A MATHEMATICAL MODEL FOR ACID MINE DRAINAGE REMOVAL AND IRON HYDROXIDE CRUST FORMATION

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A MATHEMATICAL MODEL FOR ACID MINE DRAINAGE REMOVAL AND
IRON HYDROXIDE CRUST FORMATION

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Thesis

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ABSTRACT

Acid mine drainage (AMD) is a major ecological problem in the Appalachian coal mining region. When the AMD encounters the waterways it alters the natural composition of the water by lowering the pH. The acidic, metal-rich water is harmful to biological life. Our model is a passive treatment system for thin film fluid effluents in which metals are removed and the fluids are neutralized. In turn, an iron hydroxide crust is formed due to metal removal. The model is based on the abundance of Fe(II) oxidizing bacteria (Fe(II)OB) to enhance conversion of Fe(II) to Fe(III), the availability of oxygen and the AMD Fe(II) concentration. The results predict the changes in concentrations of hydrogen, Fe(II) and Fe(III) ions over the downstream fluid run and the thickness of the crust that is formed. The model also determines the length of the fluid run needed to exhaust the Fe(II) ions from the fluid and hence, the effectiveness of the passive treatment system. Model predictions are compared to data taken from AMD at the Mushroom Farm in Mahoning County, Ohio.
Thank you to my wonderful parents, family and friends.
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CHAPTER I
INTRODUCTION

The process of coal mining has been around for over one hundred years. The coal retrieved from the ground is a leading energy source. Although coal is a natural resource, the negative impact coal mining has on the environment is undesirable.

Acidic Coal Mine Drainage (AMD) is a major ecological problem. The effects of acid mine drainage are particularly common in the Appalachian coal mining region of the United States which includes Pennsylvania, Ohio, West Virginia, Tennessee, and Kentucky. AMD has infiltrated approximately 10,000 km of waterways and aquifers [1]. The common dissolved metals in AMD are iron (Fe), aluminum (Al) and manganese (Mn). The most apparent damage is shown in the form of a Fe(III) (hydro)oxide precipitate better know as “yellowboy”. The formation of yellowboy occurs when Fe(II) contaminated AMD enters the natural waterways. Yellowboy coats algae, plants, macroinvertebrates and sediments leaving stretches of dead stream [1]. Yellowboy also lowers the pH of the water from circumneutral to acidic. Acidic water is a problem in streams which are not well buffered, however all streams are affected by the formation of yellowboy. The chemical reactions of yellowboy formation
are

\[ 4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \]  \hspace{1cm} (1.1)

\[ Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+. \]  \hspace{1cm} (1.2)

In Reaction (1.1) oxygen oxidizes Fe(II) to Fe(III). Reaction (1.2) follows as Fe(III) hydrolyzes and precipitates to form Fe(OH)_3. A common way to limit the formation of yellowboy is to remove Fe(II) before it encounters the waterways. The removal of Fe(II) will limit Reaction (1.1) and subsequently limit yellowboy in waterways (Reaction 1.2).

A variety of active and passive AMD treatment systems have been implemented. Active treatment systems use chemicals and machinery to treat AMD. Active treatments typically require the addition of alkaline reagents (limestone, hydrated lime, Mag8) using a ‘Calibrated Reagent Application Blender’ or ‘CRAB’ [2]. The ‘CRAB’ machine sprays alkaline reagent in a liquid medium. Acidic drain water plus limestone fragments are carried into the rotating drum of a machine. The drum rotation causes friction between the rocks and thus removes the metal precipitate [2]. Furthermore, this mixture is sprayed at the base of the drain. A continuous cycle occurs until the desired pH is achieved.

Another active treatment is a fluidized bed reactor (FBR). Ozkaya et al. [3] studied Fe(III) production using an artificial neural network (ANN-HEAP) to predict effluent Fe^{3+} concentration of FBR. The fluidized bed reactor stimulated oxidation of Fe(II) by a heap leaching solution. The Fe(II) concentration decreased from 8,000
to 400 mg/L within 15 days and Fe(II) oxidation was 98.5% complete [3]. The FBR model was based on a gradient descent algorithm.

Active treatment systems are capable of treating a large acidity flux but require regular addition of chemicals and can be difficult to control [2]. Also, active treatment systems have high operating costs and problems with disposal of the bulky sludge produced [4]. An alternative approach is passive treatment systems. Passive treatments are less costly, more energy efficient and require less human interaction than active approaches described above. However, the treatment could take a long period of time to remove the AMD and a variety of biological and chemical factors may alter the procedure.

A well-known passive treatment is limestone drains. The calcium carbonate in limestone neutralizes the acids. Oxidation (Reaction 1.1) and hydrolysis (Reaction 1.2) occur but the Fe(III) hydroxides coat the limestone rather than the waterways. The precipitate coating on the limestone is known as armouring. Limestone drains require little maintenance, however, build up of hydroxide precipitates may cause failure of the drains [4]. Another common passive treatment approach is anaerobic systems. Anaerobic systems depend on sulfate reducing bacteria (SRB) to increase pH and precipitate out metals. However, the precipitates may be susceptible to oxidation by atmospheric O₂ which may cause more acidic waterways and large metal flux [2].

Neculita et al. [5] conducted a study on sulfate-reducing passive bioreactors to remove Fe(II) and other metals. Over the 44 week experiment the concentration of Fe(II) decreased from 1000 mg/L to 500 mg/L. The decrease in Fe(II) concentration
significantly improved the bioreactor effectiveness. However, the sulfate-reducing bioreactor contained low counts of “culturable” SRB which may be related to the under-estimate of the number of bacteria.

A wetland-based system is an additional passive treatment system [4]. Aerobic wetlands are shallow systems that operate by surface flow and maintain oxidizing conditions. This system works to filter and stabilize the iron precipitants but other bacterial factors may contribute to the oxidation.

Since one focus of the proposed model is to oxidize Fe(II), it is important to understand the factors which dictate oxidation of this metal. Kirby et al. [6] discusses different contributions of abiotic and biological processes in Fe(II) oxidation. His model was based on a rate law for abiotic Fe(II) oxidation and a rate law of Fe(II) oxidation with the contribution of the Fe(II)OB, *Acidithiobacillus ferrooxidans*. Kirby et al. used the following differential equation to model Fe(II) oxidation,

\[
\frac{dFe^{2+}}{dt}_{\text{overall}} = -r_{\text{abiotic}} - r_{\text{biotic}}.
\]

All but one of his field sites had increased pH from anoxic limestone drains. Various sample locations were examined to determine the concentrations of Fe(II). The findings of this study showed that the abiotic Fe(II) rate law predicts an increasing oxidation rate with increasing pH, while the rate law of Fe(II) with the contribution of bacteria predicts a decreasing oxidation rate with increasing pH. However a range of factors may alter Fe(II) oxidation rates, and successful treatment requires nearly complete oxidation of Fe(II) to Fe(III) since oxidation is the rate limiting step.
Kirby et al. [7] also studied Fe(II) oxidation rates in acid mine drainage using a continuously-stirred tank reactor. The reactor is a water bath system where the stream water is pumped in and examined by probes and stirred by a motor. In this experiment, pH, dissolved oxygen, and concentration of Fe(II) were determined by “ambient” conditions while factors that might alter Fe(II) oxidation such as Fe-oxidizing bacteria were ignored. Based on the oxidation rates from the tank reactor and compared with similar studies, it is suggested that Fe(II) oxidation is influenced by both abiotic and biological factors. Furthermore, if Fe(II) oxidation is the rate limiting step in the passive treatment of AMD, the factors that influence Fe(II) oxidation should be considered.

Burke and Banwart [8] proposed another model which uses a completely mixed reactor to determine iron oxidation rates. The model includes surface-catalysed oxidation of Fe(II). Burke and Banwart used a geochemical code to determine the empirical rate laws and kinetic rate laws. The results show that Fe(II) can effectively be removed if sufficient surface area and absorption capacity of Fe(III) hydroxides are present.

The empirical rate laws were also studied by Burgos et al. [9]. The concentrations of an ionic species were formulated as

$$\frac{dC_i}{dt} = \sum_{k=1}^{N} (\nu_{ik} - \mu_{ik}) R_k,$$

where $C_i$ is the concentration of the i-th chemical species, $\nu_{ik}$ is the stoichiometry of the products, $\mu_{ik}$ is the stoichiometry of the reactants and $R_k$ is the k-th reaction rate.
In theory the summation is efficient at modelling the chemical kinetics, however, an analytic solution may not be practical. The advantage of using a reaction based model is that the rate formulations are applicable to a range of environmental conditions. The above experiments [7], [8] and [9] were all based on models that were temporally but not spatially dependent. The proposed model includes spatial dependence.

Kirby and Cravotta [10] studied the definition of net alkalinity and net acidity. Net alkalinity is the measure of a solution’s ability to react with a strong base while net acidity is the measure of a solution’s ability to react with a strong acid. Net acidity is commonly defined as the difference between acidity and alkalinity. Acidity can be calculated by,

$$\text{acidity}_{\text{calculated}} = 50[1000(10^{-pH}) + 2(Fe^{II})/56 + 3(Fe^{III})/56 + 2(Mn)/55 + 3(Al)/27],$$

where $Fe^{II}$, $Fe^{III}$, $Mn$ and $Al$ are analytical concentrations in mg/L. Although this calculation underestimates measured hydrogen ions, it overestimates the acidity from $Fe^{III}$ and $Al^{III}$ causing the errors to nearly cancel each other out. This equation incorporates more parameters than solely pH. Mine drainage waters can have a wide range of pH and $Fe^{II}/Fe^{III}$ concentrations depending on dissolved $O_2$ concentrations, $Fe^{II}$ oxidation rates, and the presence of iron-oxidizing bacteria, $Fe(OB)$. Kirby and Cravotta’s companion paper [11] studied the practical considerations of net alkalinity and net acidity. If treatment effluent is net alkaline the pH will remain near neutral after complete degassing and oxidation of the effluent, while if the treatment is net acidic the pH will decline to acidic values after oxidation and precipitation of the
dissolved metals.

Kirby et al. [12] expanded upon the Fe(II) oxidation rate in a 2009 study. The Fe(II) oxidation rate is

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

where \(a_{H^+}\) is the acidity calculated in equation (1.3). The increased pH due to CO\(_2\) degassing is critical to the treatment of net-alkaline mine drainage because it indirectly causes Fe(II) oxidation rates to increase. There were three major influences on pH change. Iron(II) oxidation and CO\(_2\) degassing cause pH to increase, while Fe(OH)\(_3\) precipitation causes pH to decrease. Kirby et al. also found that Fe(II) oxidation may require the placement of additional aeration devices downstream to ensure that O\(_2\) is replenished and does not become rate limiting.

Another important factor in the proposed model is the abundance of Fe(II) oxidizing bacteria. Johnson et al. [13] examined the influence of bacteria in acid mine drainage. The mine sites studied were in the United Kingdom, Spain and Norway. The water samples were analysed for their microbiological and physiochemical content via bioreactors. The highest numbers of iron-oxidizing bacteria were found in the more acidic AMD samples, however, the iron-oxidizing bacteria were unable to grow on the more acidic (pH 2.5-2.6) overlay of the growth medium.

Bryan and Johnson [15] studied the rate of bacterial growth. The location of this study was an abandoned copper mine in the UK. The bacterial growth was modeled as a function of temperature, pH and ferric acid. The results show isolated
Pa33, a heterotrophic iron-oxidizing acidophillic bacterium, generated diffuse zones of ferric iron. Furthermore the oxidation of ferrous iron was biological rather than an abiotic response to increasing pH.

A further experiment on bacterial communities was conducted by Senko et al. [1] at two Appalachian coal mine drainage-impact sites. The goal was to gain better understanding of AMD water chemistry, microbial activities and microbial communities. The rates of Fe(II) oxidation and precipitation were tested based on biologically mediated and abiotic reactions. The findings show that Fe(II) oxidation is dependent on the abundance of Fe(II)OB and that the availability of dissolved oxygen may have a strong control on the activity of Fe(II)OB. Overall this study shows that bacterial communities have an influence on the removal of Fe(II) in an environment similar to the Mushroom Farm.

The model is a sheetflow system which combines elements from the above passive treatment systems. The sheetflow system is depicted in Figure (1.1).

![Sheetflow System Diagram](image)

**Figure 1.1:** Proposed sheetflow system for acidic mine removal.
In Figure (1.1) the AMD emerges from the mine then flows through a sheet-flow, vegetated region and limestone bed. The sheetflow system is depicted as a thin layer of AMD flowing down a flat land surface. The sheetflow region will remove Fe and the vegetated region will remove other metals. The limestone bed will neutralize the fluids, and since the metals are removed upstream, armouring is restricted. Yellowboy is a pollutant which we want to control by promoting its precipitation. The test site of interest is the Mushroom Farm in Mahoning County, Ohio. The main goal of the system is to raise pH when necessary and precipitate out Fe(II). The model is based on the abundance of Fe(II) oxidizing bacteria (Fe(II)OB), the availability of oxygen and the AMD Fe(II) concentration. Moreover we are depicting iron hydroxide crust growth as a function of the size of the bacterial population. We assume the bacteria are contained on the surface of the crust. We expect the abundance of Fe(II)OB to change directly with the forward reaction rate of Fe(II) oxidation [16].

Although research on similar processes has been conducted, the proposed model is a passive sheetflow system which is based on the crust growth as a function of iron-oxidizing bacteria. Some of the variables under investigation in the sheetflow system are the length of the sheetflow bed, time to remove Fe(II), pH, and the impact of bacteria. Another objective is to find the growth rate of the iron hydroxide crust. The sheetflow system also depends on the transport of ionic species, through the thin film.

In the model the following assumptions will be made,

- The fluid does not carry deposited crust downstream.
• Crust is assumed to be non-porous.
• Only oxygen is allowed to transport across the liquid-air interface. No other ions are allowed to leave this interface.
• The thickness of the crust is far exceeded by the distance over which the AMD is flowing.
• Crust growth is slow.
• Bacteria are located directly on top of the crust.
• Fe(II) oxidation is occurring directly above the bacteria layer.

The results of the analytical and numerical analysis depict the concentrations of hydrogen ion, Fe(II) and Fe(III) ions along the downstream flow over a course of a year. The concentration of hydrogen ions increased over the stream run while the Fe(II) and Fe(III) decreased. The chemical reactions taper off around 3500 cm and therefore the iron hydroxide crust growth slows down. The limestone bed should be placed at 3500 cm to optimize the sheetflow system. We also found the crust growth to be 10 cm over the course of a year. In future research, we should analyze the bulk reaction rate as a function of dissolved oxygen, temperature and/or the solvability of Fe(III). Additionally, we can investigate the surface reaction rate as a function of pH.

In Chapter II, the mathematical model is formulated. In Chapter III, we have the analysis of the governing equations and boundary conditions. In Chapter IV the solution is found analytically and in Chapter V the numerical approach finalizes the results. Chapter VI contains the summary and conclusions.
CHAPTER II

FORMULATION OF THE MATHEMATICAL MODEL

The proposed mathematical model is dependent on the physical principles and chemical reactions of acidic coal mine drainage. A system of equations is needed to describe the terrain of the Mushroom Farm, the behavior of the fluid flow, the reaction of the metal ions and the movement of the air-liquid and air-crust interfaces. The model denotes the location of the crust as \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) and the air-liquid interface as \( \hat{z} = \hat{h}(\hat{x}, \hat{t}) \), where the space between the two interfaces defines the film flow. The variables with hats represent dimensional variables.

Mass conservation is depicted in (2.1) where \( \hat{u} \) represents the fluid flow downstream and \( \hat{w} \) represents the fluid flow normal to the surface,

\[
\hat{u}_x + \hat{w}_z = 0. \tag{2.1}
\]

The Navier-Stokes equations define the fluid dynamics of this flow:

\[
\hat{u}_t + \hat{u}\hat{u}_x + \hat{w}\hat{u}_z = -\frac{1}{\rho}\hat{p}_z + \nu(\hat{u}_{xx} + \hat{u}_{zz}) + g \sin \theta, \tag{2.2}
\]

\[
\hat{w}_t + \hat{u}\hat{w}_x + \hat{w}\hat{w}_z = -\frac{1}{\rho}\hat{p}_z + \nu(\hat{w}_{xx} + \hat{w}_{zz}) - g \cos \theta. \tag{2.3}
\]

Equations (2.2) and (2.3) describe the fluid dynamics of the fluid flow where \( p \) is the pressure, \( \theta \) is the angle of inclination, \( \nu \) is the fluid velocity and \( g \) is gravity.
Figure 2.1: A schematic view of the acid mine drainage model where bacteria is settled in the fluid domain.

Figure (2.1) represents a schematic view of the AMD model. The AMD flows downstream at a small angle. The crust-liquid interface is \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) and the liquid-air interface is \( \hat{z} = \hat{h}(\hat{x}, \hat{t}) \). The bacteria grow at the \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \) between the two interfaces.

The following equations define the air-liquid interface, \( \hat{z} = \hat{h}(\hat{x}, \hat{t}) \) through the kinematic condition (2.4), and the boundary conditions at this interface,

\[
\hat{h}_t = \hat{w} - \hat{u}\hat{h}_{\hat{x}}, \tag{2.4}
\]

\[
2\hat{h}_x (\hat{u}_{\hat{x}} \hat{w}_{\hat{x}}) + (1 - \hat{h}_x) (\hat{u}_{\hat{z}} + \hat{w}_{\hat{x}}) = 0, \tag{2.5}
\]

\[
-\hat{p} + \frac{\mu [\hat{u}_{\hat{x}}\hat{h}_x^2 - \hat{h}_x (\hat{u}_{\hat{z}} + \hat{w}_{\hat{x}}) + \hat{w}_{\hat{z}}]}{\sqrt{1 + \hat{h}_x^2}} = \frac{\hat{h}_{\hat{x}\hat{x}}}{(1 + \hat{h}_x^2)^{3/2}}. \tag{2.6}
\]

Here, \( \sigma \) is the surface tension of the air-liquid interface. The boundary conditions (2.5) and (2.6) imply no shear stress in the tangential direction and a normal force balance respectively. We assume no-slip conditions, \( \hat{u} = \hat{w} = 0 \), for the liquid velocities at the crust interface \( \hat{z} = \hat{s}(\hat{x}, \hat{t}) \).
The transport of $\text{O}_2$ and the ions $\text{H}^+$, $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ are given by,

\[
\frac{\partial \hat{C}_{H^+}}{\partial t} + u \frac{\partial \hat{C}_{H^+}}{\partial x} + w \frac{\partial \hat{C}_{H^+}}{\partial z} = \nabla \cdot (D_{H^+} \nabla \hat{C}_{H^+}) - k_1 \hat{C}_{Fe^{2+}}^4 \hat{C}_{O_2}^4 \hat{C}_{H^+}^4 + k_{-1} \hat{C}_{Fe^{3+}}^4 \quad (2.7)
\]

\[
\frac{\partial \hat{C}_{O_2}}{\partial t} + u \frac{\partial \hat{C}_{O_2}}{\partial x} + w \frac{\partial \hat{C}_{O_2}}{\partial z} = \nabla \cdot (D_{O_2} \nabla \hat{C}_{O_2}) - k_1 \hat{C}_{Fe^{2+}}^4 \hat{C}_{O_2}^4 \hat{C}_{H^+}^4 + k_{-1} \hat{C}_{Fe^{3+}}^4 \quad (2.8)
\]

\[
\frac{\partial \hat{C}_{Fe^{2+}}}{\partial t} + u \frac{\partial \hat{C}_{Fe^{2+}}}{\partial x} + w \frac{\partial \hat{C}_{Fe^{2+}}}{\partial z} = \nabla \cdot (D_{Fe^{2+}} \nabla \hat{C}_{Fe^{2+}}) - k_1 \hat{C}_{Fe^{2+}}^4 \hat{C}_{O_2}^4 \hat{C}_{H^+}^4 + k_{-1} \hat{C}_{Fe^{3+}}^4 \quad (2.9)
\]

\[
\frac{\partial \hat{C}_{Fe^{3+}}}{\partial t} + u \frac{\partial \hat{C}_{Fe^{3+}}}{\partial x} + w \frac{\partial \hat{C}_{Fe^{3+}}}{\partial z} = \nabla \cdot (D_{Fe^{3+}} \nabla \hat{C}_{Fe^{3+}}) + k_1 \hat{C}_{Fe^{2+}}^4 \hat{C}_{O_2}^4 \hat{C}_{H^+}^4 + k_{-1} \hat{C}_{Fe^{3+}}^4 \quad (2.10)
\]

In these governing equations, $D_i$ represents the mass diffusivity of species $i$ as listed in Table (2.1).

**Table 2.1: Mass Diffusivity of the Reactive Transport Ions**

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<tr>
<th>Ionic Species</th>
<th>Initial Concentration</th>
<th>Mass Diffusivity</th>
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<tbody>
<tr>
<td>$H^+$</td>
<td>.0631 mg/L</td>
<td>$9 \times 10^{-5}$ cm$^2$/sec</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}$</td>
<td>600 mg/L</td>
<td>$7.26 \times 10^{-5}$ cm$^2$/sec</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}$</td>
<td>5.6 mg/L</td>
<td>$6.05 \times 10^{-5}$ cm$^2$/sec</td>
</tr>
<tr>
<td>$O_2$</td>
<td>5.2 mg/L</td>
<td>$1.97 \times 10^{-5}$ cm$^2$/sec</td>
</tr>
</tbody>
</table>

Furthermore, $\hat{I} = -k_1 \hat{C}_{Fe^{2+}}^4 \hat{C}_{O_2}^4 \hat{C}_{H^+}^4 + k_{-1} \hat{C}_{Fe^{3+}}^4$, the bulk reaction rate, where $k_1$ and $k_{-1}$ are the forward and backward reaction rates and $\hat{C}_i$ is the concentration.
for the species \(i\). The forward reaction rate, \(k_1\) will be a function of bacteria concentration, controlled by the value of \(k_1\). By changing the value of \(k_1\), we simulate the concentration of bacteria. As the Fe(II) oxidation rate increases, we expect the abundance of Fe(II)OB to increase. The bulk reaction, \(\hat{I}\), is expected to be negative causing Reaction (1.1) to be a sink for hydrogen ion, oxygen and Fe(II) and a source for Fe(III).

