

# Geology and engineering processes as determinants in the quality of mining-influenced waters in Philippine copper porphyry mines

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**Abstract.** The impacts of geology and engineering processes on the quality of mining influenced waters (MIW) in Philippine copper porphyry mines were studied. Acid mine drainage-metal leaching (AMD-ML) is a common phenomenon in pyrite-rich copper porphyry deposits and said factors determine to a large extent the acidity or alkalinity of the final effluent waters discharged by an active or defunct mine to the environment. After characterization using micromineralogy, pyrite concentrates and mine tailings were leached in the laboratory (accelerated weathering) by bubbling by air to determine the main factors that affect its degradation and the subsequent formation of acidic waters. As observed in the leaching runs, interfering ions, like those of copper, act as buffers and delay the leaching out of heavy metals; similarly, various minerals dissolve, and specific ions precipitate, at various pH levels. Process lime, used in the recovery of copper from the porphyry deposits, provides a very important source of neutralizing capacity. The same behavior was observed in waters that have percolated from surrounding limestone and other alkaline rocks that find their way inside the mine. Precipitates were also characterized to determine the fate of leached-out metals after the acidification and neutralization processes.

**Keywords:** accelerated weathering, acid mine drainage, copper porphyry, micromineralogy, mining-influenced water

## 1. Introduction

**Acid mine drainage (AMD).** Acid mine drainage is a phenomenon in pyrite-rich mineral deposits [Geller *et al.* (1998), McLemore (2008)]. Pyrite is the main source of mine acidic waters and the quality of mine waters, specifically pH, is determined largely by the pyrite content of the ore, gangue, and surrounding country rocks. The chemistry involved in the degradation of pyrite to form sulfuric acid has been well covered in the literature [Chao and Sanzalone (1977), Evangelou (1995), Evangelou and Zhang (1995), Gleisner and Herbert (2002), Lottermoser (2007), Rimstidt and Vaughan (2003)]. In this study, the investigation gathered data from three sources – characterization of pyrite concentrate and tailings,

accelerated weathering runs in the laboratory, and field data from producing and defunct copper mines.

**Copper porphyry mines and pyrite.** Pyrite occurs as a gangue mineral in copper porphyry deposits, or as an alteration product; also, it occurs in waste or country rock surrounding the mineral deposit. At times, pyrite is recovered when economic conditions permit, as what Carmen Copper Corporation did in the past; the pyrite concentrates characterized in this study and used in the accelerated leaching runs were taken from a stockpile in the pier of the company.

**Geology.** Apart from the occurrence of pyrite as the main source of acidity of mine waters, its concentration in the ore and country rock determine to a high degree the mine water acidity.

**Pyrite content.** The pyrite content of the ores ranged from 0.3% to around 3.0%, a range of one order of magnitude [Apostol (1974), Baluda RP and Galapon JB (2005), Consolidated Mine, Inc. (2016), Environmental Geochemistry International Pty Ltd (2006), OceanaGold Philippines, Inc. (2016)]. However, pyrite content in waste rock was not measured because the samples sent for characterization were not representative.

**Alkaline minerals and rocks.** The acid-generating capacity of pyrites is neutralized by the presence of alkaline minerals such as calcite; further, surrounding country rocks may contain limestone and other alkaline rocks that will likewise neutralize any acidity formed [Lottermoser (2007)].

**Engineering processes.** Engineering processes include mining and beneficiation; for metal mines, where a lot of waste rock and tailings are generated, there is also the need to construct waste dumps and tailings dams or ponds. Both of the latter structures contain pyrites which generate acidic waters.

**Mining.** Extraction of the copper ore and associated pyrite breaks down the minerals either by blasting or caving; the size reduction hastens the acidification process due to the increase in surface area available for attack by oxygen and ferric ions from pyrite. Thus acidification is observed in the production areas (benches in surface mines, and production blocks in underground mines). But

neutralization by calcite in the ore (discussed above), or waters that have percolated from limestone and other alkaline rocks in the surrounding country rock, can immediately neutralize acid that has been formed.

**Beneficiation; process lime.** The run-of-mine ore is further reduced in size at the beneficiation plant, where it is crushed and ground to the liberation size somewhere around 75 to 100 microns. Lime, added at around one-half kilogram per ton of ore [Carmen Copper Corporation (2016)], is for pH control in the recovery of copper. The final tails from the recovery process thus ends up with a substantial amount of lime that can neutralize pyrite that was not recovered.

