

## **Modelling of Diffusion during Neutralisation of Acid Mine Drainage by Limestone**

**Clayton A. Mubishi<sup>1</sup>, Robert Huberts<sup>1</sup>, Reneiloe Seodigeng<sup>2</sup>, Haleden Chiririwa<sup>3\*</sup>, Tumisang Seodigeng<sup>2</sup>**

<sup>1</sup> *Department of Chemical Engineering, University of Johannesburg, P.O. Box 17011, Doornfontein 2088, South Africa.*

<sup>2</sup> *Department of Chemical Engineering, Vaal University of Technology, Private Bag X021, Vanderbijlpark, 1911, Andries Potgieter Blvd, South Africa.*

<sup>3</sup> *Biosorption and Water Research Laboratory Department of Chemistry, Vaal University of Technology, Private Bag X021, Vanderbijlpark, 1911, Andries Potgieter Blvd, South Africa.*

*\* Corresponding author*

### **Abstract**

The formation of AMD (Acid Mine Drainage) solution has a large impact on the environment with potential decant in river systems, lakes, and agriculture areas which could have catastrophic consequences on aquatic life and human health. The challenge for today is finding a way to inhibit the generation of AMD solution in order to stop the pollution of the environment. This study seeks to model  $H^+$ ,  $Fe^{2+}$  and  $Fe^{3+}$  ion diffusion during neutralisation process of acid mine drainage by limestone in order to establish if AMD can be neutralized in-situ to prevent it from polluting the environment. A model that could be used to simulate the diffusion of  $H^+$ ,  $Fe^{3+}$  and  $Fe^{2+}$  and precipitation of  $Fe^{2+}$  and  $Fe^{3+}$  was developed by comparing the values of the concentrations of the these ions to those obtained from empirical data. The best fit for AMD neutralisation was found to be for the model of the 0.5m pipe with an S.S.E (sum of squared error) of 0.434 followed by the 2m pipe with an S.S.E of 0.555 and the 1m pipe with S.S.E of 1.25. The best fit for the ferric ion diffusion and precipitation was found to be the 0.5m pipe with an S.S.E of 0.003529 followed by the 2m pipe with an S.S.E of 0.253 and a S.S.E of 0.459

for the 1m pipe. The best fit for ferrous diffusion and precipitation was for the 0.5m pipe with an S.S.E of 0.787, followed by 2m pipe with a S.S.E of 5.538 and 1m pipe with an S.S.E of 8.268.

**Keywords:** Acid mine drainage, neutralization, limestone, modelling

## INTRODUCTION

The majority of materials and metals extracted from the Earth by mining occur naturally as sulphide ores or are associated with sulphide minerals. During the extraction process of these metals, those sulphides which are not part of the ore material are dumped in waste rock dumps with other rocks [1]. Sulphuric acid is produced when metal sulphides present in mineral bearing rock are oxidized during mining operations. These sulphides are exposed to micro bacteria that are the catalysts of the oxidation reactions that produce the acid as well as other heavy metal compounds. The continual oxidation of the metal sulphides reduces the pH of the waste water that is removed during mining and is termed Acid Mine Drainage. When this waste water is introduced to naturally occurring water systems it raises the pH of the system. The natural buffering mechanisms of the water bodies will not be able to tolerate the increase of acidity of the solution. The acid then destroys all of the organisms present in the water which includes fish that humans residing near these water bodies' use for food and trade, it also make the water itself not fit for use. Other metal ions such as ferric ions present in the AMD precipitate in solution at low pH and create a "blanket" that covers the water surface, this prevents oxygen from dissolving into the water together with the acidity in the solution leads to accelerated degradation of plant and animal life [2]. Use of hydrated lime to neutralize AMD is the most cost effective method of reduce AMD [3]-[5], and mathematical models for this neutralization can be generated to control the process. Mathematical models are sets of equations that inter relate different variables and parameters that are involved in physical systems or processes [6]. These models can be used to predict the behavior of the physical process and referred to as simulation.

Models are mathematical representations of mechanisms that govern natural phenomena that are not fully recognized, controlled, or understood. They have become indispensable tools via decision support systems for policy makers and researchers to provide ways to express the scientific knowledge. The modelling process encompasses several steps that begin with a clear statement of the objectives of the model, assumptions about the model boundaries, appropriateness of the available data, design of the model structure, evaluation of the simulations, and providing feedback for recommendations and redesign processes. Accuracy measures how closely model-predicted values are to the true values. Precision measures how closely individual model-predicted values are within each other. In other words,

accuracy is the model's ability to predict the right values and precision is the ability of the model to predict similar values consistently. The assessment of adequacy of a mathematical model may often be related to its ability to yield the same ranking between observed and model-predicted values rather than model-predicted on observed values. Nonparametric tests are more resilient to abnormalities of the data such as outliers; therefore, it may generally be used to check model adequacy. Typical statistics are the Spearman correlation ( $r_s$ ) and Kendall's coefficient. The mean square error of prediction (MSEP) is the most common and reliable estimate to measure the predictive accuracy of a model [7].

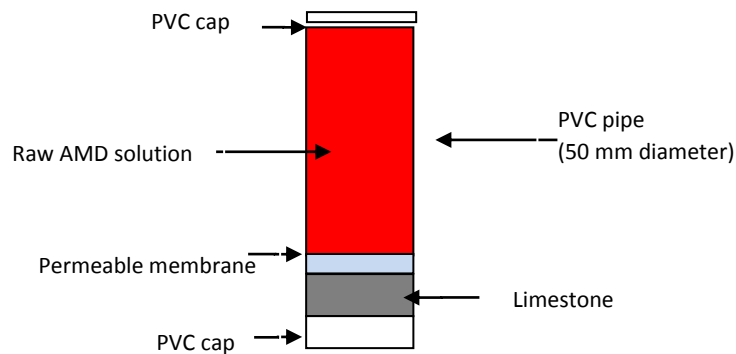
Mathematical modelling including identification and simulation has become key techniques, central to all disciplines of science and engineering. Accurate models of dynamic processes are used for design, optimization and model based monitoring and control. Modelling of chemical processes and usually based on the well-known concepts of mass and energy conservation and the laws of thermodynamics. However, in many cases in chemical reaction networks more information is needed. In these cases, appropriate formal mathematical structures to describe the velocity of individual chemical conversions have to be found. This is usually done by a human expert. In an iterative procedure experience, "intuition", a priori and empirical knowledge of the system to be modelled and measurements are used to derive a model. The present work focuses on the imitation of this human ability to reason about system structure and system behavior on a qualitative level. The efficient qualitative methods developed are coded in a computer program together with well-known quantitative identification procedures [8].

In this paper we are continuing our efforts to investigate the effect of PVC length on ferric and ferrous ion precipitation, model the diffusion of  $H^+$  ions and model the diffusion and precipitation of ferric and ferrous ions [9].

## **EXPERIMENTAL**

### **Materials**

Limestone was obtained from Phalaborwa Mining Company (PMC). Raw Acid Mine Drainage was obtained from the East Rand of Johannesburg. Barium diphenylamine sulphonate, Potassium dichromate, 32% hydrochloric acid, 98% sulphuric acid, starch indicator were bought from Merck South Africa. The experimental set up is shown in Figure 1.