At the air-liquid and liquid-crust interfaces we define the unit normal vectors
\[
\vec{n}_h = \left( \frac{-\hat{h}_x,1}{\sqrt{1+h_y^2}} \right) \quad \text{and} \quad \vec{n}_s = \left( \frac{-\hat{s}_x,1}{\sqrt{1+s_y^2}} \right).
\]
The following equations depict Henry’s law for the \(O_2\) concentration and no flux conditions for the ions at the air-liquid interface,
\[
\hat{C}_{O_2} = K_{H^+}P_{O_2}, \quad \text{(2.11)}
\]
\[
\nabla \hat{C}_{H^+} \cdot \vec{n}_h = 0, \quad \text{(2.12)}
\]
\[
\nabla \hat{C}_{Fe^{2+}} \cdot \vec{n}_h = 0, \quad \text{(2.13)}
\]
\[
\nabla \hat{C}_{Fe^{3+}} \cdot \vec{n}_h = 0. \quad \text{(2.14)}
\]

In (2.11), \(K_{H^+}\) is Henry’s constant and \(P_{O_2}\) is the partial pressure of oxygen. Henry’s law states that at a constant temperature, the oxygen dissolved is directly proportional to the partial pressure of oxygen. In Equations (2.12-2.14), there is no rate of change in the normal direction. The boundary conditions for the ionic species at
\[ \hat{z} = \hat{s}(\hat{x}, \hat{t}) \text{ are:} \]

\[ D_{O_2} \nabla \hat{C}_{O_2} \cdot \vec{n}_{\hat{z}} = F_c, \quad (2.15) \]

\[ D_{Fe^{2+}} \nabla \hat{C}_{Fe^{2+}} \cdot \vec{n}_{\hat{z}} = 0, \quad (2.16) \]

\[ D_{H^+} \nabla \hat{C}_{H^+} \cdot \vec{n}_{\hat{z}} = \kappa_1 \hat{C}_{H^+}^3 - \kappa_{-1} \hat{C}_{Fe^{3+}} \quad (2.17) \]

\[ D_{Fe^{3+}} \nabla \hat{C}_{Fe^{3+}} \cdot \vec{n}_{\hat{z}} = -\kappa_1 \hat{C}_{H^+}^3 + \kappa_{-1} \hat{C}_{Fe^{3+}}, \quad (2.18) \]

where \( F_c \) is the net flux of oxygen to the crust. The net flux can occur due to plants in the soil.

The surface reaction, Reaction (1.2), governs the formation of the Fe(III) hydroxide crust. This reaction is represented as \( J = -\kappa_1 \hat{C}_{H^+}^3 + \kappa_{-1} \hat{C}_{Fe^{3+}} \) where \( \kappa_1 \) and \( \kappa_{-1} \) are the forward and backward reaction rate coefficients. In Equation (2.18), if \( J \) is positive and iron hydroxide precipitates, \( J \) is a source for hydrogen ion and a sink for Fe(III). Equation (2.19) describes the mass balance of the surface reaction,

\[ \frac{\rho_{Fe(OH)_3} \frac{\partial \hat{s}}{\partial \hat{t}}}{\sqrt{1 + s_{\hat{z}}^2}} = (-\kappa_1 \hat{C}_{H^+}^3 + \kappa_{-1} \hat{C}_{Fe^{3+}}), \quad (2.19) \]

where \( \rho_{Fe(OH)_3} \) is the density of Fe(III) hydroxide crust. This equation determines the location of the crust.
CHAPTER III
ANALYSIS OF THE GOVERNING EQUATIONS

3.1 Nondimensional Equations

The process of nondimensionalization allows us to convert the equations to those in which the coefficients of the variables are unit-less. The independent variables, \( \hat{x}, \hat{z} \) and \( \hat{t} \) can be represented as \( Lx, dz \) and \( Tt \), respectively, where \( d \) is the average thickness of the crust plus liquid layer and \( L \) is the downstream length of the fluid run. After we nondimensionalize, the variables, \( \hat{x}, \hat{z} \) and \( \hat{t} \), will become the unit-less variables, \( x, z \) and \( t \). The variable \( T \) will be determined later.

In the mass conservation Equation (2.1), we let \( \hat{u} = U u \) and \( \hat{w} = \frac{wUd}{L} \). After taking the partial derivatives we obtain,

\[
U \frac{\hat{u}}{L} u_x + U \frac{\hat{w}}{L} w_z = 0,
\]

which simplifies to

\[
u_x + w_z = 0.
\] (3.1)

The Navier Stokes Equation (2.2) allowed us to determine the characteristic variables for \( \hat{u}, \hat{w} \) and \( \hat{p} \). In terms of nondimensional variables, we have

\[
\frac{U}{T} u_t + \frac{U^2}{L} u u_x + \frac{W U}{d} w w_z = -\frac{P}{\rho L} p_x + \frac{\mu}{\rho} \left( \frac{U}{L^2} u_{xx} + \frac{U}{d^2} \right) u_{zz} + g \sin \theta.
\]

To find \( U \) we matched the coefficients on the right-side of the equation. By equating \( \frac{\mu U}{\rho d^2} = g \) we found \( U = \frac{\rho gd^2}{\mu} \). The units of \( U \) are cm/s which is a velocity. Similarly,
to find $P$, we set $\frac{P}{\rho L} = g$, thus $P = \rho g L$. Therefore, we obtain

$$\frac{\rho d^2}{\mu T} u_t + \frac{U \rho d^2}{\mu L} uu_x + \frac{U \rho d^2}{\mu L} wu_z = -p_x + \frac{d^2}{L^2} u_{xx} + u_{zz} + \sin \theta.$$ 

The nondimensional variables are listed in Table (3.1). This table will be referenced in Chapter IV when we redimensionalize our solved equations.

Table 3.1: Nondimensional Independent and Dependent Variables

<table>
<thead>
<tr>
<th>Dimensional Variable</th>
<th>Units</th>
<th>Characteristic Scale</th>
<th>Nondimensional Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \hat{x} )</td>
<td>length (cm)</td>
<td>( L )</td>
<td>( Lx )</td>
</tr>
<tr>
<td>( \hat{z} )</td>
<td>length (cm)</td>
<td>( d )</td>
<td>( dz )</td>
</tr>
<tr>
<td>( \hat{t} )</td>
<td>time (sec)</td>
<td>( T = \frac{d^2}{\epsilon D_{Fe^{3+}}} )</td>
<td>( Tt )</td>
</tr>
<tr>
<td>( \hat{u} )</td>
<td>velocity (cm/sec)</td>
<td>( U = \frac{\rho gd^2}{\mu} )</td>
<td>( Uu )</td>
</tr>
<tr>
<td>( \hat{w} )</td>
<td>velocity (cm/sec)</td>
<td>( W = \frac{Ud}{L} )</td>
<td>( Ww )</td>
</tr>
<tr>
<td>( \hat{p} )</td>
<td>pressure (g/(cm × sec²))</td>
<td>( P = \rho g L )</td>
<td>( Pp )</td>
</tr>
<tr>
<td>( \hat{h} )</td>
<td>air-liquid interface (cm)</td>
<td>( d )</td>
<td>( hd )</td>
</tr>
<tr>
<td>( \hat{s} )</td>
<td>liquid-crust interface (cm)</td>
<td>( d )</td>
<td>( sd )</td>
</tr>
<tr>
<td>( \hat{C}_{H^+} )</td>
<td>concentration of H⁺ (mg/L)</td>
<td>( C_{H^+}^* )</td>
<td>( C_{H^+}^* C_{H^+} )</td>
</tr>
<tr>
<td>( \hat{C}_{O_2} )</td>
<td>concentration of O₂ (mg/L)</td>
<td>( C_{O_2}^* )</td>
<td>( C_{O_2}^* C_{O_2} )</td>
</tr>
<tr>
<td>( \hat{C}_{Fe^{2+}} )</td>
<td>concentration of Fe²⁺ (mg/L)</td>
<td>( C_{Fe^{2+}}^* )</td>
<td>( C_{Fe^{2+}}^* C_{H^+} )</td>
</tr>
<tr>
<td>( \hat{C}_{Fe^{3+}} )</td>
<td>concentration of Fe³⁺ (mg/L)</td>
<td>( C_{Fe^{3+}}^* )</td>
<td>( C_{Fe^{3+}}^* C_{H^+} )</td>
</tr>
</tbody>
</table>
Since $d$ is much smaller than $L$, we let $\epsilon = \frac{d}{L}$ be defined as the aspect ratio. Furthermore, $\frac{U d \rho}{\mu}$ is represented as a Reynolds number, $Re$, which is the ratio of the inertial forces to the viscous forces. We represent $\frac{\mu D_{Fe^{3+}}}{\rho}$ as a Schmidt number, $Sc$, which is the ratio of the convective to the diffusive transport of Fe(III). The time variable, $T$, will also be substituted by $\frac{d^2}{\epsilon D_{Fe^{3+}}}$, with the justification being shown in Equation (3.19), the mass balance equation. The simplified Navier-Stokes Equation (2.2) is now

\[
\frac{\epsilon}{Sc} u_t + \epsilon Re [uu_x + wu_z] = -p_x + \epsilon^2 u_{xx} + u_{zz} + \sin \theta. \tag{3.2}
\]

The other Navier-Stokes Equation (2.3) follows a similar pattern as Equation (2.2),

\[
\frac{\epsilon}{Sc} w_t + \epsilon Re [uw_x + ww_z] = -\frac{1}{\epsilon^2} p_z + \epsilon^2 w_{xx} + w_{zz} - \frac{1}{\epsilon} \cos \theta. \tag{3.3}
\]

Next, we nondimensionalize Equation (2.4), the kinematic condition,

\[
\frac{D_{Fe^{3+}}}{dU} h_t = w - uh_x. \tag{3.4}
\]

In terms of nondimensional variables, the boundary condition for the tangential force balance, Equation (2.5), is

\[
-2h_xu_x + 2w_z + \frac{1}{\epsilon^2} u_z + w_x - h_x^2 u_z - \epsilon^2 h_x w_x = 0. \tag{3.5}
\]

The nondimensional version of Equation (2.6), the normal force balance at the liquid-air interface is

\[
-p + \frac{\epsilon^2 [e^2 u_x h_x^2 - h_x (u_z + e^2 w_x) + w_z]}{\sqrt{1 + e^2 h_x^2}} = \sigma \frac{\epsilon^3 h_{xx}}{\mu U (1 + e^2 h_x^2)^{3/2}}.
\]
The coefficient, $\frac{\sigma}{\mu U}$, is expressed as $Ca$, a capillary number, which is the ratio of the surface tension force to the viscous forces. We scale the capillary number, $Ca$, to be $\frac{\bar{C}a}{\epsilon^2}$, where $\bar{C}a$ is an $O(1)$ constant. The capillary number is $O(\frac{1}{\epsilon^2})$ to be consistent with the large surface tension. Therefore we obtain

$$-p + \frac{\epsilon^2 \left[ \epsilon^2 u_x h_x^2 - h_x (u_x + \epsilon^2 w_x) + w_x \right]}{\sqrt{1 + \epsilon^2 h_x^2}} = \frac{\bar{C}a h_{xx}}{(1 + \epsilon^2 h_x^2)^{3/2}}.$$  (3.6)

The scaling parameters are listed in Table (3.2), where the explanation of the Damkohler numbers is in Equation (3.17), the boundary condition at the liquid-crust interface.

### Table 3.2: Scaling Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Scale</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reynold’s Number, $Re$</td>
<td>$\frac{U d}{v}$</td>
<td>inertial force per viscous forces</td>
</tr>
<tr>
<td>Capillary Number, $Ca$</td>
<td>$\frac{\sigma}{\mu U}$</td>
<td>surface tension force per viscous forces</td>
</tr>
<tr>
<td>Damkohler Number, $Da_{(1)}$</td>
<td>$\frac{\kappa_{1d}}{D_{Fe^{3+}}}$</td>
<td>forward reaction rate per diffusion of $Fe^{3+}$</td>
</tr>
<tr>
<td>Damkohler Number, $Da_{(-1)}$</td>
<td>$\frac{\kappa_{-1d}}{D_{Fe^{3+}}}$</td>
<td>backward reaction rate per diffusion of $Fe^{3+}$</td>
</tr>
<tr>
<td>Schmidt Number, $Sc$</td>
<td>$\frac{\mu}{D_{Fe^{3+}} \rho}$</td>
<td>viscosity per diffusion of $Fe^{3+}$</td>
</tr>
<tr>
<td>Peclet Number, $Pe$</td>
<td>$\frac{U d}{D_i}$</td>
<td>convective to diffusive transport of the ionic species $i$</td>
</tr>
</tbody>
</table>

The reactive transport expressions, Equations (2.7-2.10), have the same form, but alter based on the different ionic species of interest. After substituting the nondimensional variables (Table 3.1) and parameter variables (Table 3.2), we obtain the
following equations for the ionic species, \( i \). The only difference is a negative sign with the \( \hat{I} \) coefficient in Equation (2.10). Furthermore, we scale \( \hat{I} = \epsilon \bar{I} \), where \( \bar{I} \) contains nondimensional concentrations of the ionic species. In the bulk reaction, we are near equilibrium and therefore expect \( \hat{I} \) to be of \( O(\epsilon) \),

\[
\frac{D_{Fe^{3+}}}{D_{H^+}} C_{H^+_t} + \epsilon P_e [u C_{H^+_x} + w C_{H^+_z}] = \epsilon^2 C_{H^+_{xx}} + C_{H^+_{zz}} + \frac{\epsilon d^2}{C_{H^+}^* D_{H^+}} \bar{I}, \quad (3.7)
\]

\[
\frac{D_{Fe^{3+}}}{D_{O_2}} C_{O_{2t}} + \epsilon P_e [u C_{O_{2x}} + w C_{O_{2z}}] = \epsilon^2 C_{O_{2xx}} + C_{O_{2zz}} + \frac{\epsilon d^2}{C_{O_2}^* D_{O_2}} \bar{I}, \quad (3.8)
\]

\[
\frac{D_{Fe^{3+}}}{D_{Fe^{2+}}} C_{Fe^{2+}_t} + \epsilon P_e [u C_{Fe^{2+}_x} + w C_{Fe^{2+}_z}] = \epsilon^2 C_{Fe^{2+}_{xx}} + C_{Fe^{2+}_{zz}} + \frac{\epsilon d^2}{C_{Fe^{2+}}^* D_{Fe^{2+}}} \bar{I}, \quad (3.9)
\]

\[
\epsilon C_{Fe^{3+}_t} + \epsilon P_e [u C_{Fe^{3+}_x} + w C_{Fe^{3+}_z}] = \epsilon^2 C_{Fe^{3+}_{xx}} + C_{Fe^{3+}_{zz}} - \frac{\epsilon d^2}{C_{Fe^{3+}}^* D_{Fe^{3+}}} \bar{I}. \quad (3.10)
\]

Equation (2.11), the boundary condition at the liquid-air interface for oxygen, can be nondimensionalized as follows

\[
C_{O_2} = \frac{K_{H^+} P_{O_2}}{C_{O_2}^*}. \quad (3.11)
\]

The boundary conditions at the liquid-air interface for the other ionic species, Equations (2.12-2.14), were found by taking a dot product of the gradient vector and normal vector to the air-liquid interface. The vectors in Equation (2.12) are

\[
[\hat{C}_{H^+_x} \hat{i} + \hat{C}_{H^+_z} \hat{j}] \left[ \frac{-h_\xi \hat{i} + \hat{j}}{\sqrt{1 + h_\xi^2}} \right] = 0, \quad \text{where} \ \hat{i} \ \text{and} \ \hat{j} \ \text{represent the unit vectors}. \ \text{Therefore we have}\n\]

\[
\frac{-\hat{C}_{H^+_x} h_\xi + \hat{C}_{H^+_z}}{\sqrt{1 + h_\xi^2}} = 0.
\]
Now the nondimensional variables from Table (3.1) are used,

\[
-\epsilon^2 C_{H^+,z} h_x + C_{H^+,z} \sqrt{1 + \epsilon^2 h_x^2} = 0. \tag{3.12}
\]

Since \(\epsilon\) is small this implies \(C_{H^+,z} = 0\) and the directional derivative of \(H^+\) acts in the \(z\) direction. The same process is used in Equations (2.13-2.14),

\[
-\epsilon^2 C_{Fe^{2+,z}} h_x + C_{Fe^{2+,z}} \sqrt{1 + \epsilon^2 h_x^2} = 0 \tag{3.13}
\]

\[
-\epsilon^2 C_{Fe^{3+,z}} h_x + C_{Fe^{3+,z}} \sqrt{1 + \epsilon^2 h_x^2} = 0. \tag{3.14}
\]

Therefore we also have \(C_{Fe^{2+,z}} = 0\) and \(C_{Fe^{3+,z}} = 0\).

Equation (2.15), the boundary condition at \(z = s(x,t)\), contains \(\nabla C_i \cdot \hat{n}_s\) which is similar to Equation (2.12) except the normal vector, \(\hat{n}\), acts normal to the liquid-crust interface. The same nondimensional process occurs, however \(h_x\) is replaced by \(s_x\). Thus Equation (2.15) is

\[
-\epsilon^2 C_{O_{2,z}} s_x + C_{O_{2,z}} \sqrt{1 + \epsilon^2 s_x^2} = F, \tag{3.15}
\]

where \(F = \frac{F_c d_{O_2} C_{O_2}}{D_{O_2} C_{O_2}}\) and \(F_c\) is the net flux constant. Equation (2.16) follows the same structure except for a different ionic species. The nondimensional equation is

\[
-\epsilon^2 C_{Fe^{2+,z}} s_x + C_{Fe^{2+,z}} \sqrt{1 + \epsilon^2 s_x^2} = 0. \tag{3.16}
\]

Equations (2.17-2.18) also represent boundary conditions at \(z = s(x,t)\), and therefore follow a similar process as Equations (2.15-2.16). However, the ionic species are different and the left-hand side depends on \(J\), the surface reaction expression.

The nondimensional variables give

\[
-\epsilon^2 C_{H^+,z} s_x + C_{H^+,z} \sqrt{1 + \epsilon^2 s_x^2} = \frac{d\kappa_1 C_{H^+}^2}{D_{H^+} C_{H^+}^3} - \frac{\kappa_{-1} dC_{Fe^{3+}}^n}{D_{H^+} C_{H^+}^3} C_{Fe^{3+}}. \tag{3.17}
\]
Similarly for Equation (2.18) we obtain

\[
\frac{-\varepsilon^2 C_{Fe^{3+}} s_x + C_{Fe^{3+}x}}{\sqrt{1 + \varepsilon^2 s_x^2}} = -\frac{\kappa_1 d C_{H^+}^3}{D_{Fe^{3+}} C_{Fe^{3+}x}} C_{H^+}^3 + \frac{\kappa_{-1} d}{D_{Fe^{3+}} C_{Fe^{3+}}}.
\]

Since the coefficients of \(C_{H^+}^3\) and \(C_{Fe^{3+}}\) are nondimensionalized, they are unit-less.

We define these coefficients as Damkohler Numbers, where

\[Da(1) = \frac{\kappa_1 d}{D_{Fe^{3+}}},\]

\[Da(-1) = \frac{\kappa_{-1} d}{D_{Fe^{3+}}}.\]

Furthermore, \(Da(1) = \varepsilon \bar{Da}(1)\) and \(Da(-1) = \varepsilon \bar{Da}(-1)\). The Damkohler Numbers represent the ratio of the reaction rates versus the diffusion of \(Fe^{3+}\). We scaled these ratios to be small since the growth rate is slow. We substitute the Damkohler Numbers into the above equations to obtain

\[
\frac{-\varepsilon^2 C_{H^+} s_x + C_{H^+} x}{\sqrt{1 + \varepsilon^2 s_x^2}} = -\frac{\varepsilon \bar{Da}(1) C_{H^+}^3}{D_{H^+} C_{Fe^{3+}}} C_{H^+}^3 - \frac{\varepsilon \bar{Da}(-1) C_{Fe^{3+}}^3}{D_{H^+} C_{H^+}} C_{Fe^{3+}}^3,
\]

(3.17)

\[
-\varepsilon^2 C_{Fe^{3+}} s_x + C_{Fe^{3+}x} = -\frac{\varepsilon \bar{Da}(1) C_{Fe^{3+}}^3}{C_{Fe^{3+}}^3} C_{H^+}^3 + \varepsilon \bar{Da}(-1) C_{Fe^{3+}}.
\]

(3.18)

In terms of the nondimensional variables, Equation (2.19), the mass balance equation, is

\[
\frac{s_t}{\sqrt{1 + \varepsilon^2 s_x^2}} = -\frac{\kappa_1 C_{H^+}^3 T}{\rho_{Fe(OH)_3} d} C_{H^+}^3 + \frac{\kappa_{-1} C_{Fe^{3+}}^3 T}{\rho_{Fe(OH)_3} d} C_{Fe^{3+}}^3.
\]

We rearrange the coefficient of \(C_{Fe^{3+}}\) to solve for the characteristic variable, \(T\). We have,

\[
\bar{Da}(-1) \frac{d}{L \rho_{Fe(OH)_3}} \frac{C_{Fe^{3+}}}{TD_{Fe^{3+}}} \frac{TD_{Fe^{3+}}}{d^2} = 1.
\]

The fraction \(\frac{C_{Fe^{3+}}}{\rho_{Fe(OH)_3}}\) is unit-less since both units are concentrations. Also \(\bar{Da}(-1)\) is order 1. Thus, the remaining terms are \(\frac{TD_{Fe^{3+}}}{Ld} = 1\) and \(T = \frac{Ld}{D_{Fe^{3+}}}\). The characteristic variable, \(T\), has been substituted into the previous equations based on this calculation.
The nondimensional mass balance Equation (2.19) is

\[
\frac{\sqrt{1 + \epsilon^2 s_x^2} s_t}{\sqrt{1 + \epsilon^2 s_x^2}} = -\frac{\bar{D}_{a_{(1)}} C_{H^3}^{*}}{\rho_{Fe(OH)^3}} C_{H^+}^{*} + \frac{\bar{D}_{a_{(-1)}} C_{Fe^{3+}}^{*}}{\rho_{Fe(OH)^3}} C_{Fe^{3+}}.
\] (3.19)

The details of the nondimensional equations are listed in Appendix (A).

