

## Article

# Industrial Heap Bioleaching of Copper Sulfide Ore Started with Only Water Irrigation

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**Abstract:** Sulfuric acid solution containing ferric iron is the extractant for industrial heap bioleaching of copper sulfides. To start a heap bioleaching plant, sulfuric acid is usually added to the irrigation solution to maintain adequate acidity (pH 1.0–2.0) for copper dissolution. An industrial practice of heap bioleaching of secondary copper sulfide ore that began with only water irrigation without the addition of sulfuric acid was successfully implemented and introduced in this manuscript. The mineral composition and their behavior related to the production and consumption of sulfuric acid during the bioleaching in heaps was analyzed. This indicated the possibility of self-generating of sulfuric acid in heaps without exogenous addition. After proving by batches of laboratory tests, industrial measures were implemented to promote the sulfide mineral oxidation in heaps throughout the acidifying stages, from a pH of 7.0 to 1.0, thus sulfuric acid and iron was produced especially by pyrite oxidation. After acidifying of the heaps, adapted microbial consortium was inoculated and established in a leaching system. The launch of the bioleaching heap and finally the production expansion were realized without the addition of sulfuric acid, showing great efficiency under low operation costs.

**Keywords:** copper sulfide ore; heap bioleaching; pyrite; sulfuric acid; water irrigation



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## 1. Introduction

During the past few decades, heap bioleaching has been well employed commercially around the world, especially for copper sulfide ore, which accounts for over 20% of the world copper production [1]. For heap bioleaching, a solution containing sulfuric acid, ferric iron, and acidophilic iron- and sulfur- oxidizing microbes is used as the irrigation solution to heaps [2,3]. Copper sulfide minerals are oxidized by oxidant  $Fe^{3+}$ , thus  $Cu^{2+}$  is released into the solution, and then is usually extracted and purified by solvent extraction and the electro winning process. Those acidophilic microbes promote mineral dissolution by regenerating oxidant  $Fe^{3+}$  and oxidizing the intermediate sulfur compounds [1,4].

Unlike the tank leach, heap leaching usually processes the ore in huge amounts at the same time, so a huge amount of sulfuric acid solution is needed for the wetting and irrigation of the ore to initiate an industrial heap. Besides, it is likely that there were more gauge minerals that consume acid in the beginning of heap leaching [5]. The heap bioleaching process requires significant sulfuric acid addition to maintain a suitable acidity during agglomeration and during the leaching [6]. Acid consumption is a major economic driver of the heap leaching process and needs to be determined beforehand [7]. Preparing the heap irrigation solution by adding sulfuric acid and ferric sulfate is costly [8], therefore their minimization, especially in the beginning of heap irrigation, is important to run a heap leaching plant. Luckily, metal sulfides such as pyrite, are a source of sulfuric acid and

ferric ion, commonly found in copper sulfide deposits [9,10]. Pyrite oxidation provides acid and iron for the heap leaching. The Cu solvent extraction process also generates acid; these two processes are the important acid source for the heap bioleaching of copper sulfides [11]. Actually, acid consumption by gangue minerals exceeds the acid generating processes for most copper heap bioleaching plants. Only few heap bioleaching plants, such as Zijinshan copper mine accumulated enough acid and iron in cycling solution during leaching under the excessive pyrite oxidation [9,12]. So for most heap bioleaching plants, accelerating of the pyrite oxidation can reduce the cost of sulfuric acid addition to the heap irrigation solution.

The Monywa copper mine is located in Myanmar (22°07' N, 95°02' E) and is one of the largest secondary copper-sulfide mines in Asia [13,14]. The newly operated Letpadaung ore body has an ore reserve of over 1.5 billion tonnes, with an average copper grade of about 0.34%, and a geological reserve of metal copper of over 5 million tonnes. The new heap bioleaching plant was designed, and building began in 2013. By the end of 2015, it was ready to start, aiming at a capacity of processing 30 million tonnes of ore per year (100,000 tonnes of copper cathode per year). It was estimated that 30 million tonnes of ore will consume 225 thousand tonnes of sulfuric acid per year (the tested acid consumption at about 7.5 kg/t ore). To begin the process of heap bioleaching, a huge amount of sulfuric acid was needed. However, sulfuric acid is expensive at a price of about 500\$/t in Myanmar, and the storage facility is also costly and troublesome. Whether to buy huge amounts of sulfuric acid and to build sulfuric acid storage facilities in order to start and run the heap bioleaching was a tough decision for the company to make. This project was therefore based on the company's actual demand, to assess the need for sulfuric acid, especially at the beginning of the process of heap bioleaching. Mineralogy and acid generation potential were analyzed and batches of laboratory tests were carried out, proving the possibility of heap bioleaching without sulfuric acid addition. Several combined operations for pyrite oxidation accelerating were applied to the industrial heaps to start the heap bioleaching, and finally to expand the production to a capacity of 30 million tonnes of ore per year, starting with only water irrigation.