**Figure 1:** In-situ AMD neutralization laboratory set up

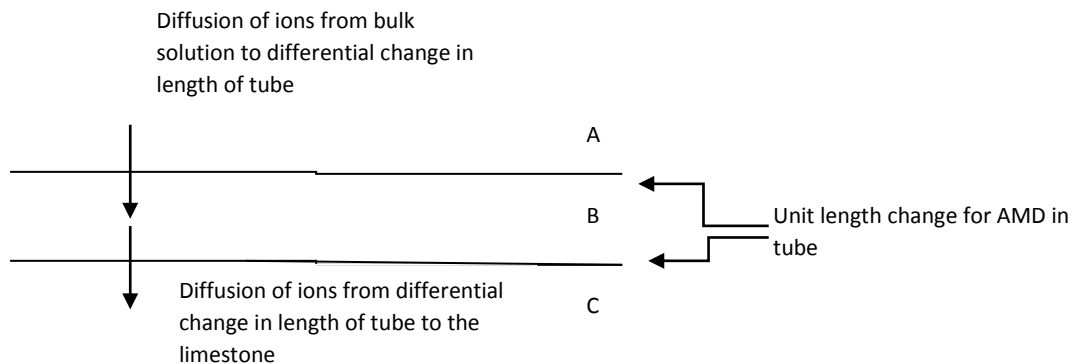
### Experimental procedure

A PVC pipe of length 2m and 50mm inside diameter was used to conduct the experiments. Raw AMD ( $1700 \text{ cm}^3$ ) was loaded into the column, 220g of Limestone was put inside a stocking and dropped into the column. The amount of limestone was calculated according to the sulphur content in the AMD solution. Samples were drawn from different column length (0.5m, 1.5m and 2m) at time intervals of 60 days.

### Analytical Methods

Titration was used for the purpose of this study to determine the concentration of ferrous and ferric irons respectively and pH determined using a pH meter. Total sulfur was determined using an Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

### Modelling approach



**Figure 2:** Representation of diffusion through two imaginary planes

Using the pH to determine the hydrogen ion concentration at a given as well as applying Fick's law to a differential change in pipe length to determine the diffusion of hydrogen ions in the small pipe length the change from A to C as illustrated in Figure 2, the total pH of the solution can be determined from equation 1:

$$[H^+] = [H_B^+] + D_H \frac{\Delta T}{\Delta x^2} ([H_A^+] - [H_B^+]) - ([H_B^+] - [H_C^+]) \quad (1)$$

Where:

$[H^+]$ : concentration of the hydrogen ions at a given time

$[H_B^+]$ : concentration of hydrogen ions within the differential change in length of the tube

$[H_A^+]$ : concentration of hydrogen ions entering the differential change of length of tube

$[H_C^+]$ : concentration of hydrogen ions leaving the differential length of tube

$D_H$ : diffusion coefficient of hydrogen ions

$\Delta T$ : change in time for the diffusion of ions

$\Delta x^2$ : differential change in length squared

The pH is also influenced by the diffusion and precipitation of the ferric ions in that at pH greater than or equal to 3, there would be precipitation of ferric ions which results in a change of pH and less than 3 there is just the diffusion of ferric ions. The equation that describes the action of ferric ions at pH of approximately 3 is given by equation 2:

$$[H^+] = [H_B^+] + D_H \frac{\Delta T}{\Delta x^2} ([H_A^+] - [H_B^+]) - ([H_B^+] - [H_C^+]) + 3[Fe^{3+}] \quad (2)$$

With  $[Fe^{3+}]$  being the concentration of ferric ions that would have precipitated

Once the pH reaches 6 ferrous ions begin to precipitate as well and can be described by equation 3:

$$[H^+] = [H_B^+] + D_H \frac{\Delta T}{\Delta x^2} ([H_A^+] - [H_B^+]) - ([H_B^+] - [H_C^+]) + 2[Fe^{2+}] \quad (3)$$

With  $[Fe^{2+}]$  being the concentration of ferrous ions that would have precipitated.

Ferrous and ferric ions play a major role in the production of AMD and the equation that describes the diffusion and precipitation of ferric ions at pH 3 is given by equation 4:

$$[Fe^{3+}] = [Fe_B^{3+}] + D_{Fe^{3+}} \frac{\Delta T}{\Delta x^2} ([Fe_A^{3+}] - [Fe_B^{3+}]) + 1/3([H^+] - 10^{-3}) \quad (4)$$

Where:

$[Fe^{3+}]$  concentration of ferric ions considering diffusion and precipitation of ferric ions

$[Fe_B^{3+}]$  Concentration of ferric ions within the differential length change and this has a value of zero at pH 3

$[Fe_A^{3+}]$  concentration of ferric ions entering the differential length change

$[H^+]$  concentration of hydrogen ions at a given time

$D_{Fe^{3+}}$  diffusion coefficient for ferric ions

The equation that describes the diffusion and precipitation of ferrous ions at pH 6 is given equation 5:

$$[Fe^{2+}] = [Fe_B^{2+}] + D_{Fe^{2+}} \frac{\Delta T}{\Delta x^2} ([Fe_A^{2+}] - [Fe_B^{2+}]) + 1/2([H^+] - 10^{-6}) \quad (5)$$

Where:

$[Fe^{2+}]$  concentration of ferrous ions considering diffusion and precipitation of ferrous ions

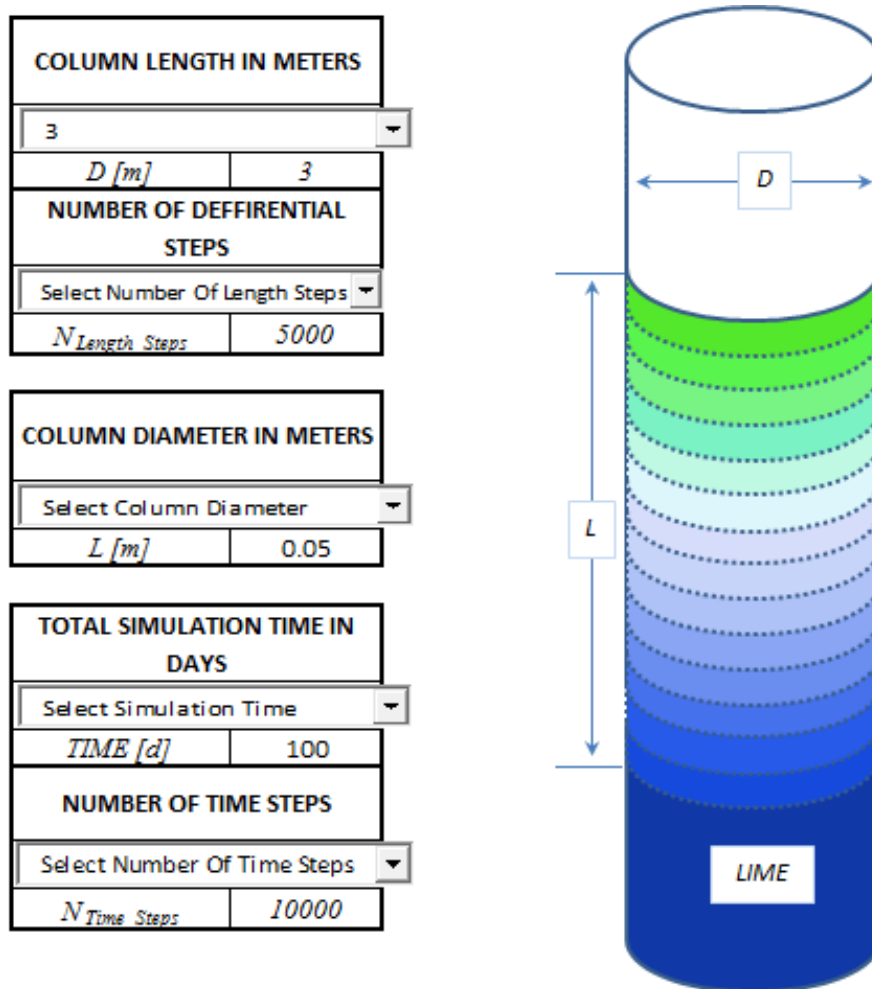
$[Fe_A^{2+}]$  concentration of ferrous ions entering the differential length change

