^4 \dot{C}_{H_0}^4 + k_{-1} \dot{C}_{Fe_3}^4 \right] \left( \frac{3 \dot{Q} \mu}{\rho g \rho d^3} \sin \theta \right)^\frac{1}{3}.
\]
APPENDIX F

NUMERICAL REACTIVE TRANSPORT CALCULATIONS

This Appendix contains Matlab code used solve the system derived in Chapter 3. This Appendix encompasses the worksheet utilized for reactive transport calculations and is used to generate data to create graphs shown in Chapter 4. This worksheet was run on Matlab 7.1. Time stepping is done by the first order Euler method, which is sufficient due to the slow crust growth. At each time step, the concentrations are calculated by ode15s, a stiff ODE system solver.

/*Main Code:*/
/*The units used for these constants are cm, mg, g, seconds, atm, liters*/
kappa1 = 1;
kappaneg1 = .17;
k1 = 2.5e-7;
kneg1 = 2.5e-3;
mu = .01;
rho = 1;
g = 980;
Fc = 1e-7;
DO2 = 1.97e-5;
KH = 41.6;
PO2 = 0.2;
theta = .03*(pi/180);
rhoFe = 3.3e6;
K = 3.7e-1;

As =-kappa1/rhoFe;
Bs = kappaneg1/rhoFe;
PAR = [kappa1 kappaneg1 k1 kneg1 mu rho g Fc DO2 KH PO2 theta rhoFe K];

Tmax = 365*24*60*60;
nmax = 10000;
dt = Tmax/nmax;

t = 0:dt:Tmax;
x = 0:10:4000;
imax = length(x);

Q = @(t) 5*(1 + 0.1*sin(4*pi*t/Tmax));
% Initial condition
for i=1:imax
    s(i,1)=1 + .9*theta*sin(6*pi*x(i)/4000);
    h(i,1)=s(i,1)+(3*Q(t(1))*mu/rho/g/sin(theta))^(1/3);
end

%c(1)is the conc of H+, c(2)is conc of Fe2+, c(3) is conc of Fe3+ and c(4)
%is the conc of O2. The initial values in this array are the initial
%values found at AMD emergence site of the mine.
for n=1:nmax-1
    fprintf(' time step %d
',n)
    factor = 1 + .1* sin(4*pi*(t(n)/Tmax));
    C0=[.0631*factor ; 600*factor ; 5.6*factor ; 3*factor]; %oxygen third
    Qn = Q(t(n));
    [x1,C] = ode15s( @(x,C) RHSnew(x,C,PAR,Qn),x,C0);
    for i=1:imax
        s(i,n+1) = s(i,n)+dt*(As*(C(i,1)^3)+Bs*(C(i,3)));
        h(i,n+1) = s(i,n)+( 3*Qn*mu/sin(theta)/rho/g)^(1/3);
    end
end

function f= RHSnew(x,C,PAR,Qn)
    kappa1 = PAR(1);
    kappa neg1 = PAR(2);
    k1 = PAR(3);
    kneg1 = PAR(4);
    mu = PAR(5);
    rho = PAR(6);
    g = PAR(7);
    Fc = PAR(8);
    DO2 = PAR(9);
    KH = PAR(10);
    PO2 = PAR(11);
    theta = PAR(12);
    rhoFe = PAR(13);
    K = PAR(14);
    scale = (3*Qn*mu/sin(theta)/rho/g)^(1/3);
    f(1) = -kappa1*(C(1)^3) + kappa neg1*C(3) + kneg1*scale*(C(3)^4)
        - k1*scale*(C(2)^4)*(C(1)^4)*C(4);
    f(1) = f(1)/Qn;
    f(2) = kneg1*scale*(C(3)^4) -k1*scale*(C(2)^4)*(C(1)^4)*C(4);
    f(2) = f(2)/Qn;
    f(3)= kappa1*(C(1)^3)- kappa neg1*C(3)- kneg1*scale*(C(3)^4)
        +k1*scale*(C(2)^4)*(C(1)^4)*C(4);
    f(3)= f(3)/Qn;
    f(4)= K*(KH*PO2-C(4))-Fc + scale*(-k1*(C(2)^4)*(C(1)^4)*C(4)+kappa1*C(3)^4 )
        +scale*(-k1*(C(2)^4)*(C(1)^4)*C(4)+kappa1*C(3)^4 )
    f(4)= f(4)/Qn;
    f = f’;
end