## 2. Mineralogy and Methods

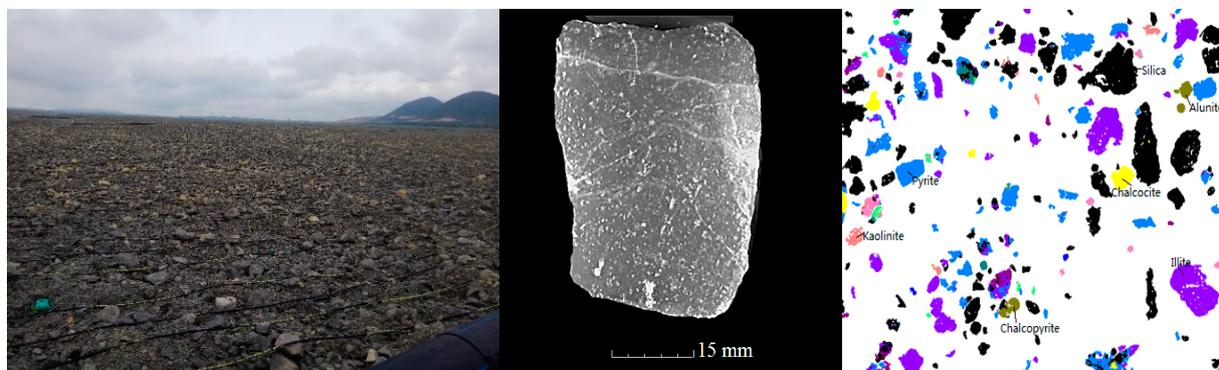
### 2.1. Mineralogy of Letpadaung Ore

The main Cu mineral in Letpadaung ore was chalcocite, and the ore also contained a small amount of chalcopyrite. It was high in pyrite content (12.13%), while low in alkali gangue mineral content (<1.0%), and the other main minerals were silica, sericite-illite-montmorillonite, and alunite (Table 1). Cu content in the ore was 0.45% of the tested ore. Iron was mainly in the form of pyrite.

**Table 1.** Mineral composition of Letpadaung ore by Mineral Liberation Analyzer (MLA).

Minerals	Formula	Percentage (%)
Chalcocite	CuS <sub>2</sub>	0.52
Chalcopyrite	CuFeS <sub>2</sub>	0.10
Pyrite	FeS <sub>2</sub>	12.13
Silica	SiO <sub>2</sub>	56.46
Alunite	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	12.93
Sericite-Illite-Montmorillonite	K <sub>2</sub> (AlFeMg) <sub>4</sub> (SiAl) <sub>8</sub> O <sub>20</sub> (OH) <sub>4</sub> ·nH <sub>2</sub> O, Al <sub>4</sub> Si <sub>8</sub> O <sub>20</sub> (OH) <sub>4</sub> ·nH <sub>2</sub> O, Al <sub>4</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>	8.32
Alkali gangue	CaMg(CO <sub>3</sub> ) <sub>2</sub> , CaCO <sub>3</sub>	<1.0
Chemical assay: Cu 0.45%, TFe 6.59% (Fe(III) 0.82%, Fe(II) 5.77%), TS 8.63%		

Ore stacking on heaps was in the size of run-of-mine (ROM), with the average size of about  $P_{80} = 200\text{mm}$  (Figure 1). The 3D-CT test (Three Dimension Computed Tomography, nano-Voxel 2000, Tianjin Sanying, China) of the ore showing the sulfide minerals mainly in the vein of the ore.



**Figure 1.** Ore morphology in heaps (left), sulfide minerals dissemination characteristics by 3D-CT tests (middle), and mineral composition by MLA tests (right).