$[Fe_B^{2+}]$  concentration of ferrous ions within the differential length change and this has a value of zero at pH 6.

$D_{Fe^{2+}}$  diffusion coefficient for ferrous ions

### Computational Tool Development

The computational tool was developed to model two scenarios, ferric and ferrous diffusion and precipitation. The algorithms for the computational flow process for the two scenarios modelled are represented through flowcharts shown in Figures 4-6. The algorithms are then programmed into Microsoft Excel VBA to solve Equations 1 to 5. Excel is used to interface the model with the user where parameters can be changed through drop-down menus as shown in Figure 3.



**Figure 3:** Computational tool user interface

The values of the concentration of hydrogen, ferric and ferrous ions at different times and length of pipe were sourced from previous experiments performed in our laboratory and values from the model were compared to experimental values [9]. The sum of squared errors was used to compare the accuracy of the model and to predict the actual neutralisation of AMD.

Microsoft Visual Basic was capable of developing a program that was based on the mathematical model. Once the program was developed the process of optimisation of AMD in situ was executed by changing the dimensions of the tube, the number of differential steps required for complete neutralisation, changes in the diffusion coefficient and the time required to complete the neutralisation.

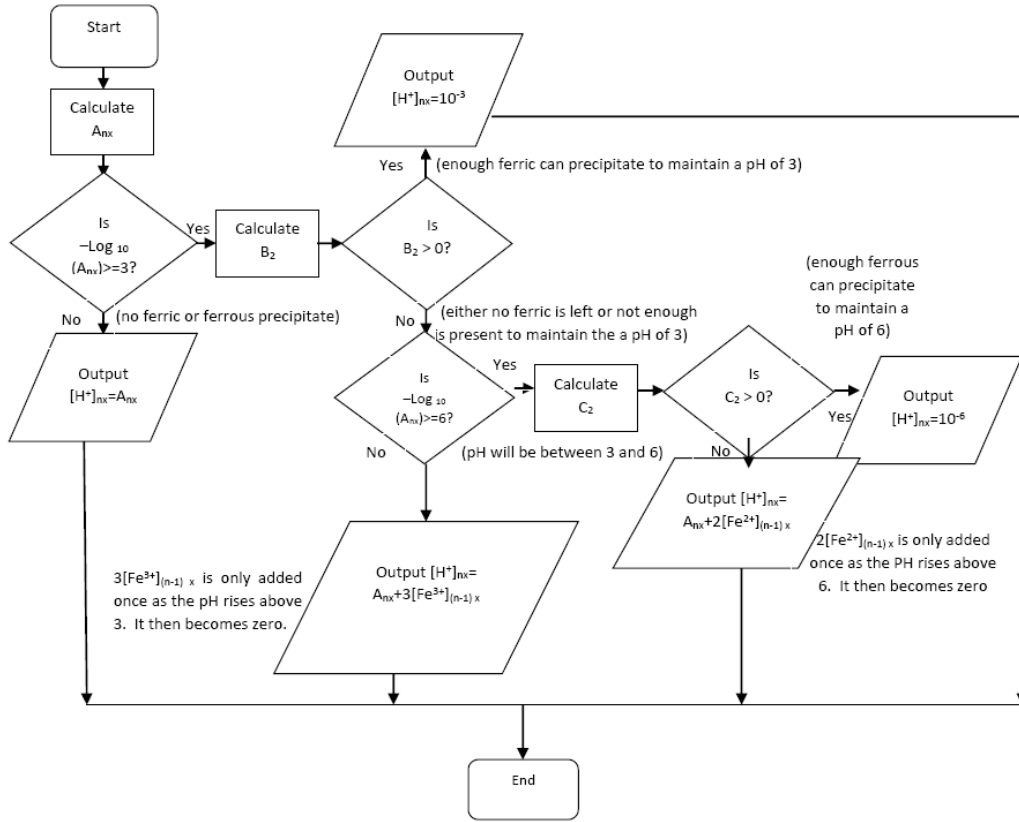


Figure 4: Flow chart of modeling approach for H<sup>+</sup>

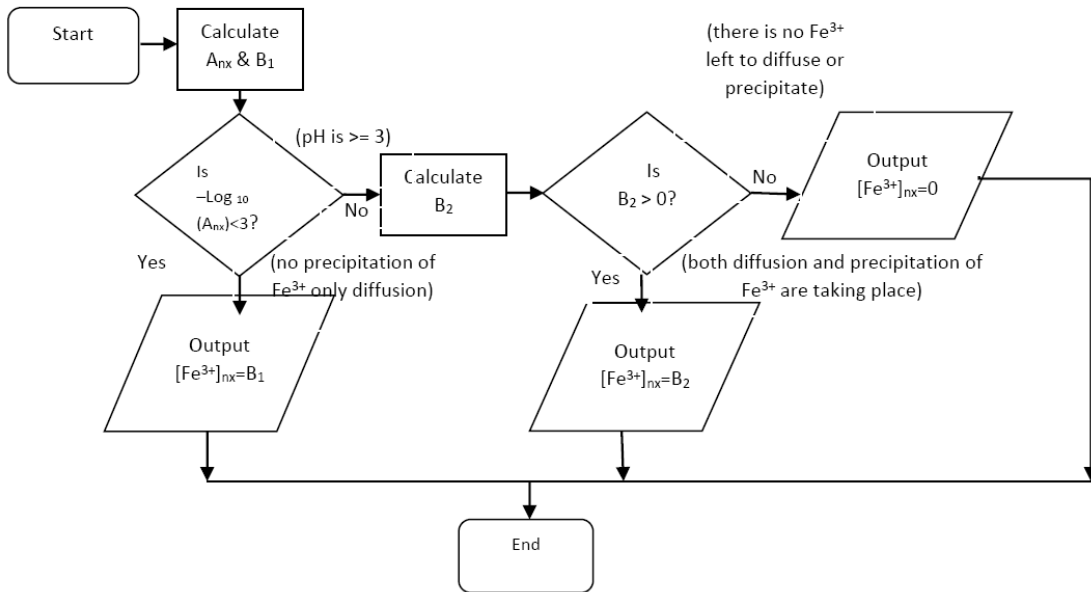


Figure 5: Flowchart of modeling approach for Fe<sup>3+</sup>



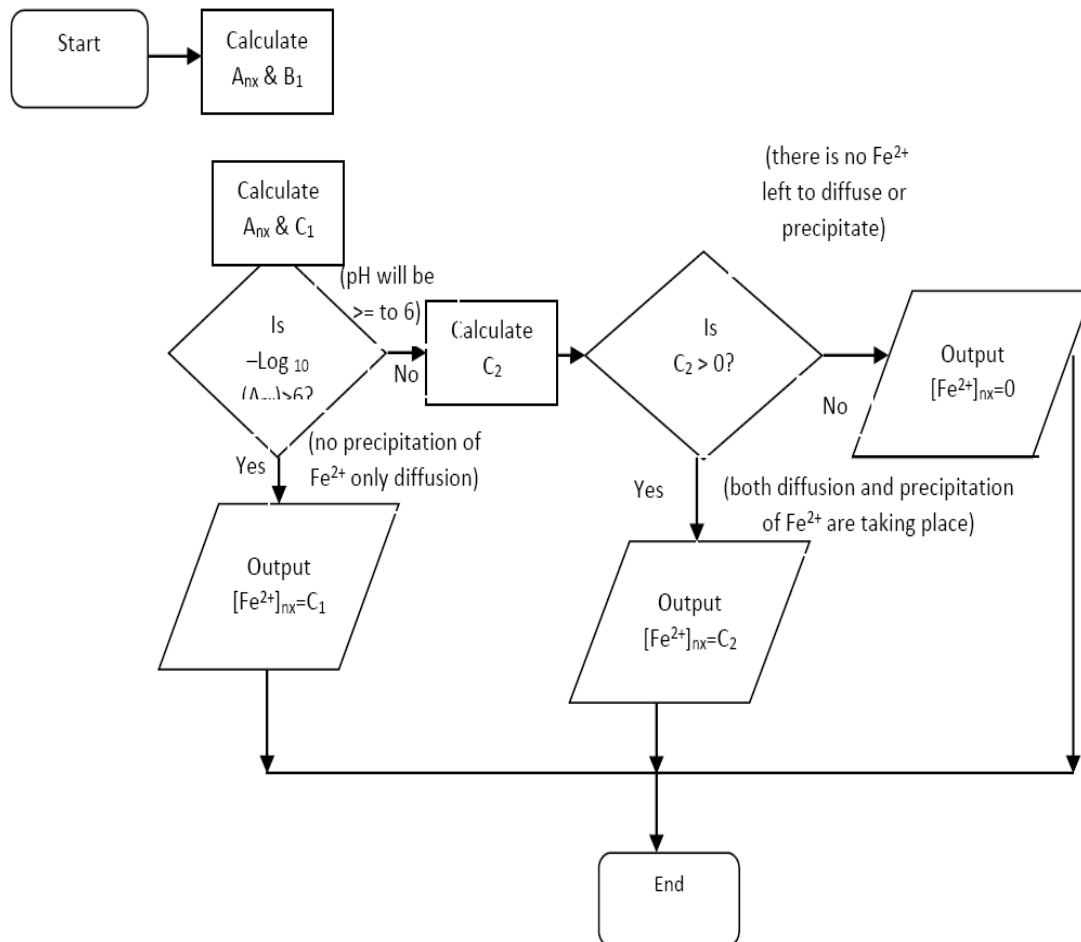
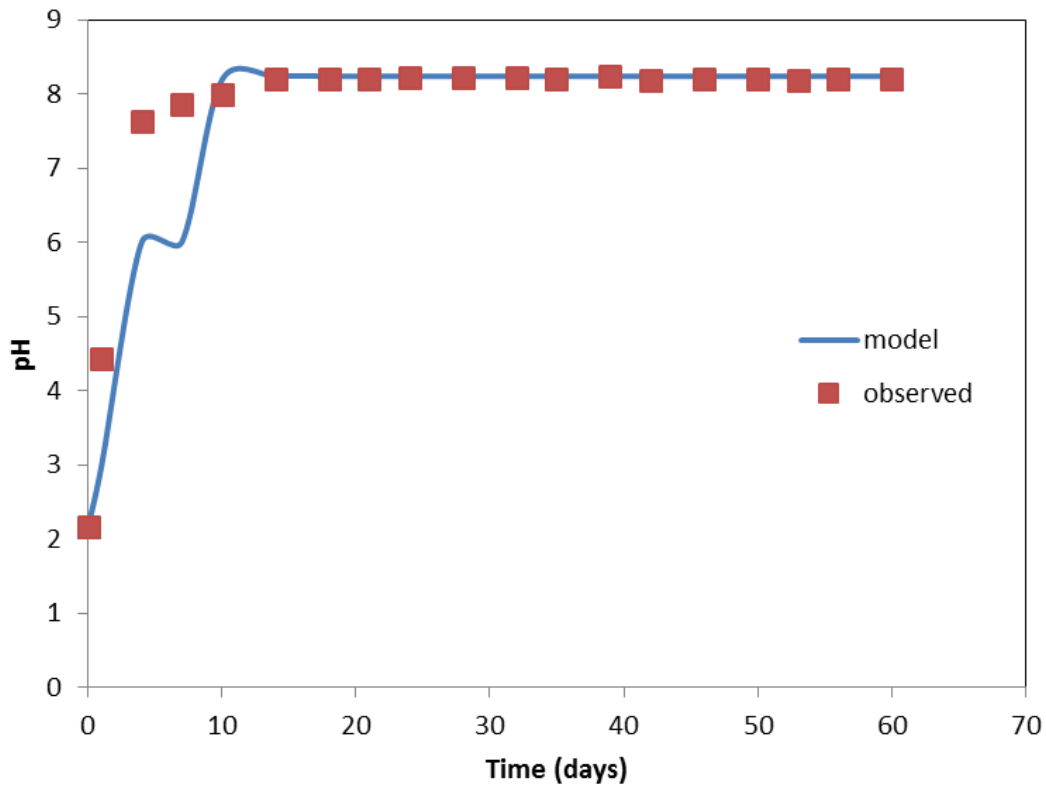