**Tailings and waste rock storage.** The final tails are stored in tailings storage facilities (tailings dams and ponds). Waste rocks, usually moved in surface mines, are stored in waste dumps where the pyrites become subjected to the elements and will generate acids; even if the pyrites in the waste rocks are larger because they have undergone just blasting (compared to that in the ore, which has been further reduced during beneficiation), the high pyrite content in the waste dumps becomes a significant source of mine acidic waters.

**Final mine effluent.** The final mine effluent waters will be a mixture of water from the mine and that from the mill (beneficiation plant); these usually converge at the tailings storage facility, or are led to a storage area for treatment, usually by the addition of lime, if necessary.

In most of the mines studied, the amount of process lime in the tails provided very strong neutralization capacity; this will be discussed in the section Results and Discussion below.

Mine effluent waters are discharged within a standard pH range (6.5 to 8.5); most mine effluent are discharged at around pH 8.0. This leaves some allowance for neutralization in case acid rock drainage (ARD) occurs downstream of the final mine effluent discharge point.

**2. Methodology and Materials.** Copper ore, pyrite and copper concentrates, and tailings were obtained from an operating mine; two other operating mines were visited for field data, and so were six defunct mines (for field data, that is). The methodology adopted was to gather data from characterization by micromineralogy, accelerated weathering laboratory leaching runs, and field data; the interpretation of results will be integrating the three data sources to be able to make general and specific observations.

**Copper porphyry mines studied.** The mines studied include most of the major copper mining projects in the Philippines. These include Carmen Copper in Cebu, Philex Padcal in Benguet, OceanaGold Didipio in Nueva Vizcaya, Benguet Corporation-Dizon Copper Silver Mine in Zambales, Maricalum in Negros Occidental, Marcopper & Mogpog in Marinduque, and Sto Niño & Boneng in Benguet.

**Characterization by micromineralogy.** Materials (fine crushed ore, pyrite and copper concentrates, and tailings) obtained for micromineralogy [Hoal *et al.* (2009)] were obtained from Carmen Copper and sent to the QEMSCAN Facility of the Colorado school of Mines in Golden CO;

the pyrite concentrate and tailings were subjected to accelerated weathering leaching runs (Please see below) which were done at the Department of Mining, Metallurgical and Materials Engineering at the College of Engineering, University of the Philippines (UP-COE-DMMME) in Diliman, Quezon City.

**Accelerated weathering laboratory leaching.** Leaching experiments [Benzazoua *et al.* (2001), Mendez-Ortiz *et al.* (2007)] have been done in the laboratory to simulate what is happening in the field; time can be interpreted as being in a logarithmic scale (accelerated weathering).

This study involved leaching pyrite concentrate and tailings with 500 grams of solid and one liter of water, with air and water bubbled through the mixture in a 2-liter glass cylinder, using aquarium water pumps. A synthetic mix of 50:50 pyrite concentrate and tailings provided interesting results.

In all, there were six (6) runs which took around one-and-a-half years to finish. Preliminary runs were made to optimize bubbler design. pH and conductivity measurements were taken after 30 minute runs; ferrous and total iron measurements were done for every 0.1 unit drop of pH; water samples and precipitates were likewise gathered for ICP-MS testing at the mineralogy and environmental laboratories of the University of the Philippines' National Institute of Geological Sciences (UP-NIGS); precipitates were obtained from the final leachate of the leaching runs by drying of in the sun. Table 1 below outlines the leaching runs and parameters used.

**Table 1.** Summary of leaching runs

Run #	Name of Run	# of Jars	# of Bubblers per Jar	Wt of Solids (gms)	Liters Water	Days of Run	Total Leaching Hours	End-pH
I	Tailings 1	3	1	500	1	10	120	7.1
II	PyrCon 1	1	1	500	1	38	250	2.0
III	PyrCon 2	3	5	500	1	117	427	2.5
IV	PyrCon 3	1	5	500	1	60	180	2.5
V	50:50	2	5	265±275	1	36	180	7.0
VI	Tailings 2	2	5	500	1	36	180	7.5

DESCRIPTION:			
RUNS	#	Materials Used	Duration of Leaching
Initial Runs	I	Tailings	22 February to 4 March 2014
	II	Clean pyrite concentrate	22 February to 28 March 2014
Final Runs	III	Pyrite conc with Cu interference	3 February to 1 June 2015
	IV	Clean pyrite concentrate	7 April to 1 June 2015
	V	50:50 mix of clean pyrite concentrate and tailings	2 Jun to 8 July 2015
	VI	Tailings	2 Jun to 8 July 2015

**Field data gathering.** Mine visits were made to measure specific parameters like pH, conductivity, ferrous and total iron.