### 3.2 Asymptotic Expansion Equations

The process of asymptotic expansion allows for variables to be expanded by a formal series. The series can be truncated after a finite number of approximations. We have the following asymptotic expansions,

\[
u = u_0 + \epsilon u_1 + \epsilon^2 u_2 + O(\epsilon^3),
\]

\[
w = w_0 + \epsilon w_1 + \epsilon^2 w_2 + O(\epsilon^3),
\]

\[
p = p_0 + \epsilon p_1 + \epsilon^2 p_2 + O(\epsilon^3).
\]

Since we solve the equations using \(O(1)\) and \(O(\epsilon)\) equations, we truncate the series after the \(\epsilon^2\) term. Additionally, use the nondimensional equations to find the asymptotic expansions. The mass continuity Equation (3.1) becomes

\[
u_{0x} + \epsilon u_{1x} + \epsilon^2 u_{2x} + w_{0z} + \epsilon w_{1z} + \epsilon^2 w_{2z} = 0 + 0\epsilon + 0\epsilon^2.
\]

After combining terms of similar \(\epsilon\) powers, we have,

\[
(u_{0z} + w_{0z}) + \epsilon(u_{1z} + w_{1z}) + \epsilon^2(u_{2z} + w_{2z}) = 0 + 0\epsilon + 0\epsilon^2.
\]

Therefore the \(O(1)\) and \(O(\epsilon)\) equations are:

\[
O(1) \quad u_{0z} + w_{0z} = 0, \quad (3.20)
\]

\[
O(\epsilon) \quad u_{1z} + w_{1z} = 0.
\]
In the Navier-Stokes Equation (3.21), the same process is followed, giving

\[(0u_0 + \epsilon \frac{1}{Sc} u_1t) + \epsilon Re[(u_0 + \epsilon u_1)(u_0 + \epsilon u_1x) + (w_0 + \epsilon w_1)(u_0 + \epsilon u_1z)] \]

\[= -(p_0x + \epsilon p_1x) + \epsilon^2(u_{0xx} + \epsilon u_{1xx}) + (u_{0zz} + \epsilon u_{1zz}) + \sin \theta] \]

Since we only are concerned with the \(O(1)\) and \(O(\epsilon)\) terms, we have

\[
O(1) - p_0x + u_{0zz} = -\sin \theta, \tag{3.21}
\]

\[
O(\epsilon) - p_1x + u_{1zz} = \frac{1}{Sc}u_0t + Re[u_0u_0x + w_0u_0z].
\]

Equation (3.3), the second Navier-Stokes equation, has terms containing \(\epsilon\) in the denominator and the asymptotic expansions do not account for \(\epsilon\) to negative powers so the first step is to multiply the equation by \(\epsilon^2\),

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

Again, since we truncate orders higher than \(\epsilon\), the expansion becomes,

\[0 = -(p_{0x} + p_{1x}) - \epsilon \cos \theta. \] The asymptotic equations are,

\[
O(1) \quad p_{0x} = 0, \tag{3.22}
\]

\[
O(\epsilon) \quad p_{1x} = -\cos \theta.
\]

The asymptotic expansions of the Kinematic Equation (3.4) are

\[
\frac{D_{Fe^{3+}}}{dU}(h_{0t} + \epsilon h_{1t}) = (w_0 + \epsilon w_1) - (u_0 + \epsilon u_1)(h_{0x} + \epsilon h_{1x}).\]

Therefore,

\[
O(1) \quad \frac{D_{Fe^{3+}}}{dU}h_{0t} = w_0 - u_0h_{0x}, \tag{3.23}
\]

\[
O(\epsilon) \quad \frac{D_{Fe^{3+}}}{dU}h_{1t} = w_1 - u_0h_{1x} - u_1h_{0x}.
\]
In Equation (3.5), the tangential force balance at \( z = h(x,t) \), we again have negative powers of \( \epsilon \) so we multiply by \( \epsilon^2 \),

\[
-2\epsilon^2 h_x u_x + 2\epsilon^2 w + u_z + \epsilon^2 w_x - \epsilon^2 h_x^2 u_z - \epsilon^4 h_x w_x = 0.
\]

The \( \epsilon^2 \) and \( \epsilon^4 \) terms are truncated and we are left with \((u_0 + \epsilon u_1) = 0\), hence

\[
O(1) \quad u_0_z = 0, \tag{3.24}
\]

\[
O(\epsilon) \quad u_1_z = 0.
\]

In Equation (3.6), the normal force balance at \( z = h(x,t) \), the higher powers of \( \epsilon \) are disregarded. In general we have

\[
-p + \frac{\epsilon^2}{1 + \epsilon^2 h_x^2} = \frac{\bar{C}a h_{xx}}{(1 + \epsilon^2 h_x^2)^{3/2}}.
\]

We use the binomial expansion to eliminate the fractional power in the denominator of the left-hand side,

\[
-p + \frac{\epsilon^2}{1 + \epsilon^2 h_x^2} = \bar{C}a h_{xx}(1 - \frac{3}{2} \epsilon^2 h_x^2 + \cdots)
\]

Based on the higher powers of \( \epsilon \), the expansion is \(-p_0 - \epsilon p_1 = (0 + \epsilon \bar{C}a h_{0xx})\), yields

\[
O(1) \quad p_0 = 0, \tag{3.25}
\]

\[
O(\epsilon) \quad -p_1 = \bar{C}a h_{0xx}.
\]

Equations (3.7-3.9), the reactive transport equations, all follow the same asymptotic expansion. The expansion for the ionic species, \( i \) is as follows,

\[
\frac{D_{Fe^{3+}}}{D_i} \epsilon (C_{i_{0x}} + \epsilon C_{i_{1x}}) + \epsilon Pe[(u_0 + \epsilon u_1) (C_{i_{0z}} + \epsilon C_{i_{1z}}) + (w_0 + \epsilon w_1)(C_{i_{0z}} + \epsilon C_{i_{1z}})]
\]

\[
= \epsilon^2 C_{i_{xx}} + (C_{i_{0xx}} + \epsilon C_{i_{1xx}}) + \frac{\epsilon d^2}{C_i^* D_i} \bar{I}.
\]

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The asymptotic expansions of $O(1)$ and $O(\epsilon)$ are listed for the given ionic species:

$$O(1) \quad C_{H_{0z}^+} = 0,$$

$$\tag{3.26}$$

$$O(\epsilon) \quad C_{H_{12z}^+} + \frac{d^2}{C_{H^+}^* D_{H^+}} \bar{I} = \frac{D_{Fe^{3+}}}{D_{H^+}} C_{H_{0z}^+} + P e[u_0 C_{H_{0z}^+} + w_0 C_{H_{0z}^+}^1], \tag{3.27}$$

$$O(1) \quad C_{O_{20z}^+} = 0,$$

$$\tag{3.28}$$

$$O(\epsilon) \quad C_{O_{21z}^+} + \frac{d^2}{C_{O_2^*} D_{O_2}} \bar{I} = \frac{D_{Fe^{3+}}}{D_{O_2}} C_{O_{20z}^+} + P e[u_0 C_{O_{20z}^+} + w_0 C_{O_{20z}^+}^1], \tag{3.29}$$

$$O(1) \quad C_{Fe^{2+0z}^+} = 0,$$

$$\tag{3.30}$$

$$O(\epsilon) \quad C_{Fe^{2+1z}^+} + \frac{d^2}{C_{Fe^{2+}^*} D_{Fe^{2+}}} \bar{I} = \frac{D_{Fe^{3+}}}{D_{Fe^{2+}}} C_{Fe^{2+0z}^+} + P e[u_0 C_{Fe^{2+0z}^+} + w_0 C_{Fe^{2+0z}^+}^1]. \tag{3.31}$$

Equation (3.10) is the same as the other ionic species except the coefficient of $C_{Fe^{3+t}}$ is 1 and the bulk reaction rate, $I$, is negative. Therefore we have

$$O(1) \quad C_{Fe^{3+0z}^+} = 0,$$

$$\tag{3.32}$$

$$O(\epsilon) \quad C_{Fe^{3+0z}^+} - \frac{d^2}{C_{Fe^{3+}^*} D_{Fe^{3+}}} \bar{I} = C_{Fe^{3+0z}^+} + P e[u_0 C_{Fe^{3+0z}^+} + w_0 C_{Fe^{3+0z}^+}^1]. \tag{3.33}$$

Equations (3.11-3.14) represent the boundary conditions at $z = h(x, t)$, the liquid-air interface. We expand $h(x, t) = h_0(x, t) + \epsilon h_1(x, t) + O(\epsilon^2)$ and refer to $h_i(x, t)$ as $h_i$. By boundary perturbation we have the Taylor’s expansion,

$$C_i(x, h_0 + \epsilon h_1 + \cdots, t) = C_{i_0}(x, h_0, t) + C_{i_1}(x, h_0, t)(\epsilon h_1 + \epsilon^2 h_2 + \cdots) + \epsilon[C_{i_1}(x, h_0, t) + C_{i_1z}(x, h_0, t)(\epsilon h_1 + \epsilon^2 h_2 + \cdots)] + O(\epsilon^2)$$

for the ionic species, $i$. Equation (3.11) is expanded as

$$(C_{O_{20}}(x, h_0, t) + \epsilon[(h_1 C_{i_{0z}}(x, h_0, t) + C_{O_{21}}(x, h_0, t))] = \frac{K_{H^+F_{O_2}}}{C_{O_2}}$$

where the
The left-hand side is a constant. The asymptotic equations become

$$
O(1) \quad C_{O_{20}}(x, h_0, t) = \frac{K_{H^+PO_2}}{C_{O_2}^*},
$$

$$
O(\epsilon) \quad C_{O_{21}}(x, h_0, t) = -h_1 C_{O_{20},y}(x, h_0, t) - C_{O_{21},y}(x, h_0, t)).
$$

Equations (3.12-3.14) follow the same expansion for the given ions:

$$
O(1) \quad C_{H_{+0z}}(x, h_0, t) = 0,
$$

$$
O(\epsilon) \quad C_{H_{+1z}}(x, h_0, t) = -h_1 C_{H_{+0zz}}(x, h_0, t),
$$

$$
O(1) \quad C_{Fe^{2+0z}}(x, h_0, t) = 0,
$$

$$
O(\epsilon) \quad C_{Fe^{2+1z}}(x, h_0, t) = -h_1 C_{Fe^{2+0zz}}(x, h_0, t),
$$

$$
O(1) \quad C_{Fe^{3+0z}}(x, h_0, t) = 0,
$$

$$
O(\epsilon) \quad C_{Fe^{3+1z}}(x, h_0, t) = -h_1 C_{Fe^{3+0zz}}(x, h_0, t).
$$

Equations (3.15-3.16) have a similar asymptotic expansion as above, however, they signify the boundary conditions at $z = s(x, t)$, the liquid-crust interface. We expand $s(x, t) = s_0(x, t) + \epsilon s_1(x, t) + O(\epsilon^2)$ and refer to $s_i(x, t)$ as $s_i$. Again by boundary perturbation we have the Taylor’s expansion,

$$
C_i(x, s_0 + \epsilon s_1 + ..., t) = C_{i0}(x, s_0, z) + C_{i1}(x, s_0, z)(\epsilon s_1 + \epsilon^2 s_2 + ...) + \epsilon [C_{i1}(x, s_0, z) + C_{i1z}(x, s_0, z)(\epsilon s_1 + \epsilon^2 s_2 + ...)] + O(\epsilon^2)
$$

for the ionic species, $i$. The asymptotic expansions
are,

\[ O(1) \quad C_{O_{2z}}(x, s_0, z) = F \quad \text{where} \quad F = \frac{F_{el}}{D_{O_2}C_{O_{2}}^*}, \quad (3.38) \]

\[ O(\epsilon) \quad C_{O_{2z}}(x, s_0, z) = -s_1 C_{O_{2zz}}(x, s_0, z), \]

\[ O(1) \quad C_{Fe^{2+0z}}(x, s_0, z) = 0, \quad (3.39) \]

\[ O(\epsilon) \quad C_{Fe^{2+1z}}(x, s_0, z) = -s_1 C_{Fe^{2+ozz}}(x, s_0, z). \]

Equation (3.17), the boundary condition for the ionic species, \( H^+ \), becomes,

\[
(C_{H^{+o}}(x, s_0, z) + \epsilon[s_1 C_{H^{+o}}(x, s_0, z) + C_{H^{+1}}(x, s_0, z)])
\]

\[
= \frac{\epsilon \tilde{D} a_{(1)} C_{H^{+}}^{*2} D_{Fe^{3+}}}{D_{H^{+}}} (C_{H^{+o}}(x, s_0, z) + \epsilon s_1 C_{H^{+1}}(x, s_0, z))^3
\]

\[
- \frac{\epsilon \tilde{D} a_{(-1)} C_{Fe^{3+}} D_{Fe^{3+}}}{D_{H^{+}} C_{H^{+}}^*} (C_{Fe^{3+0}}(x, s_0, z) + \epsilon s_1 C_{Fe^{3+1}}(x, s_0, z)).
\]

By expanding the cubic on the right hand side, the expansions become,

\[ O(1) \quad C_{H^{+o}}(x, s_0, z) = 0 \quad (3.40) \]

\[ O(\epsilon) \quad C_{H^{+1z}}(x, s_0, z) = -s_1 C_{H^{+ozz}}(x, s_0, z)
\]

\[
+ \frac{\tilde{D} a_{(1)} C_{H^{+}}^{*2} D_{Fe^{3+}}}{D_{H^{+}}} C_{H^{+o}}(x, s_0, z)^3
\]

\[
- \frac{\tilde{D} a_{(-1)} C_{Fe^{3+}} D_{Fe^{3+}}}{D_{H^{+}} C_{H^{+}}^*} C_{Fe^{3+0}}(x, s_0, z)
\]

Similarly, in Equation (3.18), the expansion for the ionic species, \( Fe^{3+} \), is

\[
(C_{Fe^{3+0z}}(x, s_0, z) + \epsilon[s_1 C_{Fe^{3+oz}}(x, s_0, z) + C_{Fe^{3+1}}(x, s_0, z)]
\]

\[
= -\frac{\epsilon \tilde{D} a_{(1)} C_{H^{+}}^{*3}}{C_{H^{+}}^*} (C_{H^{+o}}(x, s_0, z) + \epsilon s_1 C_{H^{+1}}(x, s_0, z))^3
\]

\[
+ \epsilon \tilde{D} a_{(-1)} (C_{Fe^{3+0}}(x, s_0, z) + \epsilon s_1 C_{Fe^{3+1}}(x, s_0, z)).
\]
Therefore the $O(1)$ and $O(\epsilon)$ equations are

\begin{align}
O(1) \quad C_{Fe^{3+}O_2} (x, s_0, z) &= 0, \\
O(\epsilon) \quad C_{Fe^{3+1}_3} (x, s_0, z) &= -s_1 C_{Fe^{3+}O_2} - \frac{D a_{(1)} C^{*3}_{H^+}}{C^{*}_{Fe^{3+}}} C_{H^+o} (x, s_0, z)^3 \\
&+ \bar{D} a_{(-1)} C_{Fe^{3+}o} (x, s_0, z).
\end{align}

Equation (3.19), the mass balance for the surface reaction, has the same format as above. However, we use the binomial expansion on the right-hand side to eliminate the square root in the denominator to obtain

\begin{align*}
s_t (1 - \frac{1}{2} \epsilon^2 s^2 + ...) &= -\frac{\bar{D} a_{(1)} C^{*3}_{H^+}}{\rho_{Fe(OH)_3}} (C_{H^+o} (x, s_0, z) + \epsilon s_1 C_{H^+1} (x, s_0, z))^3 \\
&+ \frac{\bar{D} a_{(-1)} C^{*}_{Fe^{3+}}}{\rho_{Fe(OH)_3}} (C_{Fe^{3+}o} (x, s_0, z) + \epsilon s_1 C_{Fe^{3+1}} (x, s_0, z)).
\end{align*}

Therefore, the asymptotic expansions of $O(1)$ and $O(\epsilon)$ are

\begin{align}
O(1) \quad s_0_t &= -\frac{\bar{D} a_{(1)} C^{*3}_{H^+}}{\rho_{Fe(OH)_3}} C_{H^+o} (x, s_0, z)^3 \\
&+ \frac{\bar{D} a_{(-1)} C^{*}_{Fe^{3+}}}{\rho_{Fe(OH)_3}} C_{Fe^{3+}o} (x, s_0, z), \\
O(\epsilon) \quad s_1_t &= -\frac{\bar{D} a_{(1)} C^{*3}_{H^+}}{\rho_{Fe(OH)_3}} [C_{H^+o} (x, s_0, z) s_1 + C_{H^+1} (x, s_0, z)]^3, \\
&+ \frac{\bar{D} a_{(-1)} C^{*}_{Fe^{3+}}}{\rho_{Fe(OH)_3}} [C_{Fe^{3+}o} (x, s_0, z) s_1 + C_{Fe^{3+1}} (x, s_0, z)].
\end{align}

Now all the equations are in terms of the asymptotic expansions of leading order and the first correction.
CHAPTER IV
ANALYTIC SOLUTION

First, we solve the hydrodynamic equations using the leading order equations. We have the system

\[
\begin{align*}
    u_{0x} + w_{0z} & = 0, \\
    -p_0 x + u_{0zz} & = -\sin \theta, \\
    p_0 & = 0,
\end{align*}
\]

subject to the boundary conditions at \( z = h_0(x,t) \),

\[
\begin{align*}
    u_{0z} & = 0, \\
    p_0 & = 0,
\end{align*}
\]

and the no-slip conditions, \( u_0 = w_0 = 0 \) at \( z = s_0(x,t) \). The leading order solution for the fluid flow equations becomes

\[
\begin{align*}
    u_0 & = \left[ -\frac{1}{2} z^2 + zh_0 + \frac{1}{2} s_0^2 - s_0 h_0 \right] \sin \theta, \\
    w_0 & = \left[ -\frac{1}{2} z^2 h_{0x} - z s_0 s_{0x} + z s_0 h_0 + z s_0 h_{0x} - \frac{1}{2} s_0^2 h_{0x} + s_0^2 s_{0x} - s_0 s_{0x} h_0 \right] \sin \theta, \\
    p_0 & = 0.
\end{align*}
\]

(4.1) \hspace{1cm} (4.2) \hspace{1cm} (4.3)

The details can be found in Appendix (B).
Next, we use the Kinematic Equation (3.4) to solve \( h_0(x,t) \). By substitution of \( u_0 \) and \( w_0 \) we have

\[
\frac{D_{Fe^{3+}}}{dU} h_{0x} = \left[ -\frac{1}{3}(h_0 - s_0)^3 \right]_x \sin \theta. \tag{4.4}
\]

Based on the dimensional variables, \( T = \frac{Ld}{F_{Fe^{3+}}} \), the left-hand side becomes \( \frac{\dot{L}}{T} \). In other words, this ratio is the time for the water to flow downstream over the time for which the crust grows. Since this ratio is very small due to a slow growing crust, we can approximate the left-hand side as 0. Thus,

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

We integrate with respect to \( x \) to obtain

\[
R(t) = [(h_0(x,t) - s_0(x,t))]^3 \sin \theta. \tag{4.5}
\]

\( R(t) \) is a function of time and referenced later.

Now we look at Equation (4.1), the velocity of the downstream. We integrate with respect to \( z \) to solve for the volumetric flow rate,

\[
\int_{s_0(x,t)}^{h_0(x,t)} u_0 \, dz = \frac{1}{3}(h_0(x,t) - s_0(x,t))^3 \sin \theta. \tag{4.6}
\]

In Equation (4.5) we found \( R(t) = [(h_0(x,t) - s_0(x,t))]^3 \sin \theta \). Therefore the volumetric flow rate is a function of time,

\[
Q(t) = \int_{s_0(x,t)}^{h_0(x,t)} u_0 \, dz = \frac{1}{3}[h_0(x,t) - s_0(x,t)]^3 \sin \theta. \tag{4.7}
\]

The function, \( Q(t) \), represents the seasonal changes over time. We expect more precipitation in the spring season than in the winter season when freezing occurs. We
now redimensionalize the volumetric flow using Table (3.1),

\[ \dot{Q}(\hat{t}) = \frac{Q\mu}{\rho gd} \].

(4.8)

We redimensionalize Equation (4.7) and solve for \( \hat{h}_0(\hat{x}, \hat{t}) \),

\[ \hat{h}_0(\hat{x}, \hat{t}) = \left( \frac{3\dot{Q}(\hat{t})}{\sin \theta} \right)^{\frac{1}{3}} + \hat{s}_0(\hat{x}, \hat{t}) \].

(4.9)

Hence, once we determine the location of the crust, \( \hat{s}_0(\hat{x}, \hat{t}) \), we will know the location of the liquid-air interface.