Figure 6: Flow chart of modeling approach for Fe<sup>2+</sup>

## RESULTS AND DISCUSSION

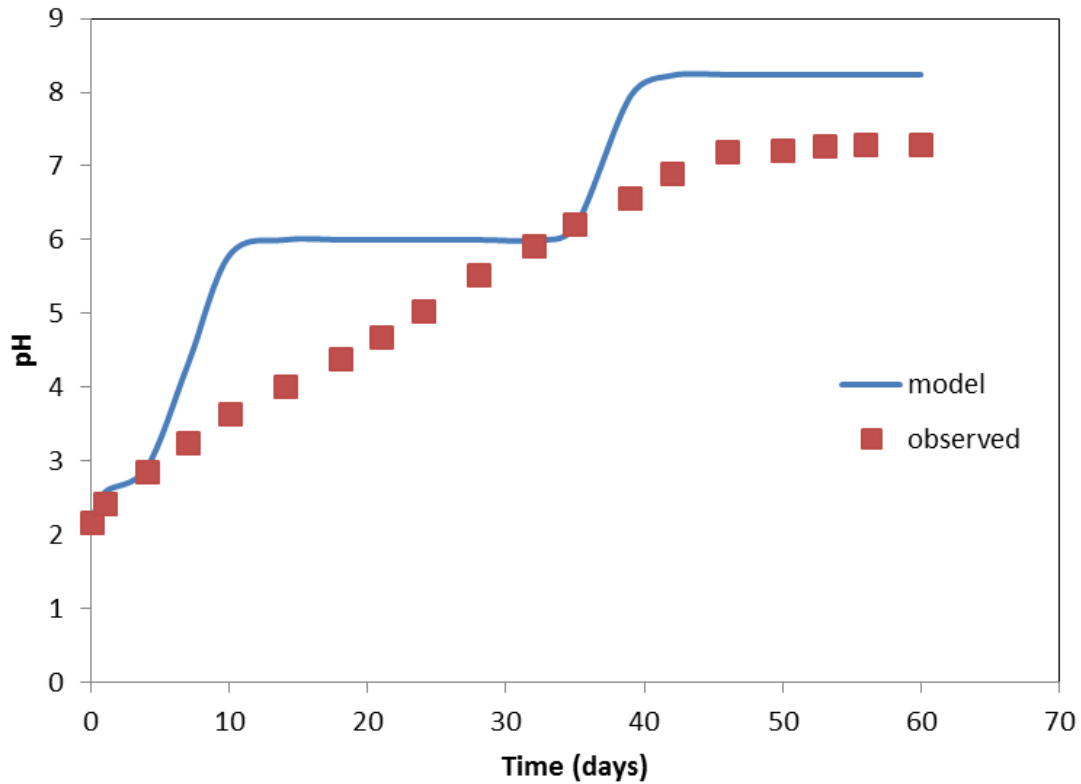
### Modelling pH against time

Figures 7-9 show the modelled results of pH against time for various column lengths (0.5m pipe, 1m pipe and 2m pipe), and this was done so as to compare how the model fits the experimental data. The model was simulated to run for the same period of as time as the experiment was carried out. It was assumed that for the neutralization of AMD, the hydrogen ions migrated to the bottom of the column by diffusion. Diffusion was caused by the difference of the hydrogen ion concentration between the AMD bulk solution at an initial pH of 2.73 and the limestone at an assumed pH of 8.24.



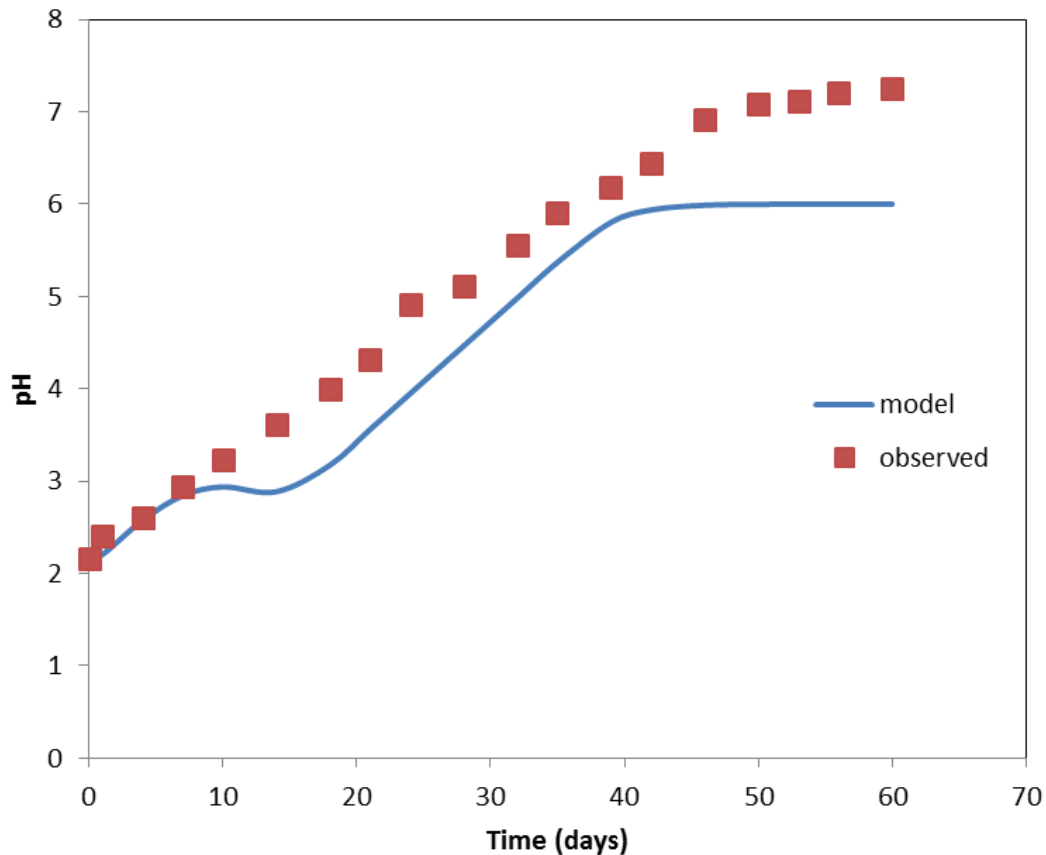
**Figure 7:** 0.5m pipe pH vs Time

Figure 7 shows the change in pH of the AMD solution for a given period of 60 days in a 0.5m PVC tube. It can be noted that there is a significant difference between the pH collected from the experiment and the ones obtained from the simulation, at day 7 and day 10. The difference could have been attributed to the value of the hydrogen ion diffusion coefficient used in the simulation was slightly different from the one that was in the experiment. The pH of the model and the ones observed in the experiment after day ten closely resemble each other, showing a good correlation between the model and the experiment. The overall sum of squared error between the model and the experimental data was determined to be 0.434, showing a good relationship between the model and the raw data.



**Figure 8:** 1m pipe pH vs Time

Figure 8 shows the change in pH of an AMD solution versus time in a 1 m PVC tube for a given period of 60 days. The pH obtained from the model are generally higher than the results obtained from the experiment, this could be because during the simulation the number of differential length steps used were not enough to allow the simulation to calculate the change in pH of the solution accurately, also the value of the diffusion coefficient used was higher than that in the experiment. The sum of squared errors for the comparison above was found to be 1.25 showing that there was a weak correlation between the model and the raw data as expected from what is represented in Figure 8.