## 2.2. Heap Sample Collection and Test

During the heap bioleaching industrial operation, irrigation solution and leachate were collected from each leaching cell every day. The redox potential of the solution was measured using Ag/AgCl reference electrode, and the pH was determined using a pH meter (SenvenGo Pro, Mettler Toledo, Switzerland). Total iron and copper concentrations in the solution were analyzed using an atomic absorption spectrophotometer (AAS) (Analytik Jena, Germany). Ferrous iron was immediately measured after sampling by titration using potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ). Copper recovery of each cell was calculated based on daily Cu accumulation from the leachate compared to the irrigation solution.

The microbial cell count was carried out immediately after leachate sampling every week in a haemocytometer ( $0.1\text{ mm}$ ,  $1/400\text{ mm}^2$ ), using a microscope (CX31, Olympus, Japan, with phase contrast condenser) equipped with a Charge Coupled Device (NC7030, Oplenic, China).  $100\times$  plan archromat objective was used to check the cell number. Each sample was counted in three haemocytometers, and each haemocytometer was counted for three times.

The leachate samples were filtered through a Millipore filter ( $0.22\text{ }\mu\text{m}$ ; diameter of  $10\text{ mm}$ ), then microbes on the filter papers were transferred into centrifuge tubes, and centrifuged at  $14,000\times g$  for  $10\text{ min}$  to collect the cells. The community DNA was extracted using FastDNA Spin kit (Bio 101, Carlsbad, CA, USA) according to the manufacturer's protocol. Primers of F515 ( $5'\text{-GTGCCAGCMGCCGCGGTAA-3}'$ ) and R806 ( $5'\text{-GGACTACVSGGGTATCTAAT-3}'$ ) were used to amplify the bacterial and archaeal 16S rRNA genes V4 hyper variable region [15]. The R806 primer contained an 8 bp barcode sequence. PCR amplification ( $25\text{ }\mu\text{L}$ ) was conducted in triplicate under the following conditions: initial denaturation at  $94\text{ }^\circ\text{C}$  for  $5\text{ min}$ , 30 cycles of denaturation at  $94\text{ }^\circ\text{C}$  for  $30\text{ s}$ , annealing at  $55\text{ }^\circ\text{C}$  for  $1\text{ min}$ , and extension at  $72\text{ }^\circ\text{C}$  for  $3\text{ min}$ , with a final extension at  $72\text{ }^\circ\text{C}$  for  $10\text{ min}$ . The purified PCR products were mixed in equal concentrations, and sequenced using Miseq (Illumina, San Diego, CA, USA) following the manufacturer's instructions. Sequencing analysis follows the procedure of Jia et al., 2016 [5].

## 3. Laboratory Testing and Industrial Steps of Water Start Heap Bioleaching

### 3.1. Sulfuric Acid Generating Potential Based on Minerology

It was shown that pyrite oxidation was the main acid generation process during Letpadaung ore heap bioleaching (Table 2). If pyrite is entirely oxidized, it would produce more than  $100\text{ kg}$  sulfuric acid per ton ore. Chalcocite (main copper mineral) dissolution

is acid consumption, but the Cu solvent extraction process is acid generation; together they produce sulfuric acid at 0.77 t/t Cu. However, this process accounted for only a small portion, because Cu content was only 0.45% (80% copper recovery will produce sulfuric acid at 2.77 t/t ore). It is shown that the acid generation potential was much higher compared with the acid consumption by the alkali gangue, so the calculation suggested an ore type of net acid generation.

**Table 2.** Main processes on acid generation and consumption during heap bioleaching of Letpadaung ore.

	Processes	Value
Acid generation	Pyrite oxidation-Jarosite formation: $4\text{FeS}_2 + 15\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SO}_4$ $3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 7\text{H}_2\text{O} \rightarrow (\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6\downarrow + 5\text{H}^+$	1.09 kg/kg FeS <sub>2</sub>
	Cu solvent extraction: $\text{CuSO}_4 + 2\text{HR} \rightarrow \text{CuR}_2 + \text{H}_2\text{SO}_4$	1.54 kg/kg cathode copper
	Gangue mineral acid consumption	7.5 kg/t ore
Acid consumption	Chalcocite oxidation: $\text{Cu}_2\text{S} + 2\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 2\text{Fe}^{2+} + \text{CuS}$ $\text{CuS} + 2\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 2\text{Fe}^{2+} + \text{S}^0$ $\text{Cu}_2\text{S} + 5\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{CuSO}_4 + \text{H}_2\text{O}$	0.77 kg/kg cathode copper

The acid consumption of the ore is measured by titration of ore powder with 100 g/L sulfuric acid, and the amount of acid consumption was calculated based on the added acid volume and acid concentration decrease.