The next step is to solve the concentration equations. Since we are only examining the leading order solutions for ion concentrations, we do not need \( h_1 \) nor \( s_1 \). We refer to \( h_0 \) as \( h \) and \( s_0 \) as \( s \).

First, we solve for the concentrations of the hydrogen ions, \( Fe(II) \) and \( Fe(III) \), the reactive ionic species. Equations (3.26, 3.30, 3.32) are \( C_{i_{0zz}} = 0 \) for the ionic species \( i \). Integration with respect to \( z \) twice yields,

\[ C_{i_0} = zA_i(x) + B_i(x) \],

where \( A_i(x) \) and \( B_i(x) \) are functions of \( x \) that must be determined. The boundary conditions at \( z = h(x, t) \) and \( z = s(x, t) \) are \( C_{i_{0z}} = 0 \) so \( A(x) = 0 \). Therefore, the leading order equations for \( H^+ \), \( Fe^{2+} \) and \( Fe^{3+} \) are simply functions of \( x \) and we find
$B_t(x)$ via the $O(\epsilon)$ equations. We solve the system,

\[ C_{H^+_{1z}} = -\frac{\bar{I}d^2}{C_{H^+}D_{H^+}}k_{-1}C_{Fe^{3+}}^4z + \frac{\bar{I}d^2}{C_{H^+}^*D_{H^+}}C_{Fe^{2+}}^4C_{H^+}^4 \int_{s(x,t)}^z k_1C_{O_2} dz \]

\[ + PeC_{H^+0z} \int_{s(x,t)}^z u_0 \, dz + B_{H^+}(x), \tag{4.10} \]

\[ C_{Fe^{2+}_{1z}} = -\frac{\bar{I}d^2}{C_{Fe^{2+}}^*D_{Fe^{2+}}}k_{-1}C_{Fe^{3+}}^4z + \frac{\bar{I}d^2}{C_{Fe^{2+}}^*D_{Fe^{2+}}}C_{Fe^{2+}}^4C_{H^+}^4 \int_{s(x,t)}^z k_1C_{O_2} dz \]

\[ + PeC_{Fe^{2+0z}} \int_{s(x,t)}^z u_0 \, dz + B_{Fe^{2+}}(x), \tag{4.11} \]

\[ C_{Fe^{3+}_{1z}} = \frac{\bar{I}d^2}{C_{Fe^{3+}}^*D_{Fe^{3+}}}k_{-1}C_{Fe^{3+}}^4z - \frac{\bar{I}d^2}{C_{Fe^{3+}}^*D_{Fe^{3+}}}C_{Fe^{2+}}^4C_{H^+}^4 \int_{s(x,t)}^z k_1C_{O_2} dz \]

\[ + PeC_{Fe^{3+0z}} \int_{s(x,t)}^z u_0 \, dz + B_{Fe^{3+}}(x), \tag{4.12} \]

subject to the boundary conditions at the liquid-crust interface, $z = s(x,t),$

\[ C_{H^+_{1z}} = \frac{\bar{D}a(1)C_{H^+}^{*2}}{D_{H^+}C_{H^+}^3}C_{H^+0}^3 - \frac{\bar{D}a(-1)C_{Fe^{3+}}^*C_{Fe^{3+}}^4}{D_{H^+}C_{H^+}^*}C_{Fe^{3+}0}, \]

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

\[ C_{Fe^{3+}_{1z}} = -\frac{\bar{D}a(1)C_{H^+}^*C_{H^+0}^3}{C_{Fe^{3+}}^*} + \bar{D}a(-1)C_{Fe^{3+0}}, \]

and the boundary conditions at the liquid-air interface, $z = h(x,t),$

\[ C_{H^+_{1z}} = 0, \]

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

\[ C_{Fe^{3+}_{1z}} = 0. \]
Applying these boundary conditions we find,

\[
P e C_{H+0} \int_{s(x,t)}^{h(x,t)} u_0 \, dz = -\frac{D a_{(1)} C_{H+}^3 D_{Fe}^2}{D_{H+}^3} C_{H+}^3 + \frac{D a_{(-1)} C_{Fe}^2 D_{Fe}^3}{D_{H+}^3} C_{Fe}^3 + \frac{\hat{I} d^2}{C_{H+}^3 D_{H+}^3} k_{-1} C_{Fe}^2 (h - s)
\]

\[
- \frac{\hat{I} d^2}{C_{H+}^3 D_{H+}^3} C_{Fe}^3 + C_{H+}^3 \int_{s(x,t)}^{h(x,t)} k_1 C_{O_2} \, dz,
\]

\[
P e C_{Fe^{2+0}} \int_{s(x,t)}^{h(x,t)} u_0 \, dz = \frac{\hat{I} d^2}{C_{H+}^3 D_{H+}^3} k_{-1} C_{Fe}^2 (h - s)
\]

\[
- \frac{\hat{I} d^2}{C_{H+}^3 D_{H+}^3} C_{Fe}^3 + C_{H+}^3 \int_{s(x,t)}^{h(x,t)} k_1 C_{O_2} \, dz,
\]

\[
P e C_{Fe^{3+0}} \int_{s(x,t)}^{h(x,t)} u_0 \, dz = \frac{\hat{I} d^2}{C_{H+}^3 D_{H+}^3} k_{-1} C_{Fe}^2 (h - s)
\]

\[
+ \frac{\hat{I} d^2}{C_{H+}^3 D_{H+}^3} C_{Fe}^3 + C_{H+}^3 \int_{s(x,t)}^{h(x,t)} k_1 C_{O_2} \, dz.
\]

Now we substitute \( \int_{s(x,t)}^{h(x,t)} u_0 \, dz = Q(t) \) from the volumetric flow Equation (4.7) and \( (h - s) = \left( \frac{3Q(t)}{\sin \theta} \right)^{\frac{1}{3}} \) from the crust growth Equation (4.4). Furthermore, we redimensionalize the equations using Table (3.1), Table (3.2) and the scaling, \( \hat{I} = \epsilon \bar{I} \). The following system of differential equations will be solved numerically in Chapter V.

\[
\dot{Q}(\hat{t}) \dot{C}_{H+ \hat{z}} = -\kappa_1 \ddot{C}_{H+} + \kappa_{-1} \ddot{C}_{Fe^{3+}}
\]

\[
+ k_{-1} \left( \frac{3Q(\hat{t}) \mu}{\sin \theta \rho g} \right)^{\frac{1}{3}} \dot{C}_{Fe^{3+}} + \dot{C}_{Fe^{2+}} \dot{C}_{H+} \int_{\dot{s}(\hat{z}, \hat{t})}^{\dot{h}(\hat{z}, \hat{t})} k_1 \dot{C}_{O_2} \, d\hat{z}, \quad (4.13)
\]

\[
\dot{Q}(\hat{t}) \dot{C}_{Fe^{2+ \hat{z}}} = k_{-1} \left( \frac{3Q(\hat{t}) \mu}{\sin \theta \rho g} \right)^{\frac{1}{3}} \dot{C}_{Fe^{3+}} + \dot{C}_{Fe^{2+}} \dot{C}_{H+} \int_{\dot{s}(\hat{z}, \hat{t})}^{\dot{h}(\hat{z}, \hat{t})} k_1 \dot{C}_{O_2} \, d\hat{z}, \quad (4.14)
\]

\[
\dot{Q}(\hat{t}) \dot{C}_{Fe^{3+ \hat{z}}} = \kappa_1 \ddot{C}_{H+} - \kappa_{-1} \ddot{C}_{Fe^{3+}}
\]

\[
- k_{-1} \left( \frac{3Q(\hat{t}) \mu}{\sin \theta \rho g} \right)^{\frac{1}{3}} \dot{C}_{Fe^{3+}} + \dot{C}_{Fe^{2+}} \dot{C}_{H+} \int_{\dot{s}(\hat{z}, \hat{t})}^{\dot{h}(\hat{z}, \hat{t})} k_1 \dot{C}_{O_2} \, d\hat{z}. \quad (4.15)
\]
Next we solve for the concentration of oxygen. We assumed that $I$ is $O(\epsilon)$ for $O_2$ causing the solution to be linear. Equation (3.28) is $C_{O_2zz} = 0$. When we integrate with respect to $z$ twice we obtain,

$$C_{O_20} = A(x)z + B(x),$$

where $A(x)$ and $B(x)$ are functions of $x$. The boundary condition at $z = s(x,t)$ is $C_{O_20z}(s) = \frac{F_c d}{D_{O_2} C^*_{O_2}}$, which represents the flux to the crust. Therefore $A(x) = \frac{F_c d}{D_{O_2} C^*_{O_2}}$.

At the boundary $z = h(x,t)$ we implement Henry’s Law to obtain,

$$C_{O_2} = \frac{F_c d}{D_{O_2} C^*_{O_2}} z + \frac{K_{H+} P_{O_2}}{C^*_{O_2}} - \frac{F_c d}{D_{O_2} C^*_{O_2}} h. \quad (4.16)$$

Now we redimensionalize the concentration equations for the $O(\epsilon)$ system. Using Table (3.1), Equation (4.16) becomes,

$$\hat{C}_{O_2} = \frac{F_c}{D_{O_2}} \hat{z} + K_{H+} P_{O_2} - \frac{F_c}{D_{O_2}} \hat{h}. \quad (4.17)$$

The equations for the ionic species, $H^+$, $Fe^{2+}$ and $Fe^{3+}$ contain $\int_{\hat{s}(\hat{x},\hat{t})}^{\hat{h}(\hat{x},\hat{t})} k_1 \hat{C}_{O_2} d\hat{z}$.

By integrating Equation (4.17) with respect to $z$ we have

$$\int_{\hat{s}(\hat{x},\hat{t})}^{\hat{h}(\hat{x},\hat{t})} k_1 \hat{C}_{O_2} d\hat{z} = k_1 \left[ -\frac{F_c}{2 D_{O_2}} (\hat{s}(\hat{x},\hat{t}) - \hat{h}(\hat{x},\hat{t}))^2 + K_{H+} P_{O_2} (\hat{h}(\hat{x},\hat{t}) - \hat{s}(\hat{x},\hat{t})) \right]. \quad (4.18)$$

By substituting Equation (4.7), the volumetric flow rate, we obtain

$$\int_{\hat{s}(\hat{x},\hat{t})}^{\hat{h}(\hat{x},\hat{t})} k_1 \hat{C}_{O_2} d\hat{z} = k_1 \left[ -\frac{F_c}{2 D_{O_2}} \left( \frac{3 \hat{Q}(\hat{t})}{\sin \theta} \right)^{\frac{2}{3}} + K_{H+} P_{O_2} \left( \frac{3 \hat{Q}(\hat{t})}{\sin \theta} \right)^{\frac{1}{3}} \right]. \quad (4.19)$$

We use Equation (4.19) in the system of differential equations for the ionic species.

The final equation to redimensionalize is Equation (3.43). Using the scalings in Table (3.1) and Table (3.2), we have

$$\hat{s}_t = -\frac{\kappa_1}{\rho_{Fe(OH)_3}} \hat{C}_{H^+}^{\frac{2}{3}} + \frac{\kappa_{Fe(OH)_3}}{\rho_{Fe(OH)_3}} \hat{C}_{Fe^{3+}}. \quad (4.20)$$
CHAPTER V
NUMERICAL SOLUTION

We solve the following system of ordinary differential equations for the reactive transport of species,

\[
\dot{Q}(\hat{t}) \dot{C}_{H^+} = -\kappa_1 \dot{C}_{H^+}^3 + \kappa_{-1} \dot{C}_{Fe^{3+}}^1 \\
+ k_{-1} \left( \frac{3\dot{Q}(\hat{t})\mu}{\sin \theta \rho g} \right)^{\frac{3}{2}} \dot{C}_{Fe^{3+}}^4 - \dot{C}_{Fe^{2+}}^4 \dot{C}_{H^+}^4 \int_{\hat{s}(\hat{x},\hat{t})}^{h(\hat{x},\hat{t})} k_1 \dot{C}_{O_2} d\hat{z},
\]

\[
\dot{Q}(\hat{t}) \dot{C}_{Fe^{2+}} = k_{-1} \left( \frac{3\dot{Q}(\hat{t})\mu}{\sin \theta \rho g} \right)^{\frac{3}{2}} \dot{C}_{Fe^{3+}}^4 - \dot{C}_{Fe^{2+}}^4 \dot{C}_{H^+}^4 \int_{\hat{s}(\hat{x},\hat{t})}^{h(\hat{x},\hat{t})} k_1 \dot{C}_{O_2} d\hat{z},
\]

\[
\dot{Q}(\hat{t}) \dot{C}_{Fe^{3+}} = \kappa_1 \dot{C}_{H^+}^3 - \kappa_{-1} \dot{C}_{Fe^{3+}}^1 \\
- k_{-1} \left( \frac{3\dot{Q}(\hat{t})\mu}{\sin \theta \rho g} \right)^{\frac{3}{2}} \dot{C}_{Fe^{3+}}^4 + \dot{C}_{Fe^{2+}}^4 \dot{C}_{H^+}^4 \int_{\hat{s}(\hat{x},\hat{t})}^{h(\hat{x},\hat{t})} k_1 \dot{C}_{O_2} d\hat{z}.
\]

We solve this system numerically using Matlab.

The Matlab code uses the ode15s solver. The ode15s solver uses multistep numerical differentiation formulas. First, we input the parameter values listed in Table (5.1). The values for the reaction rates, \( k_1, k_{-1}, \kappa_1 \) and \( \kappa_{-1} \), were chosen to be consistent with site specific data [16]. Next, we create an mfile which lists the system of equations as a vector array (Appendix C). In the main code we input the time dimension, space dimension, initial conditions and boundary conditions. The space dimension is denoted as \( x = 0 : 10 : 4000 \) where \( x \) steps from 0 cm to 4000 cm with an increment of 10 cm. The step size of 10 cm is sufficient since a smaller step size
resulted in the same concentration values and a larger step size caused error in the concentration values. The sheetflow width is set at 4000 cm to adequately capture the downflow depletion zone of Fe(II). The time dimension is denoted as $t = 0 : dt : T_{max}$ where $dt = T_{max}/n_{max}$. $T_{max} = 31,536,000$ s, the number of seconds in a year and $n_{max}$ represents the number of time steps. The $n_{max}$ value was chosen based on the tolerance of the ionic concentrations. Setting $n_{max} = 10^4$ is sufficient for accurate simulations. We also input the volumetric flow rate $\hat{Q}(\hat{t}) = 5 \times (1 + 0.1 \times \sin(\frac{4 \pi t}{T_{max}}))$, where the sine function accounts for the seasonal change.

The initial conditions for $\hat{s}(x, t)$ and $\hat{h}(x, t)$ are

$$
\hat{s}(i, 1) = 1 + 0.9 \theta \sin \left(\frac{6 \pi x(i)}{4000}\right),
$$

$$
\hat{h}(i, 1) = \hat{s}(i, 1) + \left(\frac{3 \hat{Q}(\hat{t}(1)) \mu}{g \rho \sin \theta}\right)^{\frac{1}{3}},
$$

where $s(i, 1)$ is the initial height of 1 cm plus a small magnitude of a sine function and $h(i, 1)$ is determined from Equation (4.9).

The boundary conditions for the ionic concentrations are $C_{H^+} = .0631$ mg/L,

$C_{Fe^{2+}} = 600$ mg/L and $C_{Fe^{3+}} = 5.6$ mg/L (Table 2.1). The concentrations are listed as a matrix, where the columns represent the ions $H^+$, $Fe^{2+}$ and $Fe^{3+}$ respectively. The initial concentrations were multiplied by the factor, $(1+0.1 \times (\sin(\frac{4 \pi t(n)}{T_{max}})))$, to alter the concentrations to be a function of time. We include this time parameter since the flow rate is a function of time. The ode15s solver computes the concentration of the ionic species at each time step over the 4000 cm length downstream.
Table 5.1: Parameter Values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_1$</td>
<td>$1 \text{ cm/(s} \times (\text{mg/L})^2)$</td>
<td>[16]</td>
</tr>
<tr>
<td>$\kappa_{-1}$</td>
<td>$0.17 \text{ cm/s}$</td>
<td>[16]</td>
</tr>
<tr>
<td>$k_1$</td>
<td>$2.5 \times 10^{-7} \text{ /}(s \times (\text{mg/L})^8)$</td>
<td>Derived from [10]</td>
</tr>
<tr>
<td>$k_{-1}$</td>
<td>$2.3 \times 10^{-3} \text{ /}(s \times (\text{mg/L})^3)$</td>
<td>[16]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$0.01 \text{ g/(s} \times \text{cm})$</td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>$1 \text{ g/cm}^3$</td>
<td>density of water</td>
</tr>
<tr>
<td>$g$</td>
<td>$980 \text{ cm/s}^2$</td>
<td>gravity</td>
</tr>
<tr>
<td>$F_c$</td>
<td>$1 \times 10^{-7} \text{ cm} \times \text{mg/(s} \times \text{L})$</td>
<td></td>
</tr>
<tr>
<td>$D_{O_2}$</td>
<td>$1.97 \times 10^{-5} \text{ cm}^2/\text{s}$</td>
<td></td>
</tr>
<tr>
<td>$K_{H^+}$</td>
<td>$41.6 \text{ mg/(L} \times \text{atm)}$</td>
<td></td>
</tr>
<tr>
<td>$P_{O_2}$</td>
<td>$0.2 \text{ atm}$</td>
<td>[16]</td>
</tr>
<tr>
<td>$\theta$</td>
<td>$0.03^\circ \times \pi/180$</td>
<td>[16]</td>
</tr>
<tr>
<td>$\rho_{Fe(OH)_3}$</td>
<td>$3.3 \times 10^6 \text{ mg/L}$</td>
<td>[16]</td>
</tr>
</tbody>
</table>

Now that we have the concentrations over the fluid run we look at the crust growth over time and space. The interfaces $\hat{s}(i, n)$ and $\hat{h}(i, n)$ are updated by

\[
\hat{s}(1, n + 1) = \hat{s}(i, n) + dt \times \left( \frac{\kappa_1}{\rho_{Fe(OH)_3}} \hat{C}_{H^+}^3 + \frac{\kappa_{-1}}{\rho_{Fe(OH)_3}} C_{Fe^{3+}} \right),
\]

\[
\hat{h} = \hat{s}(i, n + 1) + \left( \frac{3\dot{Q}(t(1))\mu}{g\rho \sin \theta} \right)^{\frac{1}{2}},
\]

38
where \( s(1, n+1) \) is the crust growth Equation (4.20) and \( h(1, n+1) \) is Equation (4.9).

5.1 Analysis of the Ionic Concentrations

We have the general form for the ionic concentration \( i \), \( \dot{Q}(\dot{t})\dot{C}_{i\hat{z}} = J + \int_{\hat{s}(x,t)}^{\hat{h}(x,t)} \hat{I}dz \), where \( \dot{Q}(\dot{t})\dot{C}_{i\hat{z}} \) represents the convective transport of the ionic species \( i \), \( J \) represents the surface reaction and \( \hat{I} \) represents the bulk reaction. We have precipitation when \( J \) is positive and \( \hat{I} \) is negative. The concentrations of \( \text{Fe(II)}, \text{Fe(III)} \) and the hydrogen ion are dependent on \( x \) while the concentration of oxygen is a linear function of \( z \). Furthermore, the concentrations of \( \text{Fe(II)}, \text{Fe(III)} \), the hydrogen ions and oxygen are all independent of time. Therefore, oxygen is the only component in the integral of \( \hat{I} \) which is dependent on the limits of integration.

Figure (5.1) shows the concentration of \( H^+ \) from the source of the AMD at \( x = 0 \) to the end of the sheetflow at \( x = 4000 \). The concentration of the hydrogen ion increases until about 3200 cm downstream and then levels off. The general equation is \( \dot{Q}(\dot{t})\dot{C}_{H^+_\hat{z}} = J + \int_{\hat{s}(x,t)}^{\hat{h}(x,t)} \hat{I}dz \). Since we expect \( J \) to be positive and \( I \) to be negative, the quantity \( \dot{Q}(\dot{t})\dot{C}_{H^+_\hat{z}} \) is positive and the concentration of \( H^+ \) increases at the beginning of the sheetflow. At the end of the sheetflow, the reactants are depleted and \( J \) and \( I \) tend to zero, therefore, the slope of \( \dot{Q}(\dot{t})\dot{C}_{H^+_\hat{z}} \) is zero. We anticipate the surface reaction dominating the bulk reaction. The surface reaction is a source for the hydrogen ions and a sink for \( \text{Fe(III)} \). The bulk reaction is a sink for the hydrogen ions, oxygen and \( \text{Fe(II)} \) and a source for \( \text{Fe(III)} \). The concentration increases from .0631 mg/L to .63228 mg/L over 3000 cm downstream. The initial pH is 4.2 [16] and
at 3000 cm downstream the pH decreases to 3.2. After 3200 cm, the pH levels off to 2.8 because the reaction components are depleted. Hence, the formation of yellowboy increases the acidity in the sheetflow.

![Graph showing concentration of H⁺ over the downstream fluid run.](image)

Figure 5.1: Concentration of H⁺ over the downstream fluid run.

Figure (5.2) shows the concentration of Fe²⁺ from the source of the AMD at x = 0 to the end of the sheetflow at x = 4000. The concentration of Fe(II) decreases nearly linear over the first 3000 cm before levelling off. The general equation is \( \dot{Q}(t) \dot{C}_{Fe^{2+}} = \int_{s(x,t)}^{h(x,t)} \dot{I}d\dot{z} \). We expect \( \dot{I} \) to be negative which corresponds to the negative slope of the concentration on Fe(II) over the sheetflow length, x. The negative \( \dot{I} \) also causes the bulk reaction to be a sink of Fe(II). The Fe(II) oxidizes quickly to form Fe(III). The initial concentration is 600 mg/L and decreases to 51.67 mg/L at the end of the downstream run. Also, the negative slope levels off around 3200 cm.
and becomes zero. Thus, there is no oxidation reaction after 3200 cm downstream.