**Figure 9:** 2m pipe pH vs Time

Figure 9 shows the comparison of the model and observed results for a 2m PVC pipe measuring the change in pH over time. The general trend shows that the pH increases over the 60 day period. The model increased slightly slower than the actual observed data although both sets of data got to a final pH of close to 7 at the end of 60 days. The model results are lower than the observed results, due to the fact that the data for the model was simulated with a hydrogen ion diffusion coefficient that was different than the one in the experiment. The sum of squared errors for the above data was calculated to be 0.555 which show a good correlation between the observed data and the model.

### **Modelling $\text{Fe}^{3+}$ concentration against time**

Modelled results of  $\text{Fe}^{3+}$  concentration against time for various column lengths are shown in Figures 10-12. This was done so as to compare how the model results differed from the experimental data. The model was allowed to run for the same period of as time as the experiment was carried out. The initial concentration of the

ferric ions was assumed to be reduced by diffusion of the ions from the bulk AMD solution to the bottom of the column, which initially did not have ferric ions, as well as the precipitation of the ions due to the change of pH of the solution. The plots of ferric ion concentration versus time of the model, as well as the experimental results were compared as shown in Figures 10-12 for 0.5m, 1m and 2m pipes respectively.

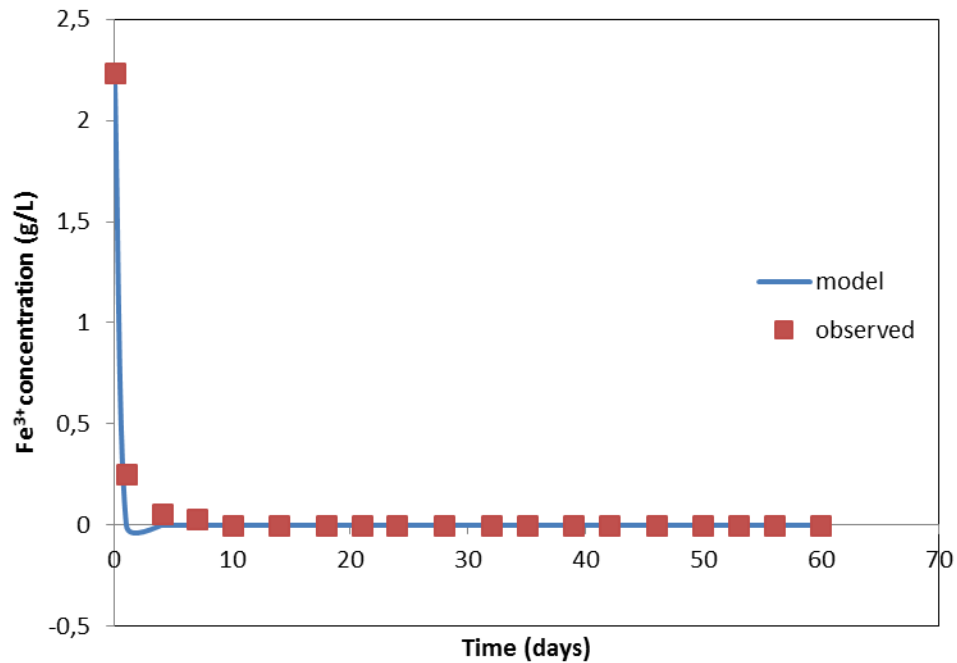
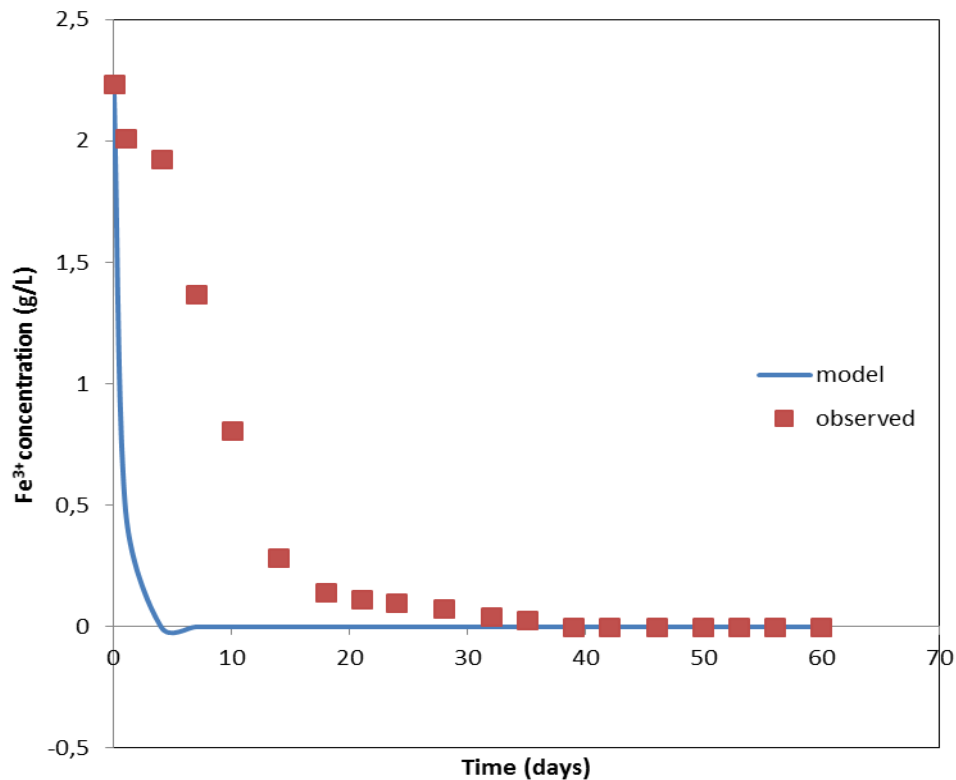


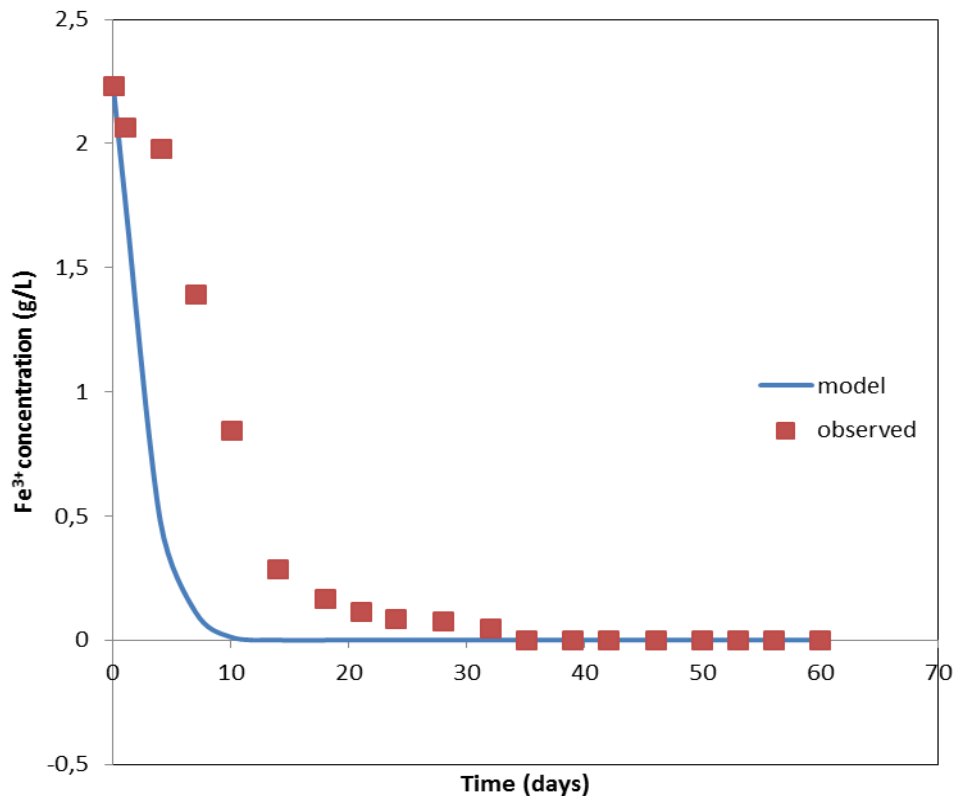
Figure 10: 0.5m pipe Ferric concentration vs Time results