Although the calculation suggested the net acid accumulation with the oxidation of sulfide minerals, whether it is possible to start heap bioleaching without sulfuric acid addition remains to be elucidated. The acid consumption and generation mismatch during heap bioleaching. Acid consumption exists mainly in the beginning of the leaching, while pyrite oxidation is not fast enough in the beginning stage, and the dissolution rate is not high enough. It was reported that pyrite oxidation rate was only around 10.5%–15.0% during the bioleaching of copper ore from Monywa mine [11]. Under this pyrite oxidation rate, although the sulfuric acid generation (pyrite oxidation + Cu solvent extraction) was higher than the acid consumption of gangue mineral, the acid accumulation in leaching solution will still take quite a long time.

### 3.2. Laboratory Column Tests Summary

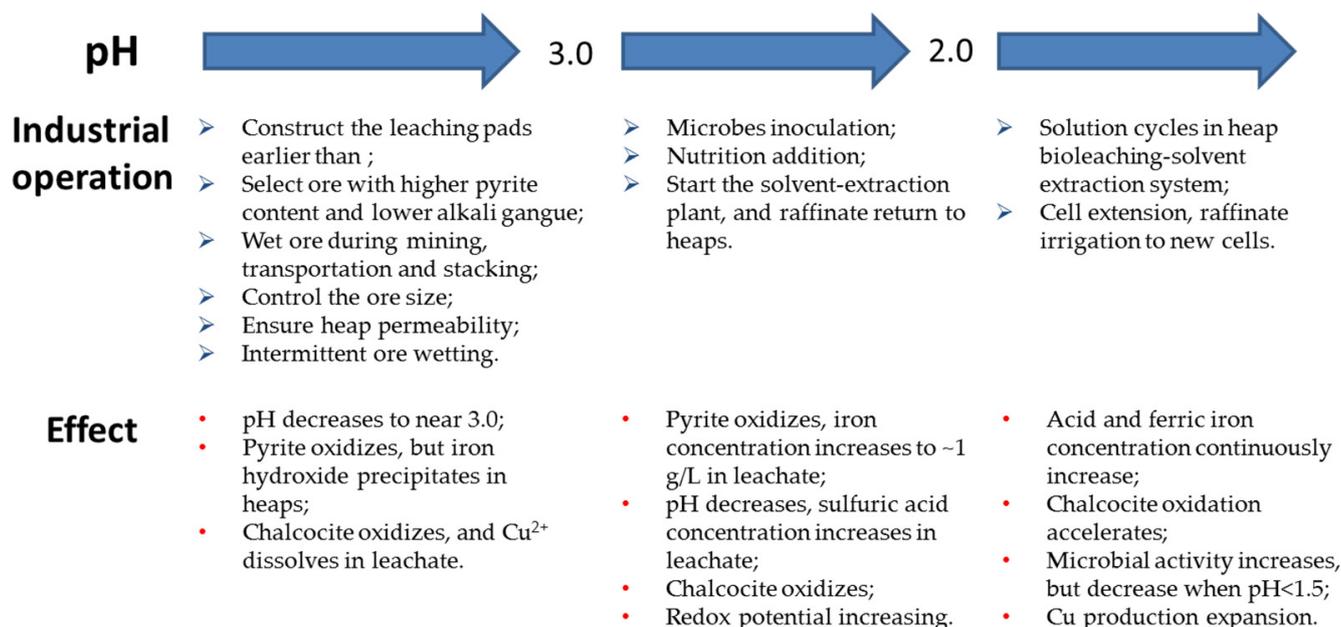
In order to obtain more convincing evidence regarding industrial application, especially in considering sulfuric acid balance, batches of laboratory column tests (in related to ore types, ore size, operation parameters, irrigation solution type, and microbial activity tests) were carried out, simulating the heap bioleaching-solvent extraction process. These tests proved that it was possible to achieve the goal of starting the heap bioleaching only by water irrigation, but some critical points should still be followed to accelerate the process: (1) select the ore with higher pyrite content and lower alkali gangue mineral; (2) wet the ore earlier to guarantee more time for sulfide mineral oxidation; (3) inoculating the iron and sulfur oxidizing bacteria will greatly promote the pyrite oxidation and copper leaching; (4) adapt the microbes in a low nutrient and high pH environment to accustom them to the environment of the heap; (5) control the ore size to ensure the exposure of sulfide minerals, but also ensure the permeability of the ore; (6) use intermittent irrigation to promote the pyrite.

