Abstract Acid mine drainage (AMD) is the outflow of acidic water from metal mines or coal mines. When exposed to air and water, metal sulfides from the deposits of the mines are oxidized and produce acid, metal ions and sulfate, which lower the pH value of the water. An open limestone channel (OLC) is a passive and low cost way to neutralize AMD. The dissolution of calcium into the water increases the pH value of the solution. A differential equation model is numerically solved to predict the variation of concentration of each species in the OLC solution. The diffusion of calcium due to iron precipitates is modeled by a linear equation. The results give the variation of pH value and the concentration of calcium.

Introduction

Acid mine drainage (AMD) is the outflow of acidic water from metal mines or coal mines. When exposed to air and water, metal sulfides from the deposits of the mines are oxidized and produce acid, metal ions and sulfate, which lower the pH value of the water. The water is then unfit for consumption, agricultural
or industrial use. AMD has become one of the largest problems for the mining industry.

There have been various methods to treat AMD. Some of them are expensive and hard to maintain. An open limestone channel (OLC) is a passive and low cost way to treat AMD. Coarse limestone boulders are placed into downstream water. The dissolution of calcium into the water will increase the pH value of the solution. Meanwhile with time passing, the oxidization of metal causes the accumulation of metal sediment at the surface of limestone which hinders the dissolution of calcium. Studies in the 1970’s [1], [2], [3] showed that limestone armored with metal oxides releases calcium at 20% the rate of an unarmored one. Experiments conducted by Zimekiewicz et al. [4] investigated factors that can improve the performance of the armored limestone.

We study the problem from a mathematical point of view. Numerous experiments have been done with data collected and analyzed. However no mathematical model has been utilized in these studies. The purpose of this paper is to set up a mathematical model which describes and predicts the performance of open limestone channel in treatment of AMD. Our model is a differential equation that computes the variation of concentrations of sample species in the solution of a downstream channel. When solving the differential equation numerically, we use Newton-Raphson method to solve for the concentrations of the species in the solution under equilibrium at each time step. The plan of this paper is as follows: in first section, we introduce the chemical reactions involved in an open limestone channel and the procedure of solving chemical equilibrium problems, the modeling differential equation is presented in the second section, and numerical results are given in section three.

Chemical Reaction

The dissolution of limestone is the main chemical reaction occurring in open limestone channel. It can be described by the following chemical formulas [5]

\[
\begin{align*}
\text{CaCO}_3(s) + 2\text{H}^+ & \rightleftharpoons \text{Ca}^{2+} + \text{H}_2\text{CO}_3^*, \\ 
\text{CaCO}_3(s) + \text{H}_2\text{CO}_3^* & \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^- \\ 
\text{CaCO}_3(s) + \text{H}_2\text{O} & \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^-
\end{align*}
\]

where \([\text{H}_2\text{CO}_3^*]=\text{[CO}_2\text{(aq)}]+ \left[\text{H}_2\text{CO}_3\right]^0\]. Square brackets \([\ ]\) define concentrations in solution, and curly brackets \(\{\}\) will be used to denote activities, both in mol/L. Activity is a measure of the “effective concentration” of a species in a mixture, in the sense that the species’ chemical potential depends on the activity of a real solution in the same way that it would depend on concentration for an ideal solution. Concentration can be related to activity using the activity coefficient \(\gamma\), where \(\{\} = \gamma[\]\). When dealing with dilute aqueous solutions, \(\gamma \approx 1\). Throughout this paper we will assume that activity is equal to concentration.

The metal sediment at the surface of limestone is considered to be \(\text{Fe(OH)}_3\)
produced by iron ions. The reaction is as follows
\[ \text{Fe}^{3+} + 3 \text{HCO}_3^- \rightarrow \text{Fe(OH)}_3(s) + 3 \text{CO}_2. \] (4)

Assuming the system is at chemical equilibrium, we can calculate the concentrations of all species in solution by applying mass balance and charge balance equations in the system. In the following we will set up a chemical equilibrium model in our system. Readers are referred to [6] for a more detailed explanation of the numerical method to solve chemical equilibrium problems.