Figure 10 shows the change in concentration of ferric ion with time for a 60 day period in a 0.5m PVC pipe. The graphs confirm that the concentration of ferric ions reduce over time in a pipe with AMD solution with limestone acting as a neutralizing agent at the bottom of the pipe. The figure above shows that the model very accurately represents the experimental data with a sum of squared errors of 0.003529. This value of S.S.E is very close to zero thus shows a very strong correlation between the experimental results and those predicted by the model.



**Figure 11:** 1m pipe Ferric concentration vs Time results

Figure 11 show the change in concentration of ferric ion concentration with time for a 60 day period in a 1m PVC pipe. The graphs confirm that the concentration of ferric ions reduce over time in a pipe with AMD solution with limestone acting as a neutralizing agent at the bottom of the pipe. The figure above shows that the model slightly represents data obtained from the experiment. This is due to the fact that the precipitation of ferric ions is governed by the change of pH of the solution, which in turn is affected by the choice of the value of hydrogen ion diffusion coefficient chosen to represent the diffusion of the hydrogen ions within the solution, also the value of the diffusion coefficient of the ferric ions affected the values of ferric ion concentration obtained from the simulation. The value of the sum of squared error obtained from the comparison was determined to be 0.459 which shows a slight resemblance of the experimental data by the model.



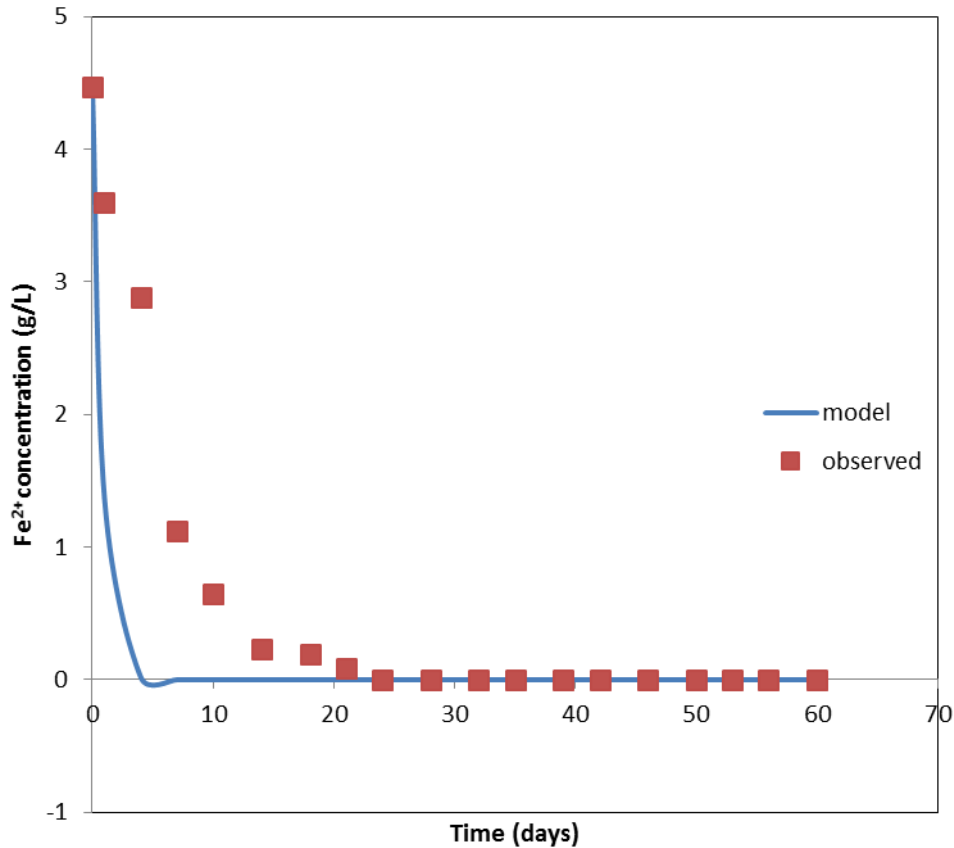
**Figure 12:** 2m pipe Ferric ion concentration vs Time

Figure 12 show the change in concentration of ferric ion concentration with time for a 60 day period in a 2m PVC pipe. The graphs confirm that the concentration of ferric ions reduce over time in a pipe with AMD solution with limestone acting as a neutralizing agent at the bottom of the pipe. The figure above shows that the model represents data obtained from the experiment to a great extent with a sum of squared error of 0.253. This is due to the fact that the value of the diffusion coefficient of the ferric ions slightly affected the values of ferric ion concentration obtained from the simulation. The diffusion coefficient used in the model was higher than the one in the experiment thus the model showed that the concentration of the ferric ions decreased much faster than that in the experiment.

**Modelling Fe<sup>2+</sup> concentration against time**

Figures 13-15 show the modelled results of Fe<sup>2+</sup> concentration against time for various column lengths. This was done so as to compare how the model results to the experimental data. The model was allowed to run for the same period of as time as the experiment was carried out. The basis of the model was that the ferrous ions diffused to the bottom of the tank due to the concentration gradient between the AMD bulk

solution and the limestone. Precipitation of ferrous ions occurs at a pH of 6 or greater thus at the AMD-limestone interface precipitation of ferrous ions occurred at a greater rate than within the bulk solution, thus reduction in the concentration of ferrous ions occurred due to the diffusion and subsequent precipitation of the ferrous ions. The plots of the pH versus time of the model as well as the experimental results were compared as shown in Figures 13-15 for 0.5m, 1m and 2m pipes respectively:

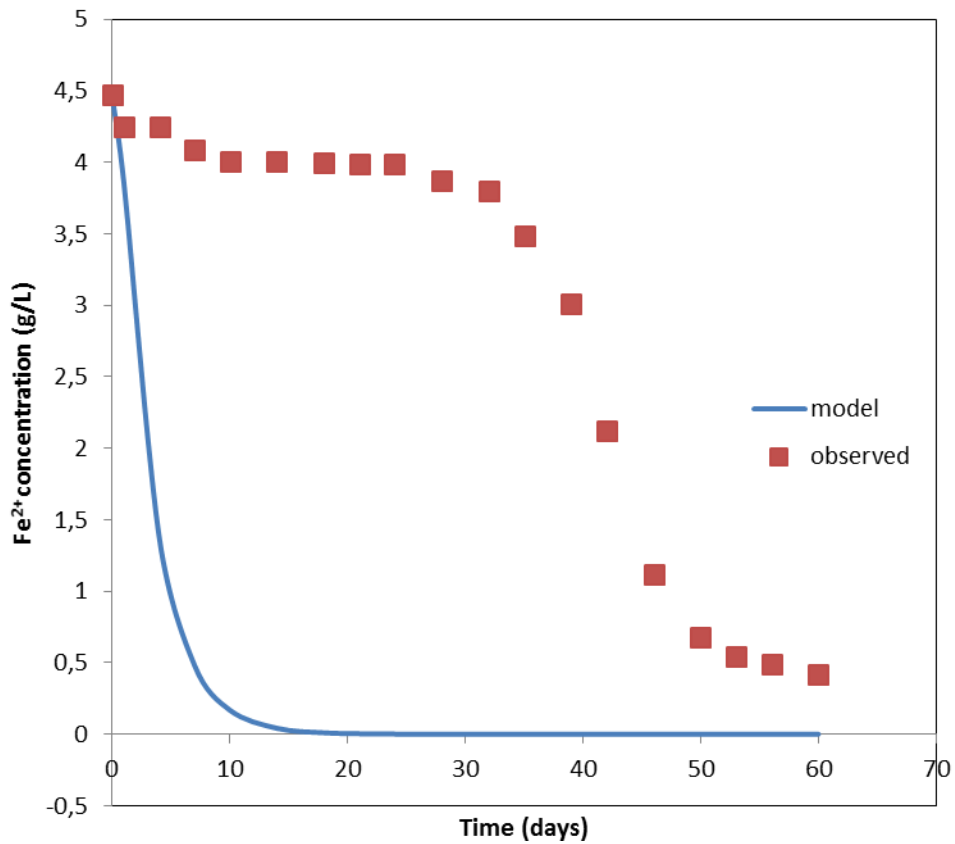


**Figure 13:** 0.5m pipe Ferrous concentration vs Time results

Figure 13 shows the change in concentration of ferrous ion concentration with time for a 60 day period in a 0.5m PVC pipe. The graphs show that the concentration of ferrous ions decreased over time until all of the ferrous ions were depleted. The comparison between the model results and the actual results show that there is a close representation of actual precipitation of ferrous ion by the model. The reduction of ferrous concentration shown by the model was faster than that obtained during the experiment. This is due to the fact that the value of the ferrous ion diffusion coefficient used to calculate the change in concentration of ferrous ions in the model was greater than the one that was in the experiment. The sum of squared errors of 0.787 however shows that there is a good correlation between the observed data and

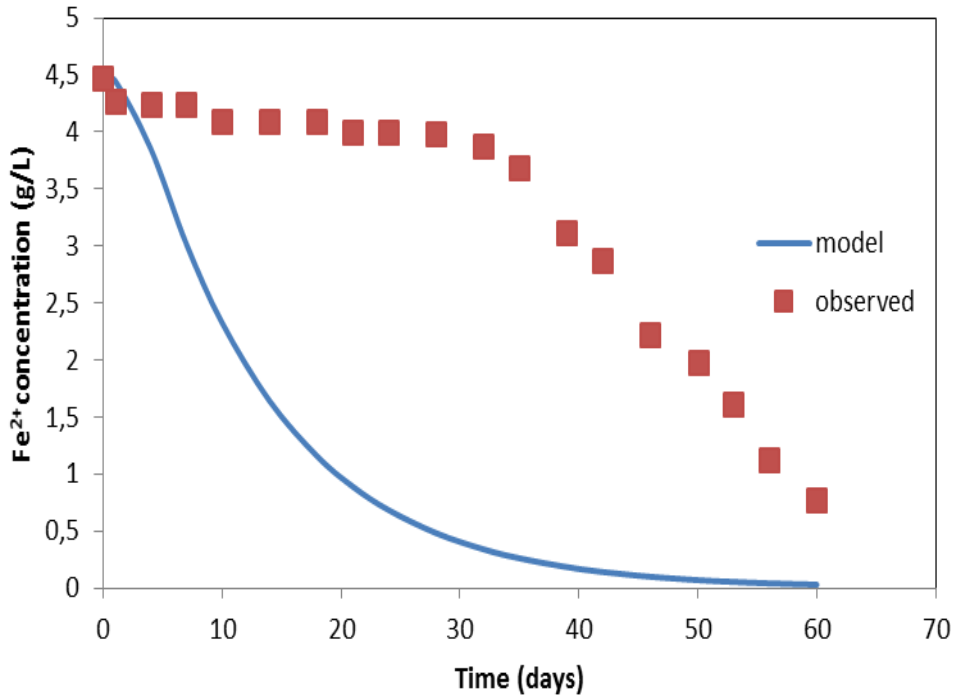


that predicted by the model.



**Figure 14:** 1m pipe Ferrous ion concentration vs Time results

Figure 14 shows the change in concentration of ferrous ion concentration with time for a 60 day period in a 1m PVC pipe. The graphs show that the concentration of ferrous ions decreased over time. The comparison between the model results and the actual results show that there was no representation of actual precipitation of ferrous ion by the model. The reduction of ferrous concentration shown by the model was much faster than that obtained during the experiment. This is due to the fact that the differential length steps used in the simulation were not enough to allow for the accuracy of the model, also the chosen value of the diffusion coefficients for hydrogen ions and ferrous were different than those in the experiment. The sum of squared errors was found to be 8.268, showed that there was no correlation between the observed data and that predicted by the model.



**Figure 15:** 2m pipe Ferrous ion concentration vs Time results

Figure 15 shows the change in concentration of ferrous ion concentration with time for a 60 day period in a 2m PVC pipe. The concentration of ferrous ions decreases over time and comparison between the model results and the actual results show that there was a very slight representation of actual precipitation of ferrous ion by the model. The reduction of ferrous concentration shown by the model was much faster than that obtained during the experiment. This is due to the fact that the differential length steps used in the simulation were not enough to allow for the accuracy of the model, also the chosen value of the diffusion coefficients for hydrogen ions and ferrous were different than those in the experiment. The sum of squared errors was determined to be 5.538 shows that there was a very slight correlation between the observed data and that predicted by the model.

## CONCLUSION

The mathematical model was able to predict the change in pH for 0.5m and 2m pipes with a slight representation of the change in pH for the 1m pipe. The model was able to accurately predict the behaviour of ferric ions undergoing diffusion and precipitation in 0.5m and 2m pipes.

## **ACKNOWLEDGEMENTS**

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