### 3.3. Steps for Water Start Heap Bioleaching

In order to start the oxidation of sulfide minerals earlier, the construction of leaching pads was given priority over the solvent extraction and electro-winning plant. Mining and ore stacking began in September 2015. Run-of-mine (ROM) at a size of about P<sub>80</sub> = 200 mm was trucked and piled up on leaching pads. By the end of 2015, six cells were constructed. These six cells were the water irrigated cells, of which, P3C6 was the first. By the end of

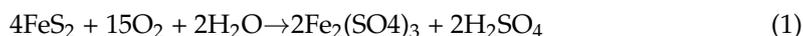
2016, about 30 cells had been stacked, while irrigation solutions for the remaining cells continued to emerge from the first six cells. Each cell (area of 700 m × 80 m) contained an estimated 500,000 tons of ore.

According to the key message obtained from the laboratory tests, promoting pyrite oxidation was important initiating heap bioleaching. Briefly, the industrial process can be divided into three stages associated with the oxidation of pyrite at different pH levels (Figure 2).



**Figure 2.** Scheme of the heap bioleaching started with only water irrigation.

(1) pH > 3.0: Ore was wetted using river water at the ratio of about 4% during mining, truck transportation and stacking, for dust suppression and most important for starting the sulfide mineral oxidation. The cells were designed by the multi-lifts, and heap height were 6 m of each lift. No agglomeration and aeration were applied during heap bioleaching. Irrigation pipelines were installed immediately and irrigated on time with water to keep the ore wet. Under the neutral or slightly acidified condition, pyrite can reacts following reaction under the effect of oxygen (Equation (1)) [16]:

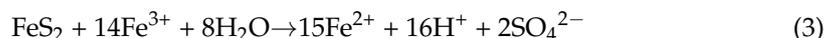
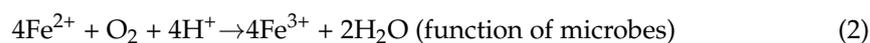


At this stage, the ore was acidified from neutral (pH 7.0) to about pH 3.0. Barely any ferric iron was detected in the leachate solution, but quite obvious yellow iron precipitates were seen in heaps, suggesting the pyrite oxidation and then hydrolysis in heaps. However, the limited active ferric iron continued to act as the oxidant to the pyrite, at least not any lower than the oxygen [17]. The hydrolysis pH for Cu<sup>2+</sup> (about 4.7) was much higher than Fe<sup>3+</sup> (about 3.0), after copper sulfide oxidizing, Cu<sup>2+</sup> was dissolved in the solution at a pH lower than 4.7. After the construction of the solvent extraction plant, the leachate was sent to the solvent extraction-electro winning plant, and finally the cathode copper was produced. Lix 984H at a concentration of 15% (v/v) was used for solvent extraction. During the solvent extraction, every 1 mol Cu extraction returned 1 mol H<sub>2</sub>SO<sub>4</sub> to the raffinate solution. Then, the raffinate returned to heaps, accelerating the leaching process.

(2) pH 2–3: If the pH value of leachate was above 3.0, the heap was irrigated cyclically until the pH value of leachate dropped down below 3.0. Additionally, the acidophilic iron and sulfur oxidation microbes were inoculated to the leachate together with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> nutrient (the ore chemical analyses showed the nitrogen was the most lacking element

for microbes in the ore). The resulting leachate was irrigated cyclically as the irrigation solution to slowly increase the concentration of sulfuric acid and ferric sulfate and initiate copper sulfide heap bioleaching.