To compute the concentrations of species at equilibrium, we consider the following reactions
\[ \text{H}_2\text{CO}_3^* \leftrightarrow \text{H}^+ + \text{HCO}_3^-, \] (5)
\[ \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}, \] (6)
\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-, \] (7)

where the species in the solution are assumed to be: \( \text{H}^+, \text{OH}^-, \text{H}_2\text{CO}_3^*, \text{HCO}_3^-, \text{CO}_3^{2-}, \text{Ca}^{2+} \). The equilibrium constants corresponding to the reactions are
\[ K_1 = \frac{\{\text{H}^+\}\{\text{HCO}_3^-\}}{\{\text{H}_2\text{CO}_3^*\}}, \] (8)
\[ K_2 = \frac{\{\text{H}^+\}\{\text{CO}_3^{2-}\}}{\{\text{HCO}_3^-\}}, \] (9)
\[ K_w = \{\text{H}^+\}\{\text{OH}^-\}. \] (10)

Here we adopted the notations used in [8] and many others, where \( K_1, K_2 \) are the equilibrium constants for carbonate and bicarbonate ion pairs, and \( K_w \) is the ionic product for water. The species satisfy the charge balance equation
\[ [\text{H}^+] + [2 \text{Ca}^{2+}] = [\text{OH}^-] + [\text{HCO}_3^-] + [2 \text{CO}_3^{2-}]. \] (11)

Writing the chemical equilibrium equation for each species in log form, we have
\[ \log[\text{OH}^-] = -\log[\text{H}^+] + \log K_w, \] (12)
\[ \log[\text{HCO}_3^-] = \log[\text{H}_2\text{CO}_3^*] - \log[\text{H}^+] + \log K_1, \] (13)
\[ \log[\text{CO}_3^{2-}] = \log[\text{H}_2\text{CO}_3^*] - 2 \log[\text{H}^+] + \log K_1 K_2. \] (14)

The equilibrium constants are defined by experiments as functions depending on temperature \( T \) (K) [7]
\[ \log K_w = 6.0875 - 4470.99 \frac{T}{T} - 0.01706T, \] (15)
\[ \log K_1 = 14.8435 - 3404.71 \frac{T}{T} - 0.03279T, \] (16)
\[ \log K_1 K_2 = 21.3415 - 6307.1 \frac{T}{T} - 0.05658T. \] (17)

Incorporating the charge balance equation (11), we obtain a nonlinear system of equations with 4 unknowns and 4 equations. We then solve the nonlinear system of equations by Newton-Raphson method.
Rate Equation

The rate of dissolution of calcite \( r \) (mmol/cm\(^2\)/s), determined by the chemical reactions (1), (2), (3), is given by the following equation \[8\]

\[
r = k_1 \{\text{H}^+_{(s)}\} + k_2 \{\text{H}_2\text{CO}_3^*\} + k_3 \{\text{H}_2\text{O}\} - k_4 \{\text{Ca}^{2+}_{(s)}\} \{\text{HCO}_3^-_{(s)}\},
\]

(18)

where the subscript \((s)\) indicates the concentration on the surface of limestone. We will use subscript \((b)\) to represent concentration in the bulk water. The first order rate constants \(k_1, k_2, k_3\) (cm/s) are defined as

\[
\log k_1 = 0.198 - \frac{444}{T},
\]

(19)

\[
\log k_2 = 2.84 - \frac{2177}{T},
\]

(20)

\[
\log k_3 = \begin{cases} 
-5.86 - \frac{317}{T} & 5 ^\circ\text{C} \leq T \leq 25 ^\circ\text{C}, \\
-1.10 - \frac{1737}{T} & 25 ^\circ\text{C} < T \leq 48 ^\circ\text{C}.
\end{cases}
\]

(21)

The rate constant of precipitation reaction \(k_4\) (cm/s) is defined as \[8\]

\[
k_4 = \frac{K_2}{K_C} \left[ k'_1 + \frac{1}{a_{\text{H}}(k_2a_{\text{H}_2\text{CO}_3^*} + k_3a_{\text{H}_2\text{O}})} \right],
\]

(22)

where \(K_2\) is the equilibrium constant for dissociation of bicarbonate, \(K_C\) is the solubility product constant for calcite, \(k'_1\) is a modified forward rate constant for reaction (1), which is roughly 10 or 20\(k_1\).

An approximation of Fick’s first law of diffusion \[6\] gives the mass flux of \(\text{Ca}^{2+}\) from the surface of limestone through the metal sediment layer, in our case, Fe(OH)\(_3\), into the bulk solution

\[
J_d = \frac{D}{\delta} ([\text{Ca}^{2+}_{(s)}] - [\text{Ca}^{2+}_{(b)}]),
\]

