

Investigating the formation of acid mine drainage of Toledo pyrite concentrate using column cells

Diosa Marie Aguila

Batangas State University, Batangas City, Philippines 4200

dmmaguila@gmail.com

Abstract. Acid mine drainage (AMD) is an inevitable problem in mining and has adverse effects in water quality. Studying AMD formation will be valuable in controlling the composition of mine waters and in planning the rehabilitation method for a mine. In this research, kinetics of AMD formation of Toledo pyrite was studied using two column experiments. The mechanisms of AMD formation and the effects of various factors on pH drop were first studied. Another column test was done for validation and to study the role of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the change of leachate pH. The first experiment revealed that time and particle size are the most significant factors. It was also observed that the sudden pH drop during the starting hours was due to cracks formed from beneficiation, and the formation of $\text{Fe}(\text{OH})_3$. The ladder behavior of pH thereafter was due to decrease in formation of $\text{Fe}(\text{OH})_3$, and the precipitates in pyrite surface that lowered the surface area available for pyrite oxidation. The results of the second experiment validated the ladder behavior of pH. It was also observed that particle size distribution and pyrite surface were affected by the change in pH. $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of leachate generally decreased as pH dropped.

1. Introduction

The Philippines is known for its vast mineral resources. According to the Mines and Geosciences Bureau (MGB), the country has 9 million hectares of land identified with high mineral potential. One of the most important base metal productions of the country is copper, amounting to almost 16 billion pesos for January to September of 2013. Along with this, considerable amount of mine tailings are also produced and needed to be monitored. To prevent underestimation of the effects of tailings and other waste materials of mining in rehabilitation especially in the formation of pit lakes, extensive and continuous studies should be done.

One of the extensively studied effects of this is acid mine drainage (AMD), which is produced when, in a mine site, a sulfide mineral is exposed to oxygen and water, creating an acidic environment. It also releases high levels of metals that may have an impact to nearby land and water bodies and their biota [1].

Pyrite oxidation has been regarded as the most acid-producing sulfidic process in nature, thus being the primary source of AMD [2]. With its cyclic nature, this process can occur indefinitely.

Pyrite may be oxidized directly by oxygen or indirectly by oxygen and iron. Indirect oxidation starts with the directly oxidizing pyrite with oxygen, producing aqueous ferrous ion, sulfate and hydrogen ion. Then, ferrous ions released will be oxidized to ferric ions. This occurs at a low pH. The ferric ions along with oxygen will then oxidize pyrite, and constitute the process called the AMD engine, which will continue to occur until there's no pyrite left to oxidize. At pH greater than 3.0, Fe^{3+} reacts with water to form ferric (oxy)hydroxide. This reaction decreases Fe^{3+} in the solution, forming yellowish precipitates, $\text{Fe}(\text{OH})_3$ [3].



However, the range of iron hydroxide/oxyhydroxide and sulfate minerals formed during pyrite oxidation is wider, depending on the amount of factors affecting the oxidation.

In view of the above, it can be reckoned that monitoring AMD and acid generating minerals exposed in the mine site as the mining progresses will not only help meeting stringent environmental requirements and regulations of the government but will also make mine rehabilitation more efficient.

According to Environmental Protection Agency (1994), there are two types of tests that are done to predict AMD: static and kinetic test. Static tests are usually done to know immediately the acid generating capacity of a mineral/rock at the mine site. Meanwhile, kinetic tests are done to predict the quality of water aiding the pyrite oxidation while manipulating the factors that may affect it. It is also done to have further information about the acid generating capacity of a mineral after doing static tests. Examples of kinetic tests are humidity cell test, Soxhlet extraction test, and column tests.

Among these, column test is easily configured to suit the factors needed to be studied and has a relatively simple model. As such, many studies have been conducted using column test.

The objective of the study is to determine the kinetics of acid mine drainage formation using the pyrite samples obtained from Toledo Mines, Philippines.