The source of the inoculated microbial community was selectively enriched from the local acid mine drainage and a nearby heap bioleaching plant containing the acidophilic iron and sulfur oxidation microbes. The iron and sulfur oxidation microbes included mainly *Acidithiobacillus*, *Leptospirillum* and *Ferroplasma*. The community were enrichment cultured under low nutrient (about 1/5 9K) with concentrations as below:  $(\text{NH}_4)_2\text{SO}_4$  of 0.5 g/L,  $\text{K}_2\text{HPO}_4$  of 0.1 g/L, KCl of 0.01 g/L,  $\text{MgSO}_4$  of 0.1 g/L,  $\text{Ca}(\text{NO}_3)_2$  of 0.002 g/L, 10 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 2 g/L elemental sulfur, and pH of 2.5. It aimed to adapt the microbes to habituation to the condition of low nutrients and higher pH at the onset of the bioleaching heap. Microbes was firstly cultured in flasks and then in 1 m<sup>3</sup> buckets, eventually to the irrigation ponds. Before the inoculation into the irrigation ponds, microbial community were analyzed by 16S rDNA as [5]. It showed that the group of *At. ferrooxidans* (42.5%), *At. caldus* (8.8%), *L. ferriphilum* (30.6%), *Ferroplasma* (10.5%), and other species.  $\text{Fe}^{2+}$  oxidation to  $\text{Fe}^{3+}$  is the rate limit process for the pyrite oxidation under acidified conditions [16]. If the pH was below 3, dissolved  $\text{Fe}^{3+}$  acted as the main oxidant to chalcocite, and the oxidation rate was much higher than under only oxygen. The chalcocite oxidation then consumed the  $\text{Fe}^{3+}$ , and generated the  $\text{Fe}^{2+}$ , but the oxidation from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  was very slow under acidic conditions, which resulted in the lacking oxidant  $\text{Fe}^{3+}$  for further chalcocite oxidation. Luckily, with the help of acidophilic iron oxidizers, this process accelerated by  $10^5$ – $10^6$  times [18–20] (Equation (2)), which ensured the continuous oxidation of pyrite (Equation (3)).



Still,  $\text{Fe}^{3+}$  and sulfuric acid at the low concentration of 1 g/L were sustained in the solution at this pH range; ferric iron then played a more important role to act as the oxidant for pyrite. This reaction was crucial for pyrite oxidation under an acidic environment, while previous research has suggested that the ferric oxidation rate was exponentially higher than the oxygen [17].

(3) pH < 2: At this stage, the water was continually irrigated to the first six cells, then the raffinate was irrigated preferably to other new cells. Under the activity of acidophilic iron and sulfur oxidation microbes,  $\text{Fe}^{3+}$  was replenished by  $\text{Fe}^{2+}$  oxidation, and the microbes also adhered on the pyrite surface were able to greatly accelerate pyrite oxidation. The first six cells acted as a producer of acid and iron, and all the cells obtained higher and higher concentrations of acid and iron; eventually all the cells started.

The use of raffinate as the irrigation solution increased the acidity in the cycling solution. With the continuous decrease in the pH to lower than 1.5, especially when pH drops down to 1.0, the microbial activity was inhibited, since the inoculated microbes was more adapted to a higher pH condition.

#### 4. Heap Bioleaching Performance

There were six cells that began with only water irrigation, and the first one (P3C6) started at November 2015. In 2016, about 40 other cells were stacked, firstly wet by water and then irrigated with the raffinate from solvent extraction plant after processing the leachate of the first 6 cells. Here, the leach performance of the first irrigated cell (P3C6) was introduced below, including the acidifying process, the copper leaching, and the microbial condition.

##### 4.1. Leachate pH Dropping during the Heap Leaching

During ore mining, transportation, and stacking, ROM ore was wetted by river water. Additionally, after being piled to heaps, river water was used as the irrigation solution to start up the heap leaching. The mining and truck stacking of one leaching cell took about two months. The ore was slightly acidified to about pH of 3.5–4.0 during this period

with the sulfide minerals oxidation by water and air (Figure 3). It was proved that sulfide minerals, including pyrite and the copper sulfides were oxidized under the moisture condition [21,22]. Pyrite oxidation under oxygen was as below (Equation (4)):