Water samples were obtained and preserved for the laboratory for ICP-MS testing; precipitates were also gathered for XRD and XRF analysis (these were also tested at the UP-NIGS). Samples included ore, waste rocks, pyrite and copper concentrates and tailings obtained from operating mines; for defunct mines, water samples were from pit lakes and surface runoff.

Geologic and other reports were obtained from the companies for more detailed information [Baluda RP and Galapon (2005), Carmen Copper Corporation (2016), Consolidated Mine, Inc. (2016), Environmental Geochemistry International Pty Ltd (2006), OceanaGold Philippines, Inc. (2016)].

### 3. Results and Discussion

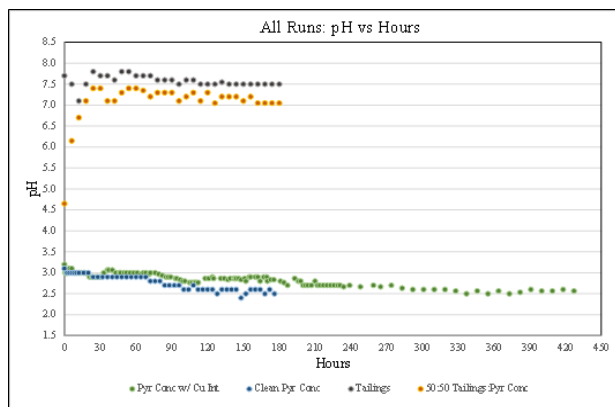
**Characterization by micromineralogy.** Results from micromineralogy include SEM and false-color imagery, mineralogical composition, grain size distribution, interlocking and liberation, associated gold and silver [Pfaff (2013)].

**Initial accelerated weathering / laboratory leaching runs.** The initial runs were made with single bubblers and stirring done manually every 4 hours; the clean pyrite concentrate reached pH 2.0 in 38 days over 250 hours of leaching time; the tailings remained at pH 7.1 in 10 days over 120 hours of leaching time.

**Final runs.** The four final runs were done with 5 bubblers and manual stirring every 30 minutes. pH vs leaching time are presented in Figure 1. The pyrites concentrate were leached to reach a pH value of 2.5; that of tailings around 7.5 and the 50:50 mix of pyrite concentrate and tailings around 7.0. The clean pyrite concentrate, which contained around 2% pyrite, reached pH 2.5 in 60 days over 180 hours of leaching time; that of the copper-contaminated pyrite concentrate took 117 days over 427 leaching hours.

For the tailings, pH never went below 7.5; this was due to the presence of process lime.

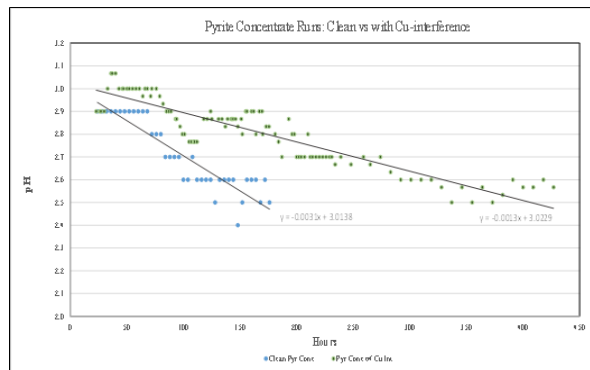
For the 50:50 pyrite concentrate to tailings mix, the pH never went below 7.0. The total pyrite content of the 50:50 mix was at 41%; this means that even if the pyrite content of tailings went up to 41%, there still enough neutralization power of the contained process lime to neutralize it to a circumneutral pH level.



**Figure 1.** Leaching runs: pH vs time

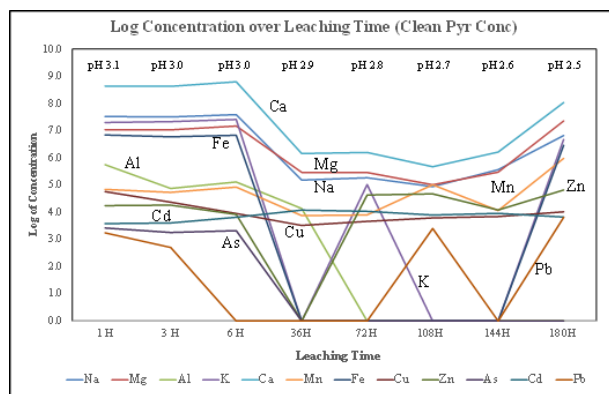
**Pyrite degradation rates.** The leaching rates show a straight-line log-log relationship of pH vs time, as shown in Figure 2.