Figure 5.2: Concentration of Fe$^{2+}$ over the downstream fluid run.

Figure (5.3) shows the concentration of Fe$^{3+}$ from the source of the AMD at $x = 0$ to the end of the sheetflow at $x = 4000$. The concentration of Fe(III) decreases over the downstream. The general equation is $\dot{Q}(t)\dot{C}_{Fe^{3+}} = -J - \int_{s(x,t)}^{h(x,t)} \hat{I}d\hat{z}$. The negative $J$ indicates the loss of Fe(III) due to precipitation of the crust, while the bulk reaction is a source of Fe(III). The concentration of Fe$^{3+}$ decreased from 5.6 mg/L to 5.03 mg/L over the 3000 cm downstream. The change in concentration of Fe(III) becomes relatively flat after 3200 cm. The surface reaction is no longer occurring and the precipitation of Fe(OH)$_3$ is limited. Therefore, the sheetflow domain ends around 3200 cm and the location of the limestone bed is determined.
5.2 Analysis of the Iron Hydroxide Crust Growth

Figure (5.4) shows the crust growth at 4000 cm downstream over the course of 1 year. The lower line denotes $\hat{s}(4000,t)$ and oscillates around 1 cm. The upper line denotes $\hat{h}(4000,t)$ and oscillates as a sine function. The thickness of the crust growth is shown at the end of the sheetflow over a year. The waves indicate the seasonal change in growth of $\hat{s}(4000,t)$ over the course of a year.

Figure (5.5) shows the total growth of $\hat{s}(\hat{x},\hat{t})$ over the year. The initial growth line at 1 cm corresponds to the initial time. The other lines represent the total growth of the liquid-crust interface at approximately 3 months, 6 months, 9 months and 1 year. These quarterly locations account for seasonal variations over a full year. By the end of the year we have a growth of 10.09 cm. At a downstream length of 3200
cm we see a convergence of the crust growth lines and they appear to level off to 1 cm. This coincides with the ionic concentrations tapering off around 3200 cm since the reactants are depleted. Therefore, the precipitation of iron hydroxide has stopped along with the crust growth.

Figure 5.4: Crust height and liquid-air interface location versus time at 4000 cm downstream.

Figure (5.6) represents the change in location of the liquid-air interface in response to the flow rate and the growth of the crust. The location of the liquid-crust interface shifts vertically with the growth of the liquid-crust interface. The initial location is 1.66 cm. The other lines represent the change in location of the liquid-air interface seasonally over a full year. Similar to Figure (5.5), the lines converge around 3200 cm and level off to around the location of the initial height. The reactants are depleted at 3200 cm and there is no crust growth.
Figure 5.5: Total growth of the liquid-crust interface at initial and seasonal locations over a year.

Figure 5.6: Initial and seasonal locations of the liquid-air interface over a year.
5.3 Analysis of the Forward Bulk Reaction Rate

Figure (5.7) represents the change in concentration of Fe(II) versus the change in the forward bulk reaction rate, $k_1$, over the distance of the sheetflow. The initial reaction rate of $2.5 \times 10^{-7} \text{1/(s } \times (\text{mg/L})^8\text{)}$ is based on site specific data and was derived from a paper by Kirby et al. [10]. There was a range of values for the bulk reaction rate and we choose a reaction rate on the high end. Therefore, for comparison, the reaction rate decreases by a factor of 10 and a factor of 100. When the forward bulk reaction rate lowers by a factor of 10, the concentration of Fe(II) at 3000 cm downstream is about 75 mg/L and levels off to 50 mg/L. When the forward bulk reaction rate lowers by a factor of 100, the concentration of Fe(II) at 3000 cm is around 120 mg/L and tapers off to 100 mg/L. Although, the decreasing trend of the concentration of Fe(II) over the sheetflow is consistent, the lower the reaction rate the lower the amount of Fe(II) is oxidized. The forward reaction rate corresponds to the abundance of bacteria. The general trend is that the reaction rate increases as the amount of bacteria increases. The initial bulk reaction rate allows for a higher amount of Fe(OB).

Figure (5.8) represents the change in crust growth at 1000 cm and 3000 cm downstream versus change in the forward bulk reaction rate. Figure (5.8A) represents the change in crust growth at 1000 cm downstream. In the model case, with a forward bulk reaction rate of $2.5 \times 10^{-7}/(\text{s } \times (\text{mg/L})^8\text{)}$ the crust growth grew from 1 cm to 10.09 cm in the first 1000 cm of the sheetflow. When the forward bulk reaction
rate decreases by a factor of 10 and 100, the crust growth grew to only 9.91 cm and 9.57 cm respectively. The decrease in forward bulk reaction rate causes a decrease in crust growth formed. In Figure 5.7, we found that a decrease in the forward bulk reaction rate caused less Fe(II) to oxidize, hence a slower crust growth. Figure (5.8B) represents the crust growth at 3000 cm downstream. When the forward bulk reaction rate decreases by a factor of 10 and 100, the crust growth grows to 6.26 cm and 5.48 cm respectively. Again, the decrease in the bulk reaction rate decreases the Fe(II) reacted which in turn causes less iron hydroxide crust to form.

![Figure 5.7: Change in concentration of Fe$^{2+}$ versus the change in forward bulk reaction rate.](image)

Figure 5.7: Change in concentration of Fe$^{2+}$ versus the change in forward bulk reaction rate.
5.8A: Crust growth at 2000 cm. 

5.8B: Crust growth at 3000 cm. 

Figure 5.8: Crust growth at 2000 cm and 3000 cm downstream versus change in the forward bulk reaction rate.

5.4 Analysis of the Backward Bulk Reaction Rate

Figure (5.9) represents the change in concentration of Fe\(^{2+}\) versus change in the backward bulk reaction rates. When the backward bulk reaction rate increases by a factor of 10, the concentration of Fe(II) is 70.4 mg/L at 3000 cm downstream which is higher than the model case. The increase in backward bulk reaction increases the amount of Fe(II) which did not oxidize, causing slower reaction rates and a slower crust growth. When the backward bulk reaction rate decreases by a factor of 10, the concentration of Fe(II) is 44.8 mg/L at 3000 cm. The decrease in backward bulk reaction rate causes more Fe(II) to react and hence more iron hydroxide crust to form.

Figure (5.10) represents the change in crust growth at 1000 cm and 3000 cm versus change in the backward bulk reaction rates. Figure (5.10A) represents the change in crust growth at 1000 cm over a year. By increasing the backward bulk reaction
rate by a factor of 10, the crust growth at 1000 cm is 9.94 cm. When the backward bulk reaction rate decreases by a factor of 10, the crust growth is 10.08 cm which is slightly higher than the model case with 10.05 cm. An increase in the backward bulk reaction rate causes less crust growth formation. Figure (5.10B) represents the change in crust growth at 3000 cm over a year. When the backward bulk reaction rate increases by a factor of 10, the crust growth is 5.40 cm which is much smaller than the model case of 6.26 cm. By decreasing the backward bulk reaction rate by a factor of 10, the crust growth is 6.66 cm. Again, an increase in the backward bulk reaction rate causes a slower crust growth while a decrease in the backward bulk reaction rate causes an increase in crust growth.

Figure 5.9: Change in concentration of Fe$^{2+}$ versus the change in forward bulk reaction rate.
5.10A: Crust growth at 2000 cm.  

5.10B: Crust growth at 3000 cm.

Figure 5.10: Crust growth at 2000 cm and 3000 cm downstream versus change in the forward bulk reaction rate.

5.5 Analysis of a Fixed Angle of Inclination

In the system of equations, the volumetric flow rate appears on both sides of the equations. We have the convective transport of ionic species \( i \), \( \hat{Q}(\hat{t})C_{i,x} \), on the left-hand side and the quantity \( (3\hat{Q}(\hat{t})\mu \sin \theta \rho g)^{1/3} \) on the right-hand side. Since the cube root of the volumetric flow rate is taken on the right-hand side, a change in the volumetric flow rate will have a greater effect on the left-hand side. In Equation (4.9) we found \( \hat{h}(\hat{x},\hat{t}) - \hat{s}(\hat{x},\hat{t}) = (3\hat{Q}(\hat{t})\mu \sin \theta)^{1/3} \). As the volumetric flow rate increases, the film thickness increases with a fixed angle of inclination. Hence, for similar concentration levels, there will be greater mass of concentrations in thicker film. In particular, we have a larger concentration of Fe(III) in the thicker film which leads to more crust growth overall.

Figure (5.11) represents the change in concentration of \( Fe^{2+} \) versus a change in the volumetric flow rate, \( \hat{Q}(\hat{t}) \), over the sheetflow. In the model, we determined the flow
rate to be \( \hat{Q}(t) = 5 \times (1 + 0.1 \times \sin(\frac{4\pi t}{T_{\text{max}}})) \), or approximately 5 cm\(^3\)/s. When we increased the volumetric flow rate to 7 cm\(^3\)/s, the concentration of Fe(II) decreased from 600 mg/L to around 200 mg/L at 3000 cm downstream. Therefore, a lower amount of Fe(II) is oxidized. When the volumetric flow rate is lowered to 3 cm\(^3\)/s, the concentration of Fe(II) decreased from 600 mg/L to 50 mg/L in the first 2000 cm. The Fe(II) oxidizes quickly and is depleted for the rest of the sheetflow.

![Graph](image)

Figure 5.11: Change in concentration of Fe\(^{2+}\) versus the volumetric flow rate.

Figure (5.12) represents the change in concentration of H\(^+\) and Fe\(^{3+}\) versus the change in the volumetric flow rate. Figure (5.12A) shows the change in the concentration of the hydrogen ions. When the volumetric flow rate increases to 7 cm\(^3\)/s, the concentration of hydrogen ions increases gradually from .06 mg/L to .20 mg/L at 3000 cm downstream. When the volumetric flow rate decreases to 3 cm\(^3\)/s, the concentra-
tion of the hydrogen ions increases gradually in the first 1500 cm and then increases rapidly between 1500 cm and 2000 cm. In the last 2000 cm, the slope of the hydrogen ion concentration is nearly zero. In Figure (5.11) we noticed a decrease in flow rate caused the Fe(II) concentration to decrease rapidly in the first 2000 cm. In the differential equation for hydrogen ions, (Equation 4.13), a smaller Fe(II) causes the bulk reaction, $I$, to be smaller and the surface reaction, $J$, to dominant thus $\dot{Q}(\dot{t})C_{H^+}$ has a positive slope. After 2000 cm downstream, the reactants are depleted causing the slope to become zero. Figure (5.12B) shows the change in the concentration of Fe(III) over the sheetflow. When the volumetric flow rate increases to 7 cm$^3$/s, the concentration of Fe(III) decreases gradually from 5.6 mg/L to 5.5 mg/L at 3000 cm downstream. When the volumetric flow rate decreases to 3 cm$^3$/s, the concentration of Fe(III) decreases from 5.6 mg/L to 4.8 mg/L in the first 2000 cm. From the differential equation for Fe(III) (Equation 4.15), the decrease in Fe(II) and increase in the hydrogen ions under the same lowered volumetric flow rate, causes the overall quantity $\dot{Q}(\dot{t})C_{Fe^{3+}}$ to be negative. Hence, a decrease in Fe(III) concentration rate.

Figure (5.13) represents the change of crust growth at 2000 cm and 3000 cm downstream in relation to the change in the volumetric flow rate, $\dot{Q}(\dot{t})$ with the angle of inclination fixed at $.03^\circ$. Figure (5.13A) shows the crust growth at 2000 cm downstream. The flow rate of 7 cm$^3$/s lies slightly above the base line of 5 cm$^3$/s, while the flow rate of 3 cm$^3$/s is drastically lower. The changes in concentration with a decrease in volumetric flow rate, show that in the first 2000 cm the ions have fully reacted.
causing the crust growth to slow down. In Figure (5.13B), the volumetric flow rate of 3 cm$^3$/s no longer has crust growth occurring. When the flow rate increases, the crust growth is higher than the growth of the initial flow rate. We expect a faster flow rate to cause less time for the bulk reaction to occur and more Fe(II) to be available to oxidize downstream. Furthermore, we determined that at a volumetric flow rate of 5 cm$^3$/s the reactants were depleted around 3200 cm and the limestone bed should be placed at 3200 cm. When the volumetric flow rate increased the reactions have less time to occur and the limestone bed should be placed further downstream to ensure the maximum amount of Fe(OH)$_3$ has formed. When the volumetric flow rate decreases the bulk reaction has more time to form Fe(OH)$_3$ and the limestone bed could be placed earlier in the sheetflow. For instance, with a volumetric flow rate of 3 cm$^3$/s the limestone bed could be placed at 2000 cm.

Figure 5.12: Change in concentration of H$^+$ and Fe$^{3+}$ in response to a change in the volumetric flow rate.

5.12A: Concentration of H$^+$.

5.12B: Concentration of Fe$^{3+}$.
Figure 5.13: The crust growth at 2000 cm and 3000 cm downstream versus change is the volumetric flow rate.

5.6 Analysis of a Fixed Volumetric Flow Rate

Now we observe the relationship between the angle of inclination and film thickness with the volumetric flow rate fixed. Figure (5.14) represents the change in concentration of Fe$^{2+}$ in response to a change in the angle of inclination. The initial angle of $0.03^\circ$ corresponds to the angle of inclination at the Mushroom Farm [16]. At 3000 cm downstream, the concentration of Fe(II) is 50.5 mg/L with the angle of inclination of $0.03^\circ$. When the angle of inclination increases to $3.0^\circ$ and $6.0^\circ$, the concentration of Fe(II) is 58.8 mg/L and 60.6 mg/L respectively at 3000 cm downstream. The increase in angle of inclination causes a decrease in the bulk reaction due to a faster flow and a thinner film thickness. Hence, more Fe(II) did not oxidize and in turn less Fe(OH)$_3$ formed and the growth rate decreases. The sheetflow system would need to
be lengthened if there were a higher degree of inclination. In future work, the angle of inclination should be a function of $x$ to simulate flow over different inclinations of the terrain.

![Graph showing change in concentration of Fe$^{2+}$ versus the angle of inclination.](image)

Figure 5.14: Change in concentration of Fe$^{2+}$ versus the angle of inclination.

Figure (5.15) represents the change in crust growth at 2000 cm and 3000 cm downstream with changes in the angle of inclination and a fixed volumetric flow rate of 5 cm$^3$/s. Figure (5.15A) represents the crust growth at 2000 cm. The crust growth with the initial angle of inclination $0.03^\circ$ changes from 1 cm to 9.89 cm at the end of a year. When the angle of inclination increases to $3.0^\circ$ and $6.0^\circ$, the crust growth grew to 9.78 cm and 9.76 cm respectively, after a year. Figure (5.15B) represents the crust growth at 3000 cm downstream. The initial crust growth at the angle of inclination of $0.03^\circ$ changes from 1 cm to 6.26 cm at 3000 cm after a year. When the
angle of inclination increases to 3.0° and 6.0°, the crust growth changes from 1.05 cm to 6.23 cm and 1.09 to 6.24 cm respectively at 3000 cm downstream at the end of year. The increase in angle of inclination causes a decrease in the crust growth due to an increase in fluid velocity. The bulk reaction has less time to react thus, the reactions occur slower and less Fe(OH)₃ growth is formed.

5.15A: Crust growth at 2000 cm. 5.15B: Crust growth at 3000 cm.

Figure 5.15: The crust growth at 2000 cm and 3000 cm downstream versus change in the angle of inclination.

5.7 Analysis of a Fixed Film Thickness

The volumetric flow equation, Equation (4.9), is \( \dot{Q}(\dot{t}) = \frac{\sin \theta \rho g}{3\mu}(\dot{h}(\dot{x}, \dot{t}) - \hat{s}(\dot{x}, \dot{t}))^3 \). In order to analyze how in the volumetric flow rate changes with respect to the angle of inclination we allow the film thickness to be fixed. In the Matlab code, a parameter for the film thickness represents the difference between the initial location of the liquid-crust interface, \( \hat{s}(\dot{x}, \dot{t}) \), and initial location of the liquid-air interface, \( \dot{h}(\dot{x}, \dot{t}) \).
Hence, the volumetric flow rate is dependent only on the angle of inclination.

Figure (5.16) represents the change in concentration of Fe$^{2+}$ with a change in angle of inclination and a fixed distance between the liquid-crust and liquid-air interface. When the angle of inclination increased to 3.0° and 6.0°, the concentration of Fe(II) is 58.8 mg/L and 61.1 mg/L at 3000 cm downstream. The greater the angle of inclination, the more Fe(II) which has not reacted due to an increase in velocity. In the differential equation for Fe(II), Equation (4.14), since we are setting the quantity

$$\left(\frac{3\hat{Q}(\hat{t}(1))\mu}{g\rho \sin \theta}\right)^{\frac{1}{3}}$$

to be constant, the right-hand of the equation does not change with a change in $\theta$. However, on the left-hand side, as $\theta$ increases the volumetric flow rate increases which causes the quantity $\hat{Q}(\hat{t})C_{Fe^{2+}x}$ to increase. Thus, the magnitude of $\hat{C}_{Fe^{2+}x}$ decreases to compensate for the increase in $\hat{Q}(\hat{t})$.

Figure (5.17) represents the change in concentration of the hydrogen ions and Fe(III) versus the change in the angle of inclination with fixed film thickness. Figure (5.17A) represents the change in concentration of the hydrogen ions. Figure (5.17B) represents the change in concentration of Fe$^{3+}$. As the angle of inclination increases there is initially a decrease in the concentration of Fe(III) due to slower Fe(II) oxidation. However, after 3200 cm the situation reverses. There is sufficient Fe(II) downstream that oxidizes leading to greater Fe(III). The situation for hydrogen is similar although opposite in response.
Figure 5.16: Change in concentration of Fe$^{2+}$ versus the angle of inclination.

5.17A: Concentration of H$^+$.  
5.17B: Concentration of Fe$^{3+}$.

Figure 5.17: Change in the angle of inclination versus the change in concentration of H$^+$ and Fe$^{3+}$.
Figure (5.18) represents the change in crust growth at 1000 cm and 3200 cm downstream versus the change in the angle of inclination with a fixed fluid thickness. Figure (5.18A) represents the crust growth at 1000 cm downstream over the year. When the angle of inclination increases to 3.0° and 6.0°, the crust growth increases to 9.96 cm and 9.90 cm, opposed to the base case crust growth of 10.05 cm. The increase in angle of inclination causes the fluid velocity to increase and less time for the reactions to occur. Therefore, in the upstream there is less crust growth. Figure (5.18B) represents the crust growth at 3200 cm downstream over a year. When the angle of inclination increases to 3.0° and 6.0°, the crust growth is 3.74 cm and 3.86 cm respectively, while in the base case the crust growth is 3.75 cm. While the increase in angle of inclination to 3.0° had relatively the same effect as the base case, the increase in angle of inclination to 6.0° causes more crust growth. As we saw in the concentration figures, the surface reaction, $J$, is beating the bulk reaction, $I$, in the upstream and the concentration lines actually cross the base case concentration lines around 3000 cm. By selecting a location after 3000 cm we notice a change in crust growth. The increase in angle of inclination causes faster reaction rates and slower crust growth. However, the reactants are depleted further down the sheetflow which causes an increase in crust growth downstream. Therefore, when there is an increase in the angle of inclination, the limestone bed should be placed further downstream.
5.18A: Crust growth at 1000 cm.  

5.18B: Crust growth at 3200 cm.

Figure 5.18: Change in the angle of inclination versus change in the crust growth at 1000 cm and 3200 cm downstream.

5.8 Analysis of the Forward Surface Reaction Rate

Figure (5.19) represents the change in concentration of Fe$^{2+}$ versus the change in the forward surface reaction rate, $\kappa_1$. The initial forward surface reaction rate is $1 \text{ cm/(s \times mg/L)}^2$ based on site specific data [16]. When the forward reaction rate increases to $100 \text{ cm/(s \times mg/L)}^2$, the concentration of Fe(II) decreases from 600 mg/L to 175 mg/L over the 3000 cm sheetflow. When the forward reaction rate decreases to $.01 \text{ cm/(s \times mg/L)}^2$, the concentration of Fe(II) decreases more rapidly, from 600 mg/L to 25 mg/L over the 3000 cm sheetflow. Since there is no $\kappa_1$ in the differential equation for Fe(II) (Equation 4.14), we need to study the concentration of the hydrogen ions and Fe(III) to fully understand the effect changes in the forward reaction rate have on the concentration of Fe(II).
Figure 5.19: Concentration of Fe$^{2+}$ versus the forward surface reaction rate.

Figure (5.20) represents change in concentration of hydrogen ions and Fe(III) versus change in the forward surface reaction rate, $\kappa_1$. Figure (5.20A) represents the change in concentration of hydrogen ions in response to the change in the forward surface reaction rate. When the forward surface reaction rate decreases to .01 cm/(s $\times$ (mg/L)$^2$), the concentration of the hydrogen ions increases slightly until around 3000 cm downstream where there is a drastic increase. The concentration of the hydrogen ions jumps from 1 mg/L to 3.5 mg/L within a couple centimeters. The smaller forward surface reaction rate causes the surface reaction, $J$, to become more positive leading to enhanced precipitation and causes the rate of change of the hydrogen ions to increase more. Figure (5.20B) represents the change in concentration of Fe(III) versus the change in the forward surface reaction rate. When the forward surface reaction rate decreases to .01 cm/(s $\times$ (mg/L)$^2$), the concentration of Fe(III) decreases dras-
tically at 3000 cm. In the beginning of the sheetflow the concentration of Fe(III) is relatively constant until 2000 cm downstream. However, the concentration of Fe(III) decreases from 5.6 mg/L to 2.3 mg/L quickly between 2800 cm and 3300 cm. The smaller forward surface reaction rate causes the surface reaction, $J$, to increase leading to enhanced precipitation. The increase in the surface reaction, $J$, is causing a faster growth. In turn, the concentration of Fe(II) decreased (Figure 5.19).