2. Methodology

2.1. Analytical Methods

The pH of the leachate were measured using a pH meter (PH-501, General). The mass of the samples was measured using an analytical balance (ATX224, Shimadzu). Screen analysis was done using Rotap and Tyler sieves. The surface morphology of pyrite was analysed by scanning electron microscope (SEM) (XL 30, Philips).

2.2. Sample Preparation

Jones Riffle was used to get 1 kg representative sample. Pyrite was then sieved using ASTM mesh sizes #25, #70, #100, #140, #200, #270, #400 and #800 to get the particle size distribution.

Three particle ranges are used in the experiment: $\geq 149 \mu\text{m}$ (P1), $\leq 149 - 105 \mu\text{m}$ (P2), and $\leq 105 \mu\text{m}$ (P3).

Samples were stored in airtight plastic bags until use to avoid surface oxidation.

2.3. Column Cells Setup

Twelve (12) Plexiglass columns (24 inch length, 1 inch inside diameter) were fabricated and were equipped with air pumps. For the design of the experiment, 3 particle ranges (P1, P2 and P3), 2 different water levels (50 mL and 100 mL) and 2 pyrite sample masses (5 g and 10 g) were used, as shown in Table 1.

The air injected in the setup is continuous and fixed throughout the experiment.

Table 1. Packing of samples in the column cell setups

Column No.	Particle Size	Water Level (ml)	Sample Mass (g)	Column No.	Particle Size	Water Level (ml)	Sample Mass (g)
1	P1	50	10	7	P2	50	5
2	P1	100	10	8	P2	100	5
3	P1	50	5	9	P3	50	10
4	P1	100	5	10	P3	100	10
5	P2	50	10	11	P3	50	5
6	P2	100	10	12	P3	100	5

Desired water quantity was poured to all columns and was let stand for an hour to let the water seep through the solids. Air was then introduced using air pumps (E-JET268 2.7L/min, 150 Pa). After an

hour, first pH measurement was conducted. Second pH measurement was done after 6 hours. The succeeding measurements were done once a day for 30 days.

3. Results

3.1. Column Study: Mechanisms

Shown in figure 1 are the pH measurements of the leachates per column cell within 30 days. The sudden pH drop during the first 6 hours is due to the available surface cracks and irregularities brought about by the comminution process. These cracks served as reactivity points where it's easiest to oxidize pyrite [4]. The graphs also show that most of the columns with the lowest particle size (P3), thus having highest surface area available, have relatively lower pH than the other measurements.

Shown in figure 2 is a SEM image of the unreacted pyrite surface showing visible cracks and other surface irregularities.

The proposed governing reactions in that phase of fast pH drop are the following:

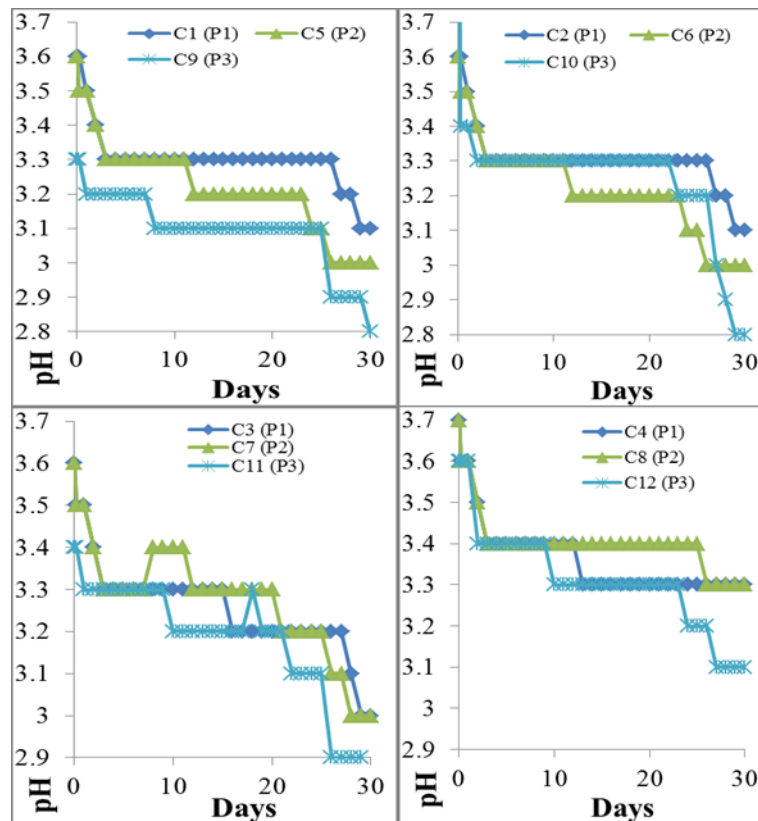
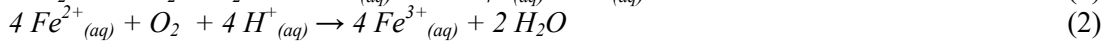
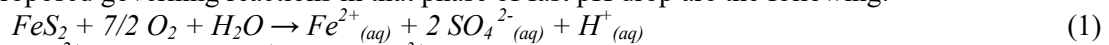