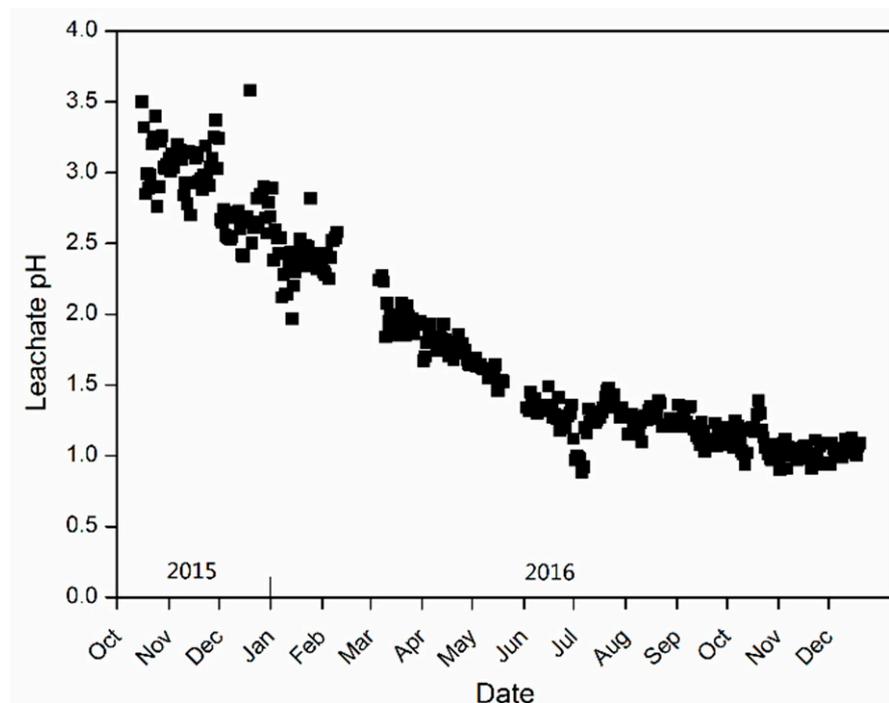


Figure 3. pH of the leachate from cell P3C6 during the heap bioleaching.

Moistening the ore was required to initiate sulfide mineral oxidation. Researchers proved that the oxygen in the sulfate was obtained more from the water [23]; the oxidation of oxygen happened together with the water. Adsorbed molecular oxygen acted as a pyrite oxidant and was incorporated into the produced sulfate in anaerobic and low oxygen experiments with low ferric iron/surface ratios [24].

Additionally, during the heap bioleaching, whether open irrigated with water or cycling irrigate with the leachate, with the continuous oxidation of pyrite, the pH continuously decreased. Especially when the pH dropped down to below 3,  $\text{Fe}^{3+}$  start sustaining in the solution, thus provide the oxidant for sulfide minerals, and later the growth of the acidophiles regenerate the oxidants  $\text{Fe}^{3+}$ , further promote the pyrite oxidizing process, produces sulfuric acid. Finally, the pH decreased to about 1.0 during the one year leaching period. The pyrite oxidation not only neutralized the acid consumption of the gangue minerals, but also greatly accumulated in the heap bioleaching solution, provided sulfuric acid to other cells.

#### 4.2. Microbial Community and Activity

After the pH dropped down to about 3.0 at January 2016, concentrated acidophilic iron and sulfur oxidation microbial community was inoculated to the irrigation solution ponds, added with  $(\text{NH}_4)_2\text{SO}_4$  at the concentration of 0.5 g/L. By analysis of the chemical composition of the ore, other elements that the microbes needed, such as K, Mg, Ca, dissolved from the ore and accumulated in the solution when the ore is acidified.

After inoculation of the microbial consortium to heaps, the cell number increased greatly, and then retained at a relatively stable level (Figure 4). Additionally, the 16S rDNA checking proved the growth of the functional microbes, showing a microbial community of dominant by *At. ferrooxidans*, and other species as *At. thiooxidans*, *At. caldus*, *L. ferriphilum*, *L. ferrooxidans*, *S. acidophilus*, *F. acidiphilium*, *Acidiphilium sp* (Table 3). Most of the microbes

were iron oxidizing bacteria, with a small portion of sulfur oxidizing bacteria. *At. ferrooxidans* is usually the dominant species in lots of the heap bioleaching plants, especially when the solution is not the acidified and not accumulate with too much salts [5,25]. *At. ferrooxidans* was high in activity of iron oxidation. Previous studies have shown that the *Leptospirillum* and *Ferroplasma* groups were dominant in extreme environments with low pH and high ionic strength [25–27]. Although the *Ferroplasma* was also inoculated to the heaps, it was not detected in the leachate. While later it may gradually grow with the lower oxygen, low pH and higher organic matter accumulation in heaps [11].