![Figure 5.20: Change in the forward surface reaction rate versus the concentration of H$^+$ and Fe$^{3+}$.](image)

5.20A: Concentration of H$^+$  
5.20B: Concentration of Fe$^{3+}$

Figure 5.20: Change in the forward surface reaction rate versus the concentration of H$^+$ and Fe$^{3+}$.

Figure (5.21) shows the change in crust growth versus the change in the forward surface reaction rate at 1000 cm and 3000 cm downstream. Figure (5.21A) shows the crust growth at 1000 cm. When the forward surface reaction rate decreases to $.01 \text{ cm/}(s \times (\text{mg/L})^2)$, the crust growth appears to be identical to the crust growth of the model. As we saw in the concentration figures, the concentrations of the ions were similar to the concentrations we observed in the beginning of the sheetflow.
When the forward surface reaction rate increases to $100 \text{ cm}/(s \times (\text{mg/L})^2)$, the crust growth has a smaller increase, from 1 cm to 9 cm, opposed to a growth of 10 cm at the lower reaction rates. The larger forward surface reaction rate, the smaller the surface reaction, $J$, and the slower the crust growth. Figure (5.21B) represents the crust growth at 3000 cm downstream. When the forward reaction rate decreases to $0.01 \text{ cm}/(s \times (\text{mg/L})^2)$, there is a large increase in crust growth. The crust grew from 1 cm to 8 cm, instead of 6.3 cm as we saw in the base case. The concentrations drastically change around 3000 cm and cause an increase in the surface reaction and a decrease in the bulk reaction, therefore causing more crust growth. When the forward surface reaction rate increases to $100 \text{ cm}/(s \times (\text{mg/L})^2)$, the crust grew from 1 cm to 3 cm, at 3000 cm downstream. The concentrations have little change at this reaction rate, therefore oxidation is occurring slower and less iron hydroxide is forming.

5.21A: Crust growth at 1000 cm.

5.21B: Crust growth at 3000 cm.

Figure 5.21: Crust growth at 1000 cm and 3000 cm versus changes in the forward surface reaction rate.
5.9 Analysis of the Backward Surface Reaction Rate

Figure (5.22) shows the change in concentration versus the change in backward surface reaction rate, $\kappa_{-1}$. The initial backward surface reaction rate is $0.17 \text{ cm}/(s \times (\text{mg/L})^8)$ based on site specific data [16]. When the reaction rate decreases to $0.085 \text{ cm}/(s \times (\text{mg/L})^8)$, the concentration of Fe(II) decreases from 600 mg/L to 200 mg/L. When the backward surface reaction rate increases to $0.34 \text{ cm}/(s \times (\text{mg/L})^8)$, the concentration of Fe(II) decreases from 600 mg/L to 50 mg/L in the first 1500 cm sheetflow. It appears that an increase in the backward reaction rate, decreases the Fe(II) remaining. Since there is no $\kappa_{-1}$ in the Fe(II) differential equation (Equation 4.14) we need to observe the change in concentration of the hydrogen ions and Fe(III).

![Graph showing concentration of Fe$^{2+}$ versus the backward surface reaction rate.]

Figure 5.22: Concentration of Fe$^{2+}$ versus the backward surface reaction rate.

Figure (5.23) represents the change in the concentration of hydrogen ions and Fe(III) versus a change in the backward surface reaction rate. Figure (5.23A) represents the
change in the concentration of hydrogen ions. When the backward surface reaction rate doubles, the concentration of the hydrogen ions increases from .06 mg/L to 1.2 mg/L in the first 1500 cm and then levels off for the rest of the sheetflow. The higher the backward surface reaction rate, the larger the surface reaction, $J$, and since the bulk reaction dominates in the beginning of the sheetflow, the differential equation for hydrogen ions (Equation 4.13) has a positive slope. When the backward reaction rate decreases by a factor of 2, the concentration of hydrogen ions increases slightly from .06 mg/L to .10 mg/L over the 3000 cm sheetflow. The decrease in the backward surface reaction rate, causes the bulk reaction, $J$, to decrease and a slower growth rate. Figure (5.23B) represents the change in concentration of Fe(III). When the backward surface reaction rate decreases, the concentration gradually decreases to 5.55 mg/L over the 3000 cm sheetflow. When the backward surface reaction rate increases, the concentration of Fe(III) decreases from 5.6 mg/L to 4.5 mg/L in the first 1500 cm of the sheetflow. The increase in the backward surface reaction rate causes the surface reaction, $J$, to increase and hence, a faster growth rate. The differential equation for Fe(III) (Equation 4.15) is in terms of a negative surface reaction term, $J$, therefore the slope of the concentration of Fe(III) is negative. The concentrations are fully reacted around 1500 cm and this coincides with the depletion of Fe(II) in the first 1500 cm.
Figure 5.23: Concentration of $H^+$ and $Fe^{3+}$ versus the backward reaction rate.

Figure (5.24) represents the change in crust growth at 1000 cm and 3000 cm versus the change in the backward surface reaction rate, $\kappa_{-1}$. Figure (5.24A) represents the change in crust growth at 1000 cm. When the backward surface reaction rate doubles, the crust height increases from 1 cm to 17 cm, which is much larger than the base case. The ionic species are fully reacting in the beginning of the sheetflow. We notice a larger backward surface reaction rate causes the surface reaction, $J$, to increase and the bulk reaction, $I$, to decrease. Again the surface reaction, $J$, is greater than the bulk reaction, $I$, in the upstream of the flow which causes the reactions to occur quickly. When the backward surface reaction rate decreases by a factor of 2, the crust growth only increases from 1 cm to 5 cm. The smaller backward surface reaction rate causes the surface reaction, $J$, to be small and the bulk reaction, $I$, to be larger which leads to smaller crust growth. Figure (5.24B) represents the change in crust growth at 3000 cm. When the backward surface reaction rate doubles, the crust growth remains constant at 1 cm. Since the reactions were occurring so quickly
in the first 1500 cm, the reactants fully react early in the sheetflow and the reactants are depleted by 3000 cm downstream. When the backward surface reaction rate decreases by a factor of 2, the crust growth increases from 1 cm to 5.5 cm. A small backward surface reaction rate causes the surface reaction, $J$, to be smaller and slower reactions overall. However, with a smaller backward surface reaction rate more reactants are left downstream which causes higher crust growth downstream.

5.24A: Crust growth at 1000 cm. 5.24B: Crust growth at 3000 cm.

Figure 5.24: Crust growth at 1000 cm and 3000 cm versus the change in the backward reaction rate.

5.10 Analysis of the Mushroom Farm Data

Figure (5.25) shows the site measured concentration of Fe$^{2+}$ in the Mushroom Farm [16] versus the numerical prediction. The initial concentration of Fe(II) is 660 mg/L, while the numerical solution started at 600 mg/L. The concentration of Fe(II) at 3000 cm down the sheetflow was 178 mg/L at the Mushroom Farm, while the numerical
solution was 52 mg/L. The decreasing trend in the numerical solution coincides with the data collected at the Mushroom Farm. The numerical solution fits the field data.

Figure 5.25: Site concentration of Fe$^{2+}$ in the Mushroom Farm versus the numerical prediction.

Figure (5.26) shows the site measured pH at the Mushroom Farm versus the numerical prediction. The initial pH at the Mushroom Farm was 4.21 and decreased to 2.85 at 3000 cm downstream [16]. The numerical prediction started at a hydrogen ion concentration of 0.0631 mg/L which correlates to an initial pH of 4.2. The numerical prediction shows the pH decreases to 3.2 at 3000 cm downstream. The pH decreases down the sheetflow since the iron hydroxide crust causes a more acidic pH. The numerical prediction fits the site measured data well.
Figure 5.26: Site measured pH in the Mushroom Farm versus the numerical prediction.

Figure 5.27: Site measured concentration of $O_2$.

Figure (5.27) represents the concentration of $O_2$ at the Mushroom Farm [16]. The initial oxygen concentration at the Mushroom Farm was 1.56 mg/L and increases to
8.55 mg/L over the 3000 cm sheetflow. The data was taken down the sheetflow with respect to the $x$ direction. The overall trend is an increase in $O_2$ over the distance from the AMD emergence. As the reactions occur downstream, the oxygen concentration reaches the atmospheric level.

Figure 5.28: Numerical prediction for the concentration of $O_2$ at the initial location and 2000 cm downstream.

Figure (5.28) represents the numerical prediction for the concentration of $O_2$. The numerical prediction for oxygen is linear in the $z$ direction, since oxygen is allowed to transport through the liquid-air interface. The model does not predict much change in the $x$ direction due to the limits examined. Figure(5.28A) represents the concentration of oxygen at the initial location. The concentration of oxygen changes from 8.312 mg/L to 8.32 mg/L. Figure (5.28B) represents the concentration of oxygen at 2000 cm from the AMD emergence. The concentration of oxygen increases from 8.317
mg/L to 8.32 mg/L at 2000 cm downstream. Hence, the AMD liquid emerges from the mine and immediately reaches the atmospheric level of $O_2$ by Henry’s Law. The predicted concentration of oxygen changes slightly but is relatively constant throughout the sheetflow. The oxygen concentration will match the downstream data of the Mushroom Farm.
CHAPTER VI
SUMMARY AND CONCLUSION

Our model is a passive sheetflow system which is based on the crust growth as a function of iron-oxidizing bacteria. Some of the variables under investigation in our sheetflow system are the length of the sheetflow bed, time to remove Fe(II), pH, and the impact of bacteria. Another objective is to find the growth rate of the iron hydroxide crust.

In our model the following assumptions will be made,

- The model is based on site specific data.
- The fluid does not carry deposited crust downstream.
- Crust is assumed to be non-porous.
- Only oxygen is allowed to leave the liquid-air interface. No other ions are allowed to leave this interface.
- The thickness of vertical growth of the crust is far exceeded by the distance over which the AMD is flowing.
- Crust growth is slow.
- Bacteria are located directly on top of the crust.
- Oxidation reactions are occurring directly above the bacteria layer.

The model analyze the physical properties of a sheetflow system by varying the volumetric flow rate, angle of inclination and fluid film thickness. Increasing the
volumetric flow rate with a fixed angle of inclination caused an increase in the fluid film thickness. When the angle of inclination increased with a fixed volumetric flow rate, the film thickness decreases due to an increase in the fluid velocity. The increase in fluid velocity allowed less time for the reactions to occur and less oxidation to occur, thus less crust formation. When the angle of inclination increased with a fixed fluid film thickness, the volumetric flow rate increased. There was an increase in fluid velocity and the reactions occurred slower. However, since the film thickness remained constant the increase in angle of inclination allowed for more reactants left at the end of the sheetflow and an increase in crust formation downstream.

The reaction rates for the surface reaction and bulk reaction were also varied in the model. An increase in the forward bulk reaction rate, \( k_1 \), caused more Fe(II) to oxidize and more iron hydroxide crust to form. The increase in the forward bulk reaction rate also simulated the increase of iron oxidizing bacteria. The backward bulk reaction rate, \( k_{-1} \), had to reverse effect. By increasing the backward bulk reaction rate, there was less Fe(II) oxidized and less crust formation. When increasing the forward surface reaction rate, \( \kappa_1 \), the surface reaction, \( J \), decreased. There was less oxidation of Fe(II) and thus, a decrease in the iron hydroxide crust. The increase in the backward surface reaction rate, \( \kappa_{-1} \), caused an increase in the surface reaction, \( J \), and more precipitation occurred. There was an increase in the amount of Fe(II) oxidized and in turn more crust growth was formed.
In our model the following results were found:

- The pH decreased from an initial 4.2 to 3.2 at 3000 cm downstream. The formation of iron hydroxide caused an increase in pH over the sheetflow.
- The metals Fe(II) and Fe(III) decreased over the first 3000 cm sheetflow. The concentration is quickly oxidizing to form Fe(III) and in turn the Fe(III) precipitates to from iron hydroxide.
- The chemical reactions slowed down by 3500 cm. The ionic species have completely reacted and are nearly depleted. The effective length of the sheetflow system is 3500 cm and the limestone bed should be placed after to ensure a limited amount of armouring.
- The crust growth grew 10 cm over the course of a year.

To improve the model, we should analyze the bulk reaction rate as a function of dissolved oxygen, temperature and/or the solvability of Fe(III). We can investigate the surface reaction rate as a function of pH. Also, the angle of inclination can be modeled as a function of x.
BIBLIOGRAPHY


APPENDIX A

ANALYSIS OF THE GOVERNING EQUATIONS

The Navier-Stokes Equation (2.2) is

\[
\frac{U}{T} u_t + \frac{U^2}{L} u u_x + \frac{U^2}{L} w w_z = -\frac{\mu U}{\rho d^2} p_x + \frac{\mu U}{\rho L^2} u_{xx} + \frac{\mu U}{\rho d^2} u_{zz} + \frac{\mu U}{\rho d^2} \sin \theta.
\]

To simplify the equation we divide by \(\frac{\mu U}{\rho d^2}\), the coefficient of \(u_{zz}\),

\[
\frac{\rho d^2}{\mu T} u_t + \frac{U \rho d^2}{\mu L} u u_x + \frac{U \rho d^2}{\mu L} w u_z = -p_x + \frac{d^2}{L^2} u_{xx} + u_{zz} + \sin \theta.
\]

The other Navier-Stokes Equation (2.3) follows a similar pattern as Equation (2.2). After taking the partial derivatives and using the nondimensional variables, we find

\[
\frac{U d}{L T} w_t + \frac{U^2 d}{L^2} u w_x + \frac{U^2 d}{L^2} w w_z = -\frac{\mu U L}{\rho d^3} p_z + \frac{\mu U d}{\rho L^2} w_{xx} + \frac{\mu U}{\rho L} w_{zz} - \frac{\mu U}{\rho d} \cos \theta.
\]

Next we will divide by \(\frac{\mu U}{\rho d L}\), the coefficient of \(w_{zz}\)

\[
\frac{\rho d^2}{\mu T} w_t + \frac{U \rho d^2}{\mu L} u w_x + \frac{U \rho d^2}{\mu L} w w_z = -\frac{L^2}{d^2} p_z + \frac{d^2}{L^2} w_{xx} + w_{zz} - \frac{L}{d} \cos \theta.
\]

Again, by substituting the Reynolds number, \(Re, \epsilon\) and \(T\) we have,

\[
\frac{D_{Fe^3}}{\nu} \epsilon w_t + \epsilon Re [uw_x + w w_z] = -\frac{1}{\epsilon^2} p_z + \epsilon^2 w_{xx} + w_{zz} - \frac{1}{\epsilon} \cos \theta. \tag{A.1}
\]

To nondimensionalize the Kinematic Equation (2.4) we define \(\hat{h} = hd\). Initially we have,

\[
\frac{d}{T} \hat{h}_t = \frac{U d}{L} w - \frac{U d}{L} u h_x.
\]
Since the coefficients of $w$ and $uh_x$ are the same, we will divide by $\frac{Ud}{L}$ to obtain

$$\frac{D_{Fw}^{\pm}}{dU} h_t = w - uh_x. \quad (A.2)$$

Equation (2.5), the tangential stress balance in terms of nondimensional variables is

$$-\frac{2dU}{L^2} h_x u_x + 2\frac{dU}{L^2} w_x h_x + \frac{U}{d} u_z + \frac{Ud}{L^2} w_x - \frac{dU}{L^2} h_x^2 u_x - \frac{d^3U}{L^4} h_x^2 w_x = 0.$$  

We divide by $\frac{dU}{L^2}$ to simplify this expression,

$$-2h_x u_x + 2w_z + \frac{1}{\epsilon^2} u_z + w_x - h_x^2 u_z - \epsilon^2 h_x w_x = 0. \quad (A.3)$$

The first of the species boundary conditions at the liquid-air interface, Equation (2.11) is nondimensionalized as follows,

$$C_{O2} = \frac{K_{H^+} P_{O2}}{C_{O2}^*}. \quad (A.4)$$

The other boundary conditions at $z = \hat{h}(\hat{x}, \hat{t})$, Equations (2.12-2.14), were found by a dot product of the gradient vector and normal vector to the air-liquid interface. The vectors in Equation (2.12) are $[\hat{C}_{H^+}^{\pm} \hat{i} + \hat{C}_{H^+}^{\pm} \hat{j}] \left[ \frac{h_x \hat{i} + \hat{j}}{\sqrt{1 + h_x^2}} \right] = 0$, where $\hat{i}$ and $\hat{j}$ represent the unit vectors. Therefore we have the equation,

$$-C_{H^+}^{\pm} h_x + C_{H^+}^{\pm} \frac{1}{\sqrt{1 + h_x^2}} = 0.$$  

Now the nondimensional variables can be used,

$$\frac{C_{H^+}^* \left[ -C_{H^+}^{\pm} h_x \frac{d}{L^2} + C_{H^+}^{\pm} \frac{1}{\epsilon} \right]}{\sqrt{1 + \frac{d^2}{L^2} h_x^2}} = 0.$$  

By factoring out $\frac{C_{H^+}^{\pm}}{d}$ and substituting $\epsilon$ we obtain,

$$\frac{C_{H^+}^* \left[ -\epsilon^2 C_{H^+}^{\pm} h_x + C_{H^+}^{\pm} \right]}{\sqrt{1 + \epsilon^2 h_x^2}} = 0.$$  

Therefore we have,
\[ -\epsilon^2 C_{H^+} h_x + C_{H^+} = 0. \] (A.5)
Since \( \epsilon \) is small this implies \( C_{H^+} = 0 \) and the directional derivative of \( H^+ \) acts in the \( z \) direction. The same process can be used in Equations (2.13-2.14),
\[ -\epsilon^2 C_{Fe^{2+}} h_x + C_{Fe^{2+}} = 0 \] (A.6)
\[ -\epsilon^2 C_{Fe^{3+}} h_x + C_{Fe^{3+}} = 0. \] (A.7)
Therefore we also have \( C_{Fe^{2+}} = 0 \) and \( C_{Fe^{3+}} = 0 \). Equation (2.16) contains \( \nabla C_i \cdot \vec{n}_s \) which is similar to Equation (2.12) except the normal vector is \( \vec{n}_s \), therefore the vector now acts at the liquid-crust interface. The same nondimensional process occurs, however \( h_x \) is replaced by \( s_x \). Thus Equation (2.16) will be,
\[ \frac{D_{O_2} C_{O_2}^*}{d} \left[ -\epsilon^2 C_{O_{2z}} s_x + C_{O_{2z}} \right] = F_c, \]
where \( F_c \) is the net flux constant. By dividing by \( \frac{D_{O_2} C_{O_2}^*}{d} \) we obtain,
\[ -\epsilon^2 C_{O_{2z}} s_x + C_{O_{2z}} = F, \] (A.8)
where \( F = \frac{F_c d}{D_{O_2} C_{O_2}^*} \).
Equations (2.17-2.18) also follow a similar process. The right-hand side of the equations look identical to Equations (2.15-2.16) accounting for the different ionic species, while the left-hand side depends on \( J \), the surface reaction expression. The nondimensional variables give us,
\[ \frac{D_{H^+} C_{H^+}^*}{d} \left[ -\epsilon^2 C_{H^+} s_x + C_{H^+} \right] = \kappa_1 C_{H^+}^* C_{H^+} - \kappa_1 C_{Fe^{3+}}^* C_{Fe^{3+}}. \]
Now we divide by \( \frac{D_{H^+}C_{Fe^{3+}}}{d} \),

\[
-\epsilon^2 C_{H^+} s_x + C_{H^+} = \frac{d\kappa_1 C_{H^+}^2 C_{H^+}^3}{D_{H^+}} - \frac{\kappa_{-1} dC_{Fe^{3+}}}{D_{H^+} C_{H^+}^3} C_{Fe^{3+}}.
\]

Similarly for (2.18) we obtain,

\[
-\epsilon^2 C_{Fe^{3+}} s_x + C_{Fe^{3+}} = \frac{-\kappa_1 dC_{H^+}^3}{D_{Fe^{3+}} C_{Fe^{3+}}} C_{H^+} + \frac{\kappa_{-1} d}{D_{Fe^{3+}} C_{Fe^{3+}}} C_{Fe^{3+}}.
\]

In terms of our nondimensional variables, Equation (2.19) is

\[
\frac{\rho_{Fe(OH)_3} d}{T} \frac{s_t}{\sqrt{1 + \epsilon^2 s_x^2}} = -\kappa_1 C_{H^+}^3 + \kappa_{-1} C_{Fe^{3+}} + \frac{\kappa_{-1} C_{Fe^{3+}}}{\rho_{Fe(OH)_3}} d C_{Fe^{3+}}.
\]

Next we divide by \( \frac{\rho_{Fe(OH)_3} d}{T} \),

\[
\frac{s_t}{\sqrt{1 + \epsilon^2 s_x^2}} = -\frac{\kappa_1 C_{H^+}^3}{\rho_{Fe(OH)_3}} d C_{H^+} + \frac{\kappa_{-1} C_{Fe^{3+}}}{\rho_{Fe(OH)_3}} d C_{Fe^{3+}}.
\]

We rearrange the coefficient of \( C_{Fe^{3+}} \) to solve for the characteristic variable, \( T \). The coefficient of \( C_{Fe^{3+}} \) is \( \frac{\kappa_{-1} C_{Fe^{3+}}}{\rho_{Fe(OH)_3}} d \). We can multiply by \( \frac{d D_{Fe^{3+}}}{d D_{Fe^{3+}}} \) in order to substitute a Damkohler number, \( Da_{(-1)} \). Thus,

\[
\frac{\kappa_{-1} C_{Fe^{3+}} T d D_{Fe^{3+}}}{\rho_{Fe(OH)_3} d} d D_{Fe^{3+}} = Da_{(-1)} \frac{C_{Fe^{3+}}}{\rho_{Fe(OH)_3}} \frac{T D_{Fe^{3+}}}{d^2} = 1.
\]

Now we will substitute \( Da_{(-1)} = \epsilon D_{a_{(-1)}} \) to change the Damkohler Number from \( O(\epsilon) \) to \( O(1) \). We scale the coefficient to be \( O(1) \),

\[
\epsilon D_{a_{(-1)}} d \frac{C_{Fe^{3+}}}{L \rho_{Fe(OH)_3}} \frac{T D_{Fe^{3+}}}{d^2} = O(1),
\]

which yields \( T = \frac{L d}{D_{Fe^{3+}}} \).
APPENDIX B
ANALYTIC SOLUTION

First we will solve the fluid flow equations using the leading order equations. From (3.22) we have \( p_{0z} = 0 \), thus \( p_0 = A(x) \), where \( A(x) \) is a function of \( x \). Using the boundary condition, Equation (3.25), we find \( A(x) = 0 \) therefore \( p_0 = 0 \). Since \( p_{0z} = 0 \), Equation (3.21) is simplified to \( u_{0zz} = -\sin \theta \). By integrating twice with respect to \( z \) we have,

\[
u_0 = -\frac{1}{2} z^2 \sin \theta + z B(x) + C(x),
\]

where \( B(x) \) and \( C(x) \) are functions of \( x \).