Figure 2 shows that the degradation rate of a pyrite concentrate with copper interference is around 2.4 times slower than that of clean pyrite concentrate; this shows that copper ions, among others, buffered the leaching process.



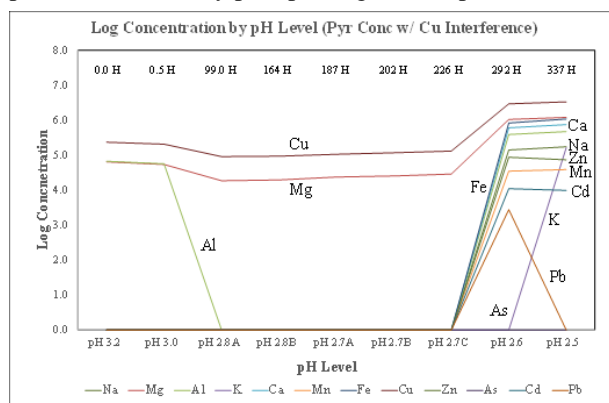
**Figure 2.** Degradation rates: clean pyrite vs Cu-interfered pyrite concentrate.

**Precipitation and re-dissolution of precipitates during leaching.** At various pH levels, dissolved ions precipitate or dissolve; this was observed in the clean pyrite precipitate leaching (Figure 3). It can be seen that metallic elements went in and out of solution at various pH levels.



**Figure 3.** Precipitation and dissolution at various pH levels, clean pyrite concentrate

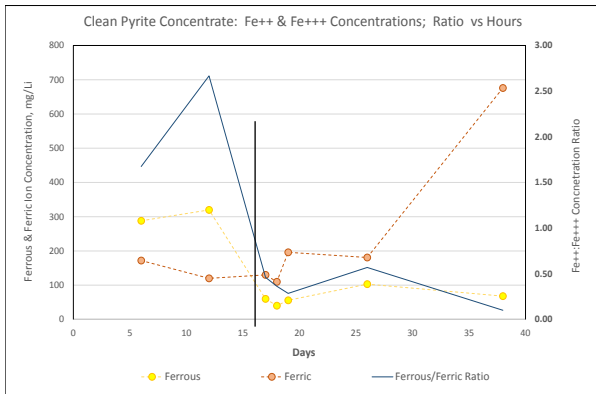
In the pyrite precipitate with Cu interference (Figure 4), it can be noted that most of the metallic elements dissolved only upon reaching a pH of 2.6; lead (Pb) exhibited a peculiar behavior by precipitating back at pH 2.5.



**Figure 4.** Precipitation and dissolution at various pH levels, pyrite concentrate with copper interference

**Ferrous and total iron.** The ratio of ferrous and ferric ions give an indication how far the acidification process has proceeded; at the start of leaching, most iron is in the ferrous state, as it proceeds, more and more ferric ions are produced. The ferric ions attack more pyrite and more acid is formed. At some point, around a ratio of 1.0, precipitation of iron starts (Figure 5); this comes in the

form of yellow precipitates that form at the walls of the bubbling jar. The precipitates are continuously formed and re-dissolved during the leaching run; they become stable once the bubbling stops.



**Figure 5.** Ferrous and ferric ions; ratios

**Precipitates from leaching runs.** Upon reaching the end of the leaching run, specifically those of the concentrates, the leachate was decanted off the bubbling apparatus and sealed in a plastic jar. From an original 2.4 liters of leachate, an iron-rich precipitate immediately formed; this was observed for the next 2 days, after which the precipitate was harvested for XRD and XRF tests. The leachate volume was reduced to 1.6 liters and the precipitate similarly collected for testing; this was also done for volumes of 0.8, 0.4 and 0.0 (fully dried off). Figure 6 shows the series of precipitates (lower row); note the series of colors from red to orange, yellow, white and finally, bluish. The last is a copper-rich precipitate.