Figure 1. pH measurements within 0-6 hours for leachate samples in C1, C5 and C9 (top left), C2, C6 and C10 (top right), C3, C7 and C11 (bottom left) and C4, C8 and C12 (bottom right)

Pyrite in contact with water and oxygen produced ferrous ion (Eq. 1). Since the system had adequate oxygen supply by means of the air pump, ferrous ions were oxidized to ferric ions (Eq. 2). At pH above 3.5, ferric ions are precipitated into amorphous ferric hydroxide (Eq. 3) which released more hydrogen ions. Thus, the fast drop of pH during the first contact of pyrite, water and oxygen was due to cracks which increased the surface available for oxidation and formation of $Fe(OH)_3$.

On the other hand, after one or two days, the leachates' pH in all column cells decreased slowly, in a ladder manner, as shown in Fig. 2. In this stage, the columns with the smallest particle size also have lower pH at the end of the experiment.

As pH decreased from 5.6 – 3.5, some of the ferric hydroxide formed dissolved back to ferric ions because of higher solubility of ferric hydroxide at lower.

This reaction consumed hydrogen ions thus effectively buffering the pH of the leachate. Also, the oxidation of ferrous ions to ferric ions became repressed at pH below approximately 4.5, thus $\text{Fe}(\text{OH})_3$ and H^+ production became repressed, too [4,5]. This means that the reaction governing this phase of slow pH decrease is the oxidation of pyrite into ferrous ions.

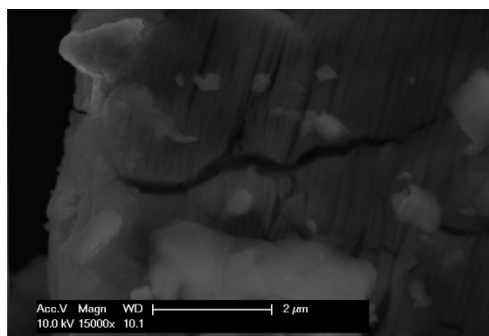


Figure 2. SEM image of unreacted pyrite surface showing cracks

3.2. Column study: Effects of factors

The effects of factors such as time, particle size, mass of samples, and volume of leachate. The levels per variable are shown in Table 2. Design Expert was used for the analysis of the results.

Mean interaction plots were used to know the effect of the factors in the variation of the result and their interactions in the experiment. The plots in figure 3 show that the most significant factor and causes higher variation in the results, the one with the steepest slope, is the time. Next most significant factor is particle size. In the previous literatures that studied effects of particle size in pH, finer particle size results to lower pH [6,7], which is consistent with the results in this study.