The boundary condition at \( z = h_0(x,t) \), Equation (3.24), is \( u_{0z} = 0 \). Thus, \( B(x) = h_0 \sin \theta \). The other boundary condition at \( z = s_0(x,t) \) is \( u_0 = 0 \) based on the no-slip condition at the liquid-crust interface, which yields

\[
C(x) = \frac{1}{2} s_0^2 \sin \theta - s_0 h_0 \sin \theta.
\]

The \( O(1) \) solution is,

\[
u_0 = -\frac{1}{2} z^2 \sin \theta + z h_0 \sin \theta + \frac{1}{2} s_0^2 \sin \theta - s_0 h_0 \sin \theta.
\]

We simplify this expression by factoring out \( \sin \theta \),

\[
u_0 = \left[ -\frac{1}{2} z^2 + z h_0 + \frac{1}{2} s_0^2 - s_0 h_0 \right] \sin \theta.
\]
Using Equation (3.20), we obtain $w_0$. By differentiating $u_0$ with respect to $x$, the equation is

$$[zh_0 + s_0s_0 - s_0h_0 - s_0h_0] \sin \theta + w_0 = 0.$$ 

Now we integrate this expression with respect to $z$ which yields,

$$w_0 = -\left[\frac{1}{2}z^2h_0 + zs_0s_0 - zs_0h_0 - zs_0h_0\right] \sin \theta + D(x),$$

where $D(x)$ is a function of $x$. The boundary condition at $z = s_0(x, t)$ is $w_0 = 0$ based on the no-slip condition. Therefore, $D(x) = \left[-\frac{1}{2}s_0^2h_0h_0 - s_0^2s_0h_0 + s_0^2h_0\right] \sin \theta$.

The flow equation becomes,

$$w_0 = \left[-\frac{1}{2}z^2h_0 - zs_0s_0 + zs_0h_0 + zs_0h_0 - \frac{1}{2}s_0^2h_0 + s_0^2s_0 - s_0s_0h_0\right] \sin \theta.$$ 

Next we use Equation (3.4) to solve $h_0(x, t)$. By substitution of $u_0$ and $w_0$ we have,

$$\frac{DF_{e^3+}}{dU} h_0 = \left[-h_0s_0s_0h_0 + s_0^2h_0h_0 + s_0^2s_0 - s_0s_0h_0 - h_0^2h_0 + s_0h_0h_0 - s_0^2h_0\right] \sin \theta.$$ 

We simplify this equation to

$$\frac{DF_{e^3+}}{dU} h_0 = \left[-\frac{1}{3}(h_0 - s_0)^3\right] x \sin \theta.$$ 

We integrate with respect to $z$ to solve for the volumetric flow rate,

$$\int_{s_0(x,t)}^{h_0(x,t)} u_0 \, dz = \int_{s_0(x,t)}^{h_0(x,t)} \left[-\frac{1}{2}z^2 + zh_0 + \frac{1}{2}s_0^2 - s_0h_0\right] \sin \theta$$

By integration we have,

$$\int_{s_0(x,t)}^{h_0(x,t)} u_0 \, dz = \left[-\frac{1}{6}h_0^3 + \frac{1}{2}h_0^3 + \frac{1}{2}h_s^2 - h_s^2s_0 + \frac{1}{6}s_0^3 - \frac{1}{2}s_0^2h_0 - \frac{1}{2}s_0^3 + s_0^2h_0\right] \sin \theta.$$
We can reduce this to
\[
\int_{s_0(x,t)}^{h_0(x,t)} u_0 \, dz = \frac{1}{3} (h_0(x,t) - s_0(x,t))^3 \sin \theta.
\]

Next, we solve for the concentration of ion, \(H^+\). Equation (3.26) is
\[
C_{H^+0_z} = 0. \text{ Integration with respect to } z \text{ twice yields,}
\]
\[
C_{H^+0} = zA(x) + B(x),
\]
where \(A(x)\) and \(B(x)\) are functions of \(x\). The boundary conditions at \(z = h(x,t)\) and \(z = s(x,t)\) are \(C_{H^+0_z} = 0\) so \(A(x) = 0\). Thus \(C_{H^+0} = B(x)\). We can find \(B(x)\) via the \(O(\epsilon)\) equation,
\[
C_{H^+1_z} = -\frac{d^2}{C_{H^+}^* D_{H^+}} \bar{I} + \frac{D_{Fe^{3+}}}{D_{H^+}} C_{H^+0_z} + Pe[u_0 C_{H^+0_x} + w_0 C_{H^+0_z}] - \int_{s(x,t)}^{h(x,t)} k_{1} C_{O_2}^* C_{Fe^{2+}}^* C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^* C_{H^+} + P e u_0 C_{H^+0_z} dz.
\]

Since \(C_{H^+0}\) is a function of \(x\), \(C_{H^+0_z} = 0\) and \(C_{H^+0_z}(s_0) = 0\). Also the bulk reaction rate, \(\bar{I} = -k_1 C_{Fe^{2+}}^4 C_{Fe^{2+}}^* C_{O_2}^* C_{O_2}^* C_{H^+}^4 C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^* C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^* C_{H^+}^4 + \int_{s(x,t)}^{h(x,t)} k_{1} C_{O_2}^* C_{Fe^{2+}}^* C_{H^+}^4 + \int_{s(x,t)}^{h(x,t)} P e u_0 C_{H^+0_z} dz\),

The boundary condition equations are in terms of \(C_{H^+0_z}\) so we will integrate once with respect to \(z\),
\[
C_{H^+1_z} = \frac{-d^2}{C_{H^+}^* D_{H^+}} k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^* C_{O_2}^* C_{H^+}^4 + \frac{d^2}{C_{H^+}^* D_{H^+}} C_{Fe^{2+}}^4 C_{Fe^{2+}}^* C_{H^+}^4 C_{H^+}^4 + \int_{s(x,t)}^{h(x,t)} k_{1} C_{O_2}^* C_{Fe^{2+}}^* C_{H^+}^4 + \int_{s(x,t)}^{h(x,t)} P e u_0 C_{H^+0_x} dz + B(x,t).
\]

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Equation (3.40) is the boundary condition at \( z = s(x,t) \). Since \( C_{H+0_z} = 0 \), the boundary condition is simplified to,

\[
C_{H+1z} = \frac{\bar{D}a_{(1)} C_{H+}^* D_{Fe^{3+}}}{D_{H+}} C_{H+0}^3 - \frac{\bar{D}a_{(-1)} C_{Fe^{3+}} D_{Fe^{3+}}}{D_{H+} C_{H+}^*} C_{Fe^{3+}0}.
\]

We will equate the above equations to obtain,

\[
-\frac{d^2}{C_{H+}^* D_{H+}} k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 + \frac{d^2}{C_{H+}^* D_{H+}} C_{Fe^{2+}}^4 C_{Fe^{2+}}^4 + C_{H+}^4 + \int_{s(x,t)}^{s(x,t)} k_1 C_O O \, dz
\]

\[
+ P e C_{H+0z} \int_{s(x,t)}^{s(x,t)} u_0 \, dz + B(x,t)
\]

\[
= \frac{\bar{D}a_{(1)} C_{H+}^* D_{Fe^{3+}}}{D_{H+}} C_{H+0}^3 - \frac{\bar{D}a_{(-1)} C_{Fe^{3+}} D_{Fe^{3+}}}{D_{H+} C_{H+}^*} C_{Fe^{3+}0}.
\]

The integration limits are both \( s(x,t) \) so the integral terms equal 0 and we acquire,

\[
B(x,t) = \frac{d^2 k_{-1}}{C_{H+}^* D_{H+}} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 s + \frac{\bar{D}a_{(1)} C_{H+}^* D_{Fe^{3+}}}{D_{H+}} C_{H+0}^3 - \frac{\bar{D}a_{(-1)} C_{Fe^{3+}} D_{Fe^{3+}}}{D_{H+} C_{H+}^*} C_{Fe^{3+}0}.
\]

The \( C_{H+1z} \) equation becomes,

\[
C_{H+1z} = -\frac{d^2}{C_{H+}^* D_{H+}} k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 s
\]

\[
+ \frac{d^2}{C_{H+}^* D_{H+}} C_{Fe^{2+}}^4 C_{Fe^{2+}}^4 + C_{H+}^4 + \int_{s(x,t)}^{s(x,t)} k_1 C_O O \, dz
\]

\[
+ P e C_{H+0z} \int_{s(x,t)}^{s(x,t)} u_0 \, dz + \frac{d^2}{C_{H+}^* D_{H+}} k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4 s
\]

\[
+ \frac{\bar{D}a_{(1)} C_{H+}^* D_{Fe^{3+}}}{D_{H+}} C_{H+0}^3 - \frac{\bar{D}a_{(-1)} C_{Fe^{3+}} D_{Fe^{3+}}}{D_{H+} C_{H+}^*} C_{Fe^{3+}0}.
\]
The boundary condition at $z = h(x, t)$ is $C_{H+1} = 0$. Therefore we have,

$$
0 = -\frac{d^2}{C_{H+1} D_{H+}} k_{-1} C_{Fe^{3+}}^{4} + C_{Fe^{3+}}^{4} h
+ \frac{d^2}{C_{H+1} D_{H+}} C_{Fe^{2+}}^{4} C_{Fe^{2+}}^{4} + C_{H+1}^{4} C_{H+1}^{4} \int_{s(x,t)}^{h(x,t)} k_{1} C_{O_2} C_{O_2}^{4} dz
+ Pe C_{H^{+}} \int_{s(x,t)}^{h(x,t)} u_{0} dz + \frac{d^2}{C_{H+1} D_{H+}} k_{-1} C_{Fe^{3+}}^{4} + C_{Fe^{3+}}^{4} s
+ \frac{d^2}{C_{H+1} D_{H+}} C_{Fe^{2+}}^{4} C_{Fe^{2+}}^{4} + C_{H+1}^{4} C_{H+1}^{4} \int_{s(x,t)}^{h(x,t)} k_{1} C_{O_2} C_{O_2}^{4} dz.
$$

From Equations (4.7) we substitute $\int_{s(x,t)}^{h(x,t)} u_{0} dz = Q(t)$ and $h(x, t) - s(x, t) = \left(\frac{3Q(t)}{\sin \theta}\right)\frac{1}{2}$, we have

$$
Pe Q(t) C_{H^{+}} = -\frac{\bar{D} a_{(1)} C_{H}^{4} C_{Fe^{3+}}^{4} + \bar{D} a_{(1)} C_{Fe^{3+}}^{4} C_{Fe^{3+}}^{4}}{D_{H+} C_{H+}^{4} C_{H+}^{4}} + \frac{d^2}{C_{H+1} D_{H+}} k_{-1} \left(\frac{3Q(t)}{\sin \theta}\right) C_{Fe^{3+}}^{4} + C_{Fe^{3+}}^{4}
+ \frac{d^2}{C_{H+1} D_{H+}} C_{Fe^{2+}}^{4} C_{Fe^{2+}}^{4} + C_{H+1}^{4} C_{H+1}^{4} \int_{s(x,t)}^{h(x,t)} k_{1} C_{O_2} C_{O_2}^{4} dz.
$$

We further simplify this expression by redimensionalizing the variables in Table (3.1) and Table (3.2). Also we have the redimensional Equation (4.8) and set $\bar{I} = \frac{I}{\epsilon}$,

$$
\frac{dp g d^2 \hat{Q}(\hat{t}) \mu}{D_{H^{+}} \mu g d^3 \hat{C}_{H^{+}}} = -\frac{k_{1} C_{H}^{4} C_{Fe^{3+}}^{4} + \hat{C}_{H^{+}}^{3} + \frac{k_{-1} C_{Fe^{3+}}^{4} C_{Fe^{3+}}^{4}}{D_{Fe^{3+}} C_{H+}} \hat{C}_{Fe^{3+}}^{4}}{D_{Fe^{3+}} C_{Fe^{3+}} + C_{H+}^{4} C_{H+}^{4}}
+ \frac{d^2}{\epsilon C_{H+1} D_{H+}} \left(\frac{3 \hat{Q}(\hat{t}) \mu}{\rho g d^3 \sin \theta}\right) \hat{C}_{Fe^{3+}}^{4} - \frac{d^2 \hat{C}_{Fe^{2+}}^{4} + \hat{C}_{H+}^{4}}{\epsilon C_{H+1} D_{H+}} \int_{s(\hat{x}, \hat{t})}^{h(\hat{x}, \hat{t})} k_{1} \hat{C}_{O_2} d\hat{z}.
$$

Thus,

$$
\frac{\hat{Q}(\hat{t})}{D_{H^{+}}} \hat{C}_{H^{+}}^{4} = -\frac{k_{1} C_{H}^{4} C_{Fe^{3+}}^{4} + \frac{k_{-1} C_{Fe^{3+}}^{4} C_{Fe^{3+}}^{4}}{D_{Fe^{3+}} C_{H+}} \hat{C}_{Fe^{3+}}^{4}}{D_{Fe^{3+}} C_{Fe^{3+}} + C_{H+}^{4} C_{H+}^{4}}
+ \frac{d^2}{\epsilon C_{H+1} D_{H+}} \left(\frac{3 \hat{Q}(\hat{t}) \mu}{\rho g d^3 \sin \theta}\right) \hat{C}_{Fe^{3+}}^{4} - \frac{d^2 \hat{C}_{Fe^{2+}}^{4} + \hat{C}_{H+}^{4}}{\epsilon C_{H+1} D_{H+}} \int_{s(\hat{x}, \hat{t})}^{h(\hat{x}, \hat{t})} k_{1} \hat{C}_{O_2} d\hat{z}.
$$
When we nondimensionalized Equation (3.7) we divided by \( \frac{D_{H^+} + C_{H^+}^*}{d^2} \) and we will simplify this equation by multiplying by \( \frac{D_{H^+} + C_{H^+}^*}{d^2} \),

\[
\frac{\hat{Q}(\hat{t}) L}{d^2} \hat{C}_{H^+} = -\kappa_1 \frac{\hat{C}_{H^+}^3}{d\epsilon} + \kappa_{-1} \frac{\hat{C}_{Fe^{3+}}}{d\epsilon} + k_{-1} \left( \frac{3\hat{Q}(\hat{t}) \mu}{\rho g \sin \theta} \right)^\frac{1}{3} \hat{C}_{Fe^{3+}}^4 + \hat{C}_{Fe^{2+}} \int_{\hat{s}(\hat{x},\hat{t})}^{h(\hat{x},\hat{t})} k_1 \hat{C}_{O_2} d\hat{z}.
\]

The redimensional Equation (3.26) is now,

\[
\hat{Q}(\hat{t}) \hat{C}_{H^+} = -\kappa_1 \hat{C}_{H^+}^3 + \kappa_{-1} \hat{C}_{Fe^{3+}} + k_{-1} \left( \frac{3\hat{Q}(\hat{t}) \mu}{\rho g \sin \theta} \right)^\frac{1}{3} \hat{C}_{Fe^{3+}}^4 - \hat{C}_{Fe^{2+}} \int_{\hat{s}(\hat{x},\hat{t})}^{h(\hat{x},\hat{t})} k_1 \hat{C}_{O_2} d\hat{z}.
\]

The next ion of interest is \( Fe^{2+} \). The \( O(1) \) Equation (3.30) is \( C_{Fe^{2+}O_{zz}} = 0 \).

Integrating with respect to \( z \) twice yields,

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

where \( A(x) \) and \( B(x) \) are functions of \( x \). At \( z = h(x,t) \) and \( z = s(x,t) \), \( C_{Fe^{2+0}} = 0 \) thus \( A(x) = 0 \). We are left to solve for \( C_{Fe^{2+0}} = B(x) \). We will use the \( O(\epsilon) \) equation to solve for \( B(x) \). The \( O(\epsilon) \) equation for \( Fe^{2+} \) is

\[
C_{Fe^{2+1zz}} = \frac{d^2}{C_{Fe^{2+}} D_{Fe^{2+}}} \tilde{I} = \frac{D_{Fe^{3+}}}{D_{Fe^{2+}}} C_{Fe^{2+0}} + Pe\left[u_0 C_{Fe^{2+0z}} + w_0 C_{Fe^{2+0z}}\right].
\]

Since \( C_{Fe^{2+0}} \) is a function of only \( x \), \( C_{Fe^{2+0z}} = 0 \) and \( C_{Fe^{2+zz}} = 0 \). Also we replace \( \tilde{I} \) with \(-k_1 C_{Fe^{2+}}^4 C_{Fe^{2+}} C_{O_2} C_{O_2} C_{H^+}^4 C_{H^+}^4 + k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4\),

\[
C_{Fe^{2+1zz}} = \frac{d^2}{C_{Fe^{2+}} D_{Fe^{2+}}} \left[k_1 C_{Fe^{2+}}^4 C_{Fe^{2+}} C_{O_2} C_{O_2} C_{H^+}^4 C_{H^+}^4 - k_{-1} C_{Fe^{3+}}^4 C_{Fe^{3+}}^4\right] + Pe u_0 C_{Fe^{2+0z}}.
\]
The boundary conditions involve $C_{Fe^{2+1}z}$ so we integrate once with respect to $z$,

$$
C_{Fe^{2+1}z} = -\frac{d^2}{C_{Fe^{2+}D_{Fe^{2+}}}^*}k_{-1}C_{Fe^{3+}C_{Fe^{3+}}^*}^4 + D_{Fe^{2+}}^* \int^z k_{1}C_{O_2}C_{O_2}^* d z
+ PeC_{Fe^{2+0z}} \int^z u_0 d z + B(x, t).
$$

Equation (3.39) is the boundary condition at $z = s(x, t)$. Since $C_{Fe^{2+1}z}$, we have

$$
0 = -\frac{d^2}{C_{Fe^{2+}D_{Fe^{2+}}}^*}k_{-1}C_{Fe^{3+}C_{Fe^{3+}}^*}^4 + D_{Fe^{2+}}^* \int^s k_{1}C_{O_2}C_{O_2}^* d z
+ PeC_{Fe^{2+0z}} \int^s u_0 d z + B(x, t).
$$

The integration limits are both $s(x, t)$ so the integrals are 0. Hence,

$$
B(x) = \frac{d^2}{C_{Fe^{2+}D_{Fe^{2+}}}^*}k_{-1}C_{Fe^{3+}C_{Fe^{3+}}^*}^4 + D_{Fe^{2+}}^* s.
$$

The equation for $C_{Fe^{2+1}z}$ is now,

$$
C_{Fe^{2+1}z} = -\frac{d^2}{C_{Fe^{2+}D_{Fe^{2+}}}^*}k_{-1}C_{Fe^{3+}C_{Fe^{3+}}^*}^4 + z
+ \frac{d^2}{C_{Fe^{2+}D_{Fe^{2+}}}^*}C_{Fe^{2+}C_{Fe^{2+}}^*}^4 + C_{H^+}^4 \int^{z(x,t)} k_{1}C_{O_2}C_{O_2}^* d z
+ PeC_{Fe^{2+0z}} \int^{z(x,t)} u_0 d z + \frac{d^2}{C_{Fe^{2+}D_{Fe^{2+}}}^*}k_{-1}C_{Fe^{3+}C_{Fe^{3+}}^*}^4 + s.
$$

The boundary condition at $z = h(x, t)$ is Equation (3.36). Again $C_{Fe^{2+1}z}(x, t) = 0,$
The redimensional Equation (3.30) is,

\[ 0 = -\frac{d^2}{C_{Fe^{2+}}^{*} D_{Fe^{2+}}} k_{-1} C_{Fe^{3+}}^{4*} C_{Fe^{3+}}^{4*} + h \]

\[ + \frac{d^2}{C_{Fe^{2+}}^{*} D_{Fe^{2+}}} C_{Fe^{2+}}^{C_{Fe^{2+}}^{4*} C_{Fe^{2+}}^{C_{H^{+}}^{4*}} + h s_{(x,t)}^{h(x,t)} k_{1} C_{O^{2}}^{*} C_{O^{2}} d z \]

\[ + Pe C_{Fe^{2+}}^{*} s_{(x,t)}^{h(x,t)} u_{0} d z + \frac{d^2}{C_{Fe^{2+}}^{*} D_{Fe^{2+}}} k_{-1} C_{Fe^{3+}}^{4*} C_{Fe^{3+}}^{4*} + s. \]