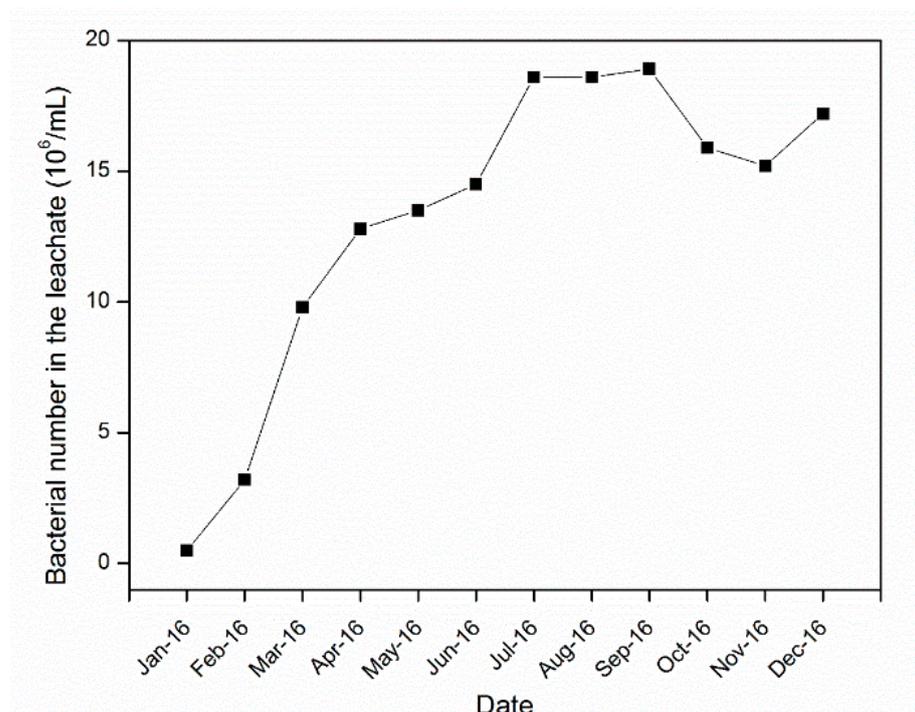


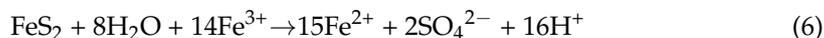
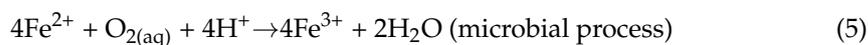
Figure 4. Microbes number in the leachate of cell P3C6.

Table 3. Microbial community in heaps of cell P3C6 in May 2016.

Genus	Species	Percentage (%)
<i>Acidithiobacillus</i>	<i>At.ferrooxidans</i>	57.1
	<i>At. thiooxidans</i>	4.2
	<i>At. caldus</i>	8.2
<i>Leptospirillum</i>	<i>L. ferriphilum</i>	10.5
	<i>L. ferrooxidans</i>	3.6
<i>Sulfobacillus</i>	<i>S. acidophilus</i>	1.2
<i>Ferroplasma</i>	<i>F.acidiphilium</i>	5.2
<i>Acidiphilium</i>	<i>Acidiphiliumsp.</i>	8.3
Other		1.7

The process of pyrite bioleaching involves two rate-controlling sub-processes: chemical leaching of pyrite by ferric ion and bacterial oxidation of ferrous ion to regenerate ferric ion (Equations (5) and (6)) [28]. After the reaction with pyrite,  $Fe^{3+}$  was reduced to  $Fe^{2+}$ , but the  $Fe^{2+}$  oxidation by  $O_2$  is very slow. The rate of pyrite dissolution decreases with increased sulfate concentration and ferrous concentration, as verified by an electrochemical

method [29,30]. Luckily, these inoculated iron oxidizing acidophiles, dominated by *At. thiooxidans*, can oxidize the  $\text{Fe}^{2+}$  quickly.



With the growth of the microbes (Figure 4), the redox potential continuously increased (Figure 5). Among the factors that affect pyrite dissolution, the solution Eh is the most critical and is directly correlated with rate. Below the redox potential of 650 mV (vs. SHE), pyrite is barely oxidized, even though microbes adhere on the pyrite surface [31,32]. It was reported that the pyrite oxidation was 5 times faster with the elevation of redox potential by 100 mV [33]. So the increased redox potential greatly improved the pyrite oxidation.