(23)

where \(D\) (L\(^2\)/s) is the diffusion rate of \(\text{Ca}^{2+}\) in Fe(OH)\(_3\) as porous media \[9\], \(\delta\) (L) is the thickness of the metal sediment, \([\text{Ca}^{2+}_{(s)}]\) is the concentration of \(\text{Ca}^{2+}\) at the surface of the limestone, and \([\text{Ca}^{2+}_{(b)}]\) is the concentration of \(\text{Ca}^{2+}\) in the bulk solution. For dissolution from a surface of area \(A\) (m\(^2\)) into a fluid of volume \(V\) (m\(^3\)), the mass balance necessitates that the rate of change of the concentration in the bulk solution is

\[
\frac{d[\text{Ca}^{2+}]}{dt} = \frac{A}{V} J_d.
\]

(24)

Combining it with the rate law (18) and the rate equation \(\frac{V}{A} \frac{d[\text{Ca}^{2+}]}{dt} = r\), we obtain

\[
\frac{D}{\delta} ([\text{Ca}^{2+}_{(s)}] - [\text{Ca}^{2+}_{(b)}])
\]

\[
= \frac{1}{10} \{k_1[\text{H}^+_{(s)}] + k_2[\text{H}_2\text{CO}_3^*] + k_3[\text{H}_2\text{O}] - k_4[\text{Ca}^{2+}_{(s)}][\text{HCO}_3^-_{(s)}]\},
\]

(25)
where the constant $\frac{1}{10}$ is used to adjust the units. This is overall a nonlinear equation dependent on the concentrations of calcium ions on the surface of the limestone, as well as in the water. The concentration of calcium ions in the water is obtained by solving the differential equation (24). A nonlinear equation solver is then utilized to solve (25) for the surface concentration of $\text{Ca}^{2+}$, given the concentration in the bulk water.

Because of the low solubility of $\text{Fe}^{3+}$, it tends to precipitate when the pH value raises to some certain threshold. To calculate the iron precipitation, we consider the following reaction and its corresponding equilibrium equation [6]

$$\text{Fe(OH)}_3 + 3\text{H}^+ \rightleftharpoons \text{Fe}^{3+} + 3\text{H}_2\text{O},$$

$$\log[\text{Fe}^{3+}] = 3.2 - 3\text{pH}.$$ (27)

In each time step of the differential equation, the iron precipitation and therefore the thinkness of the layer $\delta$ is calculated, so that this effect is incorporated in the differential equation solver to reflect the diffusion of calcium ions through the precipitation layer on the surface of limestone.

**Numerical Result**

The experiment was done by engineering students at Saint Francis University under the “Limestone Channel at Swank 13 Mine” project [10]. The Swank 13 mine is an abandoned underground coal mine in Reade Township, northern Cambria County, Pennsylvania. An acid flow emerges from the abandoned mine and was directed down a 1000 feet channel lined with about a foot thickness of limestone, in order to neutralize the acidity and precipitate the Fe and Al. Numerous data were collected from the field and numerical computations were conducted in Matlab to fit the real data. We used optimization toolbox to solve the nonlinear equation (25). *ode45* is used to compute the change of concentrations of calcium ions along the channel. Tables 1, 2, and 3 list some sample measurement data we made for depth of water, velocity of water flow in the channel, and surface area of typical limestone at different locations in the channel, respectively. Since only the ratio of the surface area of limestone and volume of water is needed in our equation, we can obtain a rough estimate by multiplying the number of limestone and the average surface area in one unit volume of water.

The numerical results obtained by computations are plotted in Figure 1 and Figure 2.

Figure 1 shows the change of concentration of calcium and iron ions along the channel, as well as the change of pH value, obtained by our model. We can observe the release of calcium and pH value is increased accordingly. When the pH value achieves a threshold value, iron precipitates start to appear. Figure 2 shows the comparison of our numerical results and measurements from the channel with three sets of data. Both show the predicted improvement of water quality.
Conclusion and Future Discussion

In this project we have set up a mathematical model of open limestone channel using Fick’s first law and the rate law of calcite dissolution. The diffusion process is approximated by linear decrease, which is the steady state equation. The computational results suggest that without diffusion, the acid water could be completely neutralized. However, both numerical and experimental data show that the effect of open limestone channel treatment is greatly reduced by the iron sediments, which is consistent with the conclusion made in [4]. There are several other factors to be considered in our model in the future. The velocity of water flow in the channel may take away some of the iron sediments. A coefficient may be added accordingly. A time delay may be considered in the diffusion process.
Figure 1: Change of Concentration of Different Species

Figure 2: Comparison of Results

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References


[8] L. N. Plummer, T. M. L. Wigley, and D. L. Parkhurst, The kinetics of calcite dissolution in CO$_2$-water systems at 5 to 60°C and 0.0 to 1.0 atm CO$_2$, American Journal of Science 278 (1978) 179–216.