Now we substitute \( s_{(x,t)}^{h(x,t)} u_{0} d z = Q(t) \) and \( h(x, t) - s(x, t) = \left( \frac{3Q(t)}{\sin \theta} \right)^{\frac{1}{2}} \) from Equation (4.7),

\[ Pe C_{Fe^{2+}}^{*} Q(t) = \frac{d^2}{C_{Fe^{2+}}^{*} D_{Fe^{2+}}} k_{-1} \left( \frac{3Q(t)}{\sin \theta} \right)^{\frac{1}{2}} C_{Fe^{3+}}^{4*} C_{Fe^{3+}}^{4*} + \]

\[ - \frac{d^2 C_{Fe^{2+}}^{4*} C_{Fe^{2+}}^{4*} C_{H^{+}}^{4*}}{C_{Fe^{2+}}^{*} D_{Fe^{2+}}} s_{(x,t)}^{h(x,t)} k_{1} C_{O^{2}}^{*} d z. \]

We redimensionalize the variables using Table (3.1) and Table (3.2). We also have

\[ Q(t) = \frac{\dot{Q}(t) \mu}{\rho g d^{2}} \] and \( I = \frac{I}{\epsilon}, \)

\[ \frac{d \rho g d^{2} \dot{Q}(t) \mu}{D_{Fe^{2+}}^{*} \rho g d^{3}} C_{Fe^{2+}}^{*} = \frac{d^2 k_{-1}}{\epsilon C_{Fe^{2+}}^{*} D_{Fe^{2+}}} \left( \frac{3\dot{Q}(t) \mu}{\rho g d^{3} \sin \theta} \right)^{\frac{1}{2}} C_{Fe^{3+}}^{4*} + \]

\[ - \frac{d^2 C_{Fe^{2+}}^{4*} C_{H^{+}}^{4*}}{C_{Fe^{2+}}^{*} D_{Fe^{2+}}} s_{(x,t)}^{h(x,t)} k_{1} \dot{C}_{O^{2}} d \hat{z}. \]

Next we multiply by \( \frac{D_{Fe^{2+}}^{*} C_{Fe^{2+}}^{*}}{d^2}, \)

\[ \frac{\dot{Q}(t)}{d^2} C_{Fe^{2+}}^{*} C_{Fe^{2+}}^{*} = \frac{k_{-1}}{\epsilon d} \left( \frac{3\dot{Q}(t) \mu}{\rho g \sin \theta} \right)^{\frac{1}{2}} C_{Fe^{3+}}^{4*} - \frac{1}{\epsilon d} \dot{C}_{Fe^{2+}}^{4*} \dot{C}_{H^{+}}^{4*} s_{(x,t)}^{h(x,t)} k_{1} \dot{C}_{O^{2}} d \hat{z}. \]

The redimensional Equation (3.30) is,

\[ \dot{Q}(t) \dot{C}_{Fe^{2+}}^{*} = \frac{k_{-1}}{\epsilon d} \left( \frac{3\dot{Q}(t) \mu}{\rho g \sin \theta} \right)^{\frac{1}{2}} C_{Fe^{3+}}^{4*} - \dot{C}_{Fe^{2+}}^{4*} \dot{C}_{H^{+}}^{4*} s_{(x,t)}^{h(x,t)} k_{1} \dot{C}_{O^{2}} d \hat{z}. \]

The final concentration equation is Equation (3.32). We have \( C_{Fe^{3+}}^{*} a_{zz} = 0. \)

By integration with respect to \( z \) we obtain,

\[ C_{Fe^{3+}}^{0} = A(x) z + B(x), \]

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where $A(x)$ and $B(x)$ are functions of $x$. Similar to the ions $H^+$ and $Fe^{2+}$, the boundary conditions at $z = s(x,t)$ and $z = h(x,t)$ are $C_{Fe^{3+}_0} = 0$. Therefore, $C_{Fe^{3+}_0} = B(x)$. Again we will solve the $O(\epsilon)$ equation,

$$C_{Fe^{3+}_{1zz}} - \frac{\bar{I}d^2}{C_{Fe^{3+}}D_{Fe^{3+}}} = C_{Fe^{3+}_0} + Pe[u_0C_{Fe^{3+}_0z} + w_0C_{Fe^{3+}_0z}].$$

We found $C_{Fe^{3+}_0}$ to be a function of $x$, so the derivatives with respect to $t$ and $z$ are 0. Also the bulk reaction is

$$\bar{I} = -k_1C_{Fe^{2+}Fe^{2+}}^{4s}C_{O_2}^{C_H^{C_H^*}C_H^*} + k_{-1}C_{Fe^{3+}}^{4s}C_{Fe^{3+}}^{4s},$$

$$C_{Fe^{3+}_{1zz}} = \frac{d^2}{C_{Fe^{3+}}D_{Fe^{3+}}} [-k_1C_{Fe^{2+}Fe^{2+}}^{4s}C_{O_2}^{C_H^{C_H^*}C_H^*} + k_{-1}C_{Fe^{3+}}^{4s}C_{Fe^{3+}}^{4s} + Peu_0C_{Fe^{3+}_0z}].$$

We integrate with respect to $z$ since the boundary conditions involve $C_{Fe^{3+}_{1z}}$,

$$C_{Fe^{3+}_{1z}} = \frac{d^2}{C_{Fe^{3+}}D_{Fe^{3+}}} \left[ -k_1C_{Fe^{3+}_{1zz}}^{4s} + \int_z^{s(x,t)} k_1C_{O_2}^{C_H^{C_H^*}C_H^*} dz \right] + PeC_{Fe^{3+}_0z} \int_{s(x,t)}^z u_0 dz + B(x,t).$$

Equation (3.42) is the boundary condition at $z = s(x,t)$. We have $C_{Fe^{3+}_0} = 0$ so the boundary condition becomes,

$$C_{Fe^{3+}_{1z}} = -\frac{\bar{D}a_{(1)}C_{H^+}^{3s}C_{H^+}^{3s} + \bar{D}a_{(-1)}C_{Fe^{3+}_0}}{C_{Fe^{3+}}^{3s}}.$$

By equating the above equations we obtain,

$$\frac{d^2}{C_{Fe^{3+}}D_{Fe^{3+}}}k_{-1}C_{Fe^{3+}}^{4s} + \int_{s(x,t)}^{s(x,t)} k_{1}C_{O_2}^{C_H^{C_H^*}C_H^*} dz + PeC_{Fe^{3+}_0} \int_{s(x,t)}^{s(x,t)} u_0 dz + B(x) = -\frac{\bar{D}a_{(1)}C_{H^+}^{3s}C_{H^+}^{3s} + \bar{D}a_{(-1)}C_{Fe^{3+}_0}}{C_{Fe^{3+}}^{3s}}.$$
The integrals are 0 since the integration limits are both \( s(x, t) \). Therefore,

\[
B(x, t) = - \frac{d^2}{C^*_{Fe^{3+}} D_{Fe^{3+}}} k_{-1} C^4_{Fe^{3+}} C^{4*}_{Fe^{3+}} s - \frac{\bar{D} a_{(1)} C^{3*}_H}{C^*_{Fe^{3+}}} C^3_{H+0} + \bar{D} a_{(-1)} C_{Fe^{3+}0}.
\]

The equation for \( C^*_{Fe^{3+1_z}} \) is now,

\[
C^*_{Fe^{3+1_z}} = \frac{\frac{d^2}{C^*_{Fe^{3+}} D_{Fe^{3+}}} k_{-1} C^4_{Fe^{3+}} C^{4*}_{Fe^{3+}} z}{C^*_{Fe^{3+}} D_{Fe^{3+}}} - \frac{d^2 C^4_{Fe^{2+}} C^{4*}_{Fe^{2+}} C^4_{H+} + C^{4*}_{H+}}{C^*_{Fe^{3+}} D_{Fe^{3+}}} \int_{s(x,t)}^{z} k_1 C_{O2} C^*_2 d z
\]

\[+ P e C^*_{Fe^{3+0_z}} \int_{s(x,t)}^{h(x,t)} u_0 \, d z - \frac{d^2 k_{-1}}{C^*_{Fe^{3+}} D_{Fe^{3+}}} C^4_{Fe^{3+}} C^{4*}_{Fe^{3+}} s - \frac{\bar{D} a_{(1)} C^{3*}_{H+}}{C^*_{Fe^{3+}}} C^3_{H+0} + \bar{D} a_{(-1)} C_{Fe^{3+}0}.
\]

The boundary condition at \( z = h(x, t) \) is \( C^*_{Fe^{3+1_z}} = 0 \),

\[
0 = \frac{\frac{d^2}{C^*_{Fe^{3+}} D_{Fe^{3+}}} k_{-1} C^4_{Fe^{3+}} C^{4*}_{Fe^{3+}} h}{C^*_{Fe^{3+}} D_{Fe^{3+}}} - \frac{d^2 C^4_{Fe^{2+}} C^{4*}_{Fe^{2+}} C^4_{H+} + C^{4*}_{H+}}{C^*_{Fe^{3+}} D_{Fe^{3+}}} \int_{s(x,t)}^{h(x,t)} k_1 C_{O2} C^*_2 d z
\]

\[+ P e C^*_{Fe^{3+0_z}} \int_{s(x,t)}^{h(x,t)} u_0 \, d z - \frac{d^2 k_{-1}}{C^*_{Fe^{3+}} D_{Fe^{3+}}} C^4_{Fe^{3+}} C^{4*}_{Fe^{3+}} s - \frac{\bar{D} a_{(1)} C^{3*}_{H+}}{C^*_{Fe^{3+}}} C^3_{H+0} + \bar{D} a_{(-1)} C_{Fe^{3+}0}.
\]

We substitute Equation (4.7), \( \int_{s(x,t)}^{h(x,t)} u_0 \, d z = Q(t) \) and \( h(x, t) - s(x, t) = \left( \frac{3 Q(t)}{\sin \theta} \right)^{\frac{1}{3}} \),

\[
P e C^*_{Fe^{3+}} Q(t) = \frac{\bar{D} a_{(1)} C^{3*}_{H+}}{C^*_{Fe^{3+}}} C^3_{H+0} - \bar{D} a_{(-1)} C_{Fe^{3+}}
\]

\[+ \frac{\frac{d^2}{C^*_{Fe^{3+}} D_{Fe^{3+}}} k_{-1} \left( \frac{3 Q(t)}{\sin \theta} \right)^{\frac{1}{3}} C^4_{Fe^{3+}} C^{4*}_{Fe^{3+}}}{C^*_{Fe^{3+}} D_{Fe^{3+}}} \int_{s(x,t)}^{h(x,t)} k_1 C_{O2} C^*_2 d z.
\]
Now we redimensionalize the equation. We use Table (3.1) and Table (3.2). We also have 
\[ Q(t) = \hat{Q}(\hat{t}) \mu \] and \[ I = \frac{\hat{t}}{\epsilon} \],

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

Therefore,

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

We further simplify by multiplying by \( \frac{D_{Fe^{3+}} C_{Fe^{3+}}}{d^2} \),

\[
\hat{Q}(\hat{t}) L_{Fe^{3+}} \hat{C}_{Fe^{3+}} = \frac{\kappa_1 d}{D_{Fe^{3+}} + \epsilon C_{Fe^{3+}}} C_{H^+}^{3} - \frac{\kappa_{-1} d}{D_{Fe^{3+}} + \epsilon} C_{Fe^{3+}} - \frac{d^2 k_{-1}}{\epsilon C_{Fe^{3+}} + \epsilon D_{Fe^{3+}}} \left( \frac{3\hat{Q}(\hat{t})\mu}{\rho gd^3 \sin \theta} \right)^{\frac{1}{2}} \hat{C}_{Fe^{3+}}^{4} d\hat{z}.
\]

The redimensional Equation (3.32) is now,

\[
\hat{Q}(\hat{t}) \hat{C}_{Fe^{3+}} = \kappa_1 \hat{C}_{H^+}^{3} - \kappa_{-1} \hat{C}_{Fe^{3+}} - \frac{k_{-1}}{\sin \theta \rho g} \left( \frac{3\hat{Q}(\hat{t})\mu}{\rho gd^3 \sin \theta} \right)^{\frac{1}{2}} \hat{C}_{Fe^{3+}}^{4} + \hat{C}_{Fe^{3+}} \hat{C}_{H^+}^{4} + \int_{\hat{s}(\hat{x}, \hat{t})}^{\hat{h}(\hat{x}, \hat{t})} k_1 \hat{C}_{O_2} d\hat{z}.
\]

Next we solve the concentration for oxygen. We assumed that \( I \) is \( O(\epsilon) \) for \( O_2 \) causing the solution to be linear. Equation (3.28) is \( C_{O_{2zz}} = 0 \). When we integrate with respect to \( z \) twice we obtain,

\[ CO_{20} = A(x)z + B(x), \]

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where \( A(x) \) and \( B(x) \) are functions of \( x \). The boundary condition at \( z = s(x,t) \) is \( C_{O_2 z}(s) = \frac{F_{c d}}{D_{O_2} C_{O_2}^*} \), which represents the flux to the crust. By taking the derivative of \( C_{O_2} \) with respect to \( z \) we are left with \( A(x) \). Therefore \( A(x) = \frac{F_{c d}}{D_{O_2} C_{O_2}^*} \). At the boundary condition \( z = h(x,t) \) we implement Henry’s Law, \( C_{O_2} = \frac{K_{H P_2}}{C_{O_2}^*} \),

\[
\frac{F_{c d}}{D_{O_2} C_{O_2}^*} h + B(x) = \frac{K_{H P_2}}{C_{O_2}^*}.
\]

Therefore, \( B(x) = \frac{K_{H P_2}}{C_{O_2}^*} - \frac{F_{c d}}{D_{O_2} C_{O_2}^*} h \). The solved equation for \( C_{O_2} \) is

\[
C_{O_2} = \frac{F_{c d}}{D_{O_2} C_{O_2}^*} z + \frac{K_{H P_2}}{C_{O_2}^*} - \frac{F_{c d}}{D_{O_2} C_{O_2}^*} h.
\]

Now we redimensionalize the concentration equations for the \( O(\epsilon) \) system (Table 3.1). Equation (3.28) now contains redimensional variables,

\[
\hat{C}_{O_2} = \frac{F_{c d}}{D_{O_2}} \hat{z} + K_{H P_2} - \frac{F_{c d}}{D_{O_2}} \hat{h}.
\]

The solved equations for the ionic species, \( H^+ \), \( Fe^{2+} \) and \( Fe^{3+} \) contain \( \int^{\hat{h}(\hat{x},\hat{t})}_{\hat{s}(\hat{x},\hat{t})} k_1 \hat{C}_{O_2} d\hat{z} \).

By integrating Equation (4.17) with respect to \( z \) we have

\[
\int^{h(\bar{x},\bar{t})}_{\bar{s}(\bar{x},\bar{t})} k_1 \hat{C}_{O_2} d\hat{z} = \int^{h(\bar{x},\bar{t})}_{\bar{s}(\bar{x},\bar{t})} k_1 \left[ \frac{F_{c d}}{D_{O_2}} \hat{z} + K_{H P_2} - \frac{F_{c d}}{D_{O_2}} \hat{h} \right] d\hat{z},
\]

\[
\int^{\hat{h}(\hat{x},\hat{t})}_{\hat{s}(\hat{x},\hat{t})} k_1 \hat{C}_{O_2} d\hat{z} = k_1 \left[ \frac{F_{c d}}{2D_{O_2}} \hat{z}^2 + K_{H P_2} \hat{z} - \frac{F_{c d}}{D_{O_2}} \hat{h} \hat{z} \right]\bigg|^{\hat{h}(\hat{x},\hat{t})}_{\hat{s}(\hat{x},\hat{t})},
\]

\[
\int^{\hat{h}(\hat{x},\hat{t})}_{\hat{s}(\hat{x},\hat{t})} k_1 \hat{C}_{O_2} d\hat{z} = k_1 \left[ \frac{F_{c d}}{2D_{O_2}} \hat{h}^2 + K_{H P_2} \hat{h} - \frac{F_{c d}}{D_{O_2}} \hat{h} \hat{s} \right] - k_1 \left[ \frac{F_{c d}}{2D_{O_2}} \hat{s}^2 + K_{H P_2} \hat{s} - \frac{F_{c d}}{D_{O_2}} \hat{h} \hat{s} \right]
\]

We now have the integral of \( \hat{C}_{O_2} \) in terms of \( \hat{h} \) and \( \hat{s} \),

\[
\int^{h(\bar{x},\bar{t})}_{\bar{s}(\bar{x},\bar{t})} k_1 \hat{C}_{O_2} d\hat{z} = k_1 \left[ -\frac{F_{c d}}{2D_{O_2}} (\hat{s}(\hat{x},\hat{t}) - \hat{h}(\hat{x},\hat{t}))^2 + K_{H P_2} (\hat{h}(\hat{x},\hat{t}) - \hat{s}(\hat{x},\hat{t})) \right].
\]
The final equation to redimensionalize is Equation (3.43). Using the scalings in Table (3.1) and Table (3.2), we have,

\[
\frac{d^2}{d\epsilon D_{Fe^{3+}}} \hat{s}_i = -\frac{\kappa_1 d C_{H^+}^{*3}}{D_{Fe^{3+}} \epsilon \rho_{Fe^{(OH)_3}}} C_{H^+}^{3} + \frac{\kappa_{-1} d C_{Fe^{3+}}^{*3}}{D_{Fe^{3+}} \epsilon \rho_{Fe^{(OH)_3}}} C_{Fe^{3+}}.
\]

Thus,

\[
\frac{d}{\epsilon D_{Fe^{3+}}} \hat{s}_i = -\frac{\kappa_1 d}{D_{Fe^{3+}} \epsilon \rho_{Fe^{(OH)_3}}} \hat{C}_{H^+}^{3} + \frac{\kappa_{-1} d}{D_{Fe^{3+}} \epsilon \rho_{Fe^{(OH)_3}}} \hat{C}_{Fe^{3+}}.
\]

We multiply by \( \frac{\epsilon D_{Fe^{3+}}}{d} \) and obtain,

\[
\hat{s}_i = \frac{\kappa_1}{\rho_{Fe^{(OH)_3}}} \hat{C}_{H^+}^{3} + \frac{\kappa_{-1}}{\rho_{Fe^{(OH)_3}}} \hat{C}_{Fe^{3+}}.
\]

This concludes the necessary redimensionalization of equations.
% parameters
kappa1 = 1;
kappaneg1 = .17;
k1 = 2.5e-7;
k1neg1 = 2.3e-3;
mu = 0.01;
rho = 1;
g = 980;
Fc = 1e-7;
DO2 = 1.97e-5;
KH = 41.6;
P02 = 0.2;
theta = .03*pi/180; % degrees to radians
rhoFe = 3.3e6;
PAR = [kappa1 kappaneg1 k1 kneg1 mu rho g Fc DO2 KH P02 theta rhoFe];

Tmax = 31536000; % 365*24*60*60;
nmax = 1e4;
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/g/rho/sin(theta))^(1/3);
end

% left boundary conditions for ion concentrations
for n = 1:nmax-1
    % Concentrations H^+, Fe^2+, Fe^3+
    factor = 1 + 0.1*sin(4*pi*(t(n)/Tmax));
    C0 = [.0631*factor; 600*factor; 5.6*factor];
    Qn = Q(t(n));
    Sn = s(:,n);
    Hn = h(:,n);
    [x1,C] = ode15s(@(x,C) RHS11(x,C,PAR,Qn),x,C0);
    As = -kappa1/rhoFe;
    Bs = kappaneg1/rhoFe;
    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+1)+(3*Qn*mu/g/rho/sin(theta))^(1/3);
    end
end

function f=RHS11(x,C,PAR,Qn)
scale = (3*Qn*PAR(5)/sin(PAR(12))/PAR(6)/PAR(7))^(1/3);
\begin{verbatim}
INTEGRAL = (-PAR(8)/(2*PAR(9))*scale^2 + PAR(10)*PAR(11)*scale)*PAR(3);
f = [(-PAR(1)*C(1)^3 + PAR(2)*C(3) + PAR(4)*scale*C(3)^4 - INTEGRAL*C(2)^4*C(1)^4)/Qn
    (PAR(4)*scale*C(3)^4 - INTEGRAL*C(2)^4*C(1)^4)/Qn
    (PAR(1)*C(1)^3 - PAR(2)*C(3) - PAR(4)*scale*C(3)^4 + INTEGRAL*C(2)^4*C(1)^4)/Qn];
end
\end{verbatim}

Table C.1: Matlab Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Matlab Name</th>
<th>Location in vector PAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_1$</td>
<td>kappa1</td>
<td>PAR(1)</td>
</tr>
<tr>
<td>$\kappa_{-1}$</td>
<td>kappaneg1</td>
<td>PAR(2)</td>
</tr>
<tr>
<td>$k_1$</td>
<td>k1</td>
<td>PAR(3)</td>
</tr>
<tr>
<td>$k_{-1}$</td>
<td>kneg1</td>
<td>PAR(4)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>mu</td>
<td>PAR(5)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>rho</td>
<td>PAR(6)</td>
</tr>
<tr>
<td>$g$</td>
<td>g</td>
<td>PAR(7)</td>
</tr>
<tr>
<td>$F_c$</td>
<td>Fc</td>
<td>PAR(8)</td>
</tr>
<tr>
<td>$D_{O_2}$</td>
<td>DO2</td>
<td>PAR(9)</td>
</tr>
<tr>
<td>$K_H$</td>
<td>KH</td>
<td>PAR(10)</td>
</tr>
<tr>
<td>$P_{O_2}$</td>
<td>PO2</td>
<td>PAR(11)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>theta</td>
<td>PAR(12)</td>
</tr>
<tr>
<td>$\rho_{Fe(OH)_3}$</td>
<td>rhoFe</td>
<td>PAR(13)</td>
</tr>
</tbody>
</table>