**Figure 6.** Precipitates. From the leachate after accelerated weathering laboratory runs (lower row); precipitates from an operating mine (upper row)

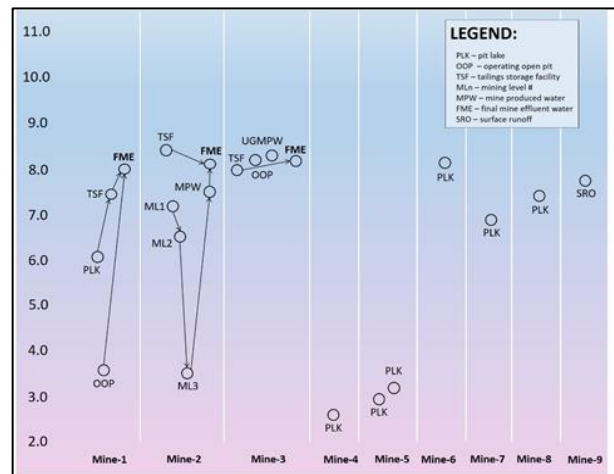
**Precipitates from the field.** Precipitates were also gathered from the field and tested using XRF. The upper two vials at the top in Figure 6 came from neighboring draw points of an underground mine; the one on the left from an active draw point and the other from a closed draw point.

**Field data.** A summary of the field data are presented in Table 2.

**Table 2.** Summary of field data

MINE #	PIT LAKE / OPEN PIT / TAILINGS POND / UG MINE	pH	Conductivity	Ferrous Conc'n	Fe <sub>total</sub> Conc'n	Ferric Conc'n	Fe <sup>++</sup> /Fe <sup>+++</sup>
Mine-3	Pit Lake	2.6	1,805	16.50	32.30	15.80	1.04
Mine-4	Pit Lake 1	2.9	1,618	3.20	3.80	0.60	5.33
Mine-1	Open Pit	3.1	5,100	0.80	5.10	4.30	0.19
Mine-4	Pit Lake 2	3.2	1,978	1.20	2.60	1.40	0.86
Mine-2	Underground Mine	3.3	8,546	560.00	688.00	128.00	4.38
Mine-1	Pit Lake	6.1	5,980	0.13	0.20	0.07	1.86
Mine-6	Pit Lake	6.9	705	0.09	0.20	0.11	0.82
Mine-2	Underground Mine	7.2	5,865	0.40	7.20	6.80	0.06
Mine-7	Pit Lake	7.4	514	0.04	0.09	0.05	0.80
Mine-1	Tailings Pond	7.4	3,815	0.62	-	-	-
Mine-8	Open Pit (runoff water)	7.7	1,067	0.15	-	-	-
Mine-5	Pit Lake	8.1	1,308	0.00	-	-	-

pH plots, showing values measured at various parts of the process flows, give a quick view of the levels of acidity in various part of the mine, mill, tailings dam, and the final mine effluent, are presented in Figure 7.



**Figure 7.** pH plots of all the mines

Note that there are two mines that are relatively acidic; the reason for acidic mines can be that there are still pyrite-rich materials (ore and waste), or there are no alkaline rocks in the vicinity of the mine [Reyes *et al.* (1985)].

Most mines visited, especially operating ones, have final mine effluents with pH values between 7.0 and 8.0; several pit lakes exhibited alkaline mine waters. Mines having alkaline waters either have alkaline rocks in the surroundings [Apostol (1974), Baluda and Galapon (2005)], or, have high calcite content in the ore [Environmental Geochemistry International Pty Ltd (2006)], or are in skarn-like environments [Consolidated Mine, Inc. (2016), Environmental Geochemistry International Pty Ltd.(2006)].

Thus, acidic mine waters exist in the mine and the extent to which it occurs depends on the presence of alkaline minerals and rocks. In fact in one underground mine studied, the mine waters at the lowest parts of the mine went from a pH of 7.2 to 3.2 from the upper levels to the lowest; as the water drained out of the underground openings, the acidic waters combined with alkaline waters that percolated from the edges of the mine area; from the blocks, the pH went up to 7.5 along the 3-km drain tunnel before the portal. Inflow waters along the drain tunnel having a pH around 8.0 have increased the pH; upon exiting the portal, the pH is reduced to 7.4 because of carbon dioxide from the atmosphere.

**4. Conclusions.** This study has led to the following conclusions:

Acid mine drainage occurs in all copper porphyry deposits but to a somewhat limited extent; acidification occurs where there is fragmentation of the pyrite during mining.

Process lime added during the recovery of copper provides a strong capacity in the neutralization of acidity formed due to the degradation of pyrite in the ore or waste rock.

The presence of limestones in the surrounding waste and country rocks provide further neutralization capacity; percolating waters neutralize acidic water when

comingling with underground or surface waters that have passed through the orebody being mined.

Precipitates contain metals that come from dissolved minerals; thus, leached metals are recaptured by the precipitates, this is accompanied by an increase in pH, as some of the acidity is also consumed during the precipitation process.

### Acknowledgements

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