Table 2. Level of factors

Parameter	-1	0	1
Time (day)	1	15	30
Mass (g)	5	-	10
Volume (ml)	50	-	100
Particle Size	P3	P2	P1

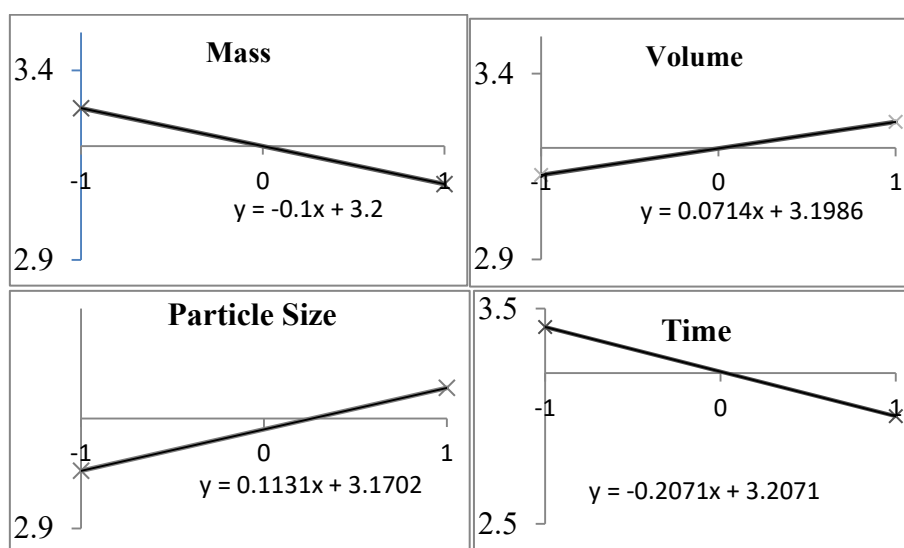


Figure 3. Mean interaction plots for pH of the leachate based on the factors

4. Conclusion

1. The formation of acid mine drainage in Philippine pyrite in column cell experiment was initiated by the formation of $\text{Fe}(\text{OH})_3$ precipitates which increased the formation of hydrogen ions. The fast decrease of pH at the start was due to the cracks formed from the beneficiation process that increased the surface area of the pyrite available for reaction. A gradual decrease in pH afterwards until the end of experiment was governed by the decrease in rate of oxidation of pyrite due to the precipitates in the pyrite surface that lowered the surface area available for pyrite oxidation.
2. Among the factors, contact time and particle size showed the most influence in pH.

Acknowledgments

The author would like to thank Engineering Research and Development for Technology (ERDT) for supporting the financial aspects of this endeavour.

References

- [1] Lowson R 1982 Aqueous Oxidation of Pyrite by Molecular Oxygen *Chemical Reviews* 82, pp 461–497
- [2] Chandra A and Gerson A 2010 The mechanisms of pyrite oxidation and leaching: A fundamental perspective *Surface Science Reports* 65, pp 293–315
- [3] Evangelou V 1995 *Pyrite oxidation and its control* (Florida: CRC Press, Inc.)
- [4] Lottermoser B 2007 *Mine Wastes: Characterization, Treatment and Environmental Impacts* (Heidelberg: Springer)
- [5] Barik R and Mohapatra M 2011 Facile precipitation of iron oxide with in situ $\text{Fe}(\text{II})$ in $\text{Fe}_2(\text{SO}_4)_3\text{NaOH}(\text{N}_2\text{H}_4)_2\text{H}_2\text{SO}_4\text{H}_2\text{O}$ medium *Indian Journal of Chemical Technology* vol 18 pp 107–112
- [6] Butler B 2009 Effect of pH, ionic strength, dissolved organic carbon, time, and particle size on metals release from mine drainage impacted streambed sediments *Water Research* 43 1392 – 1402
- [7] Erguler G Erguler Z Akcakoca H and Ucar A 2014 The effect of column dimensions and particle size on the results of kinetic column test used for acid mine drainage (AMD) prediction *Minerals Engineering* 55 pp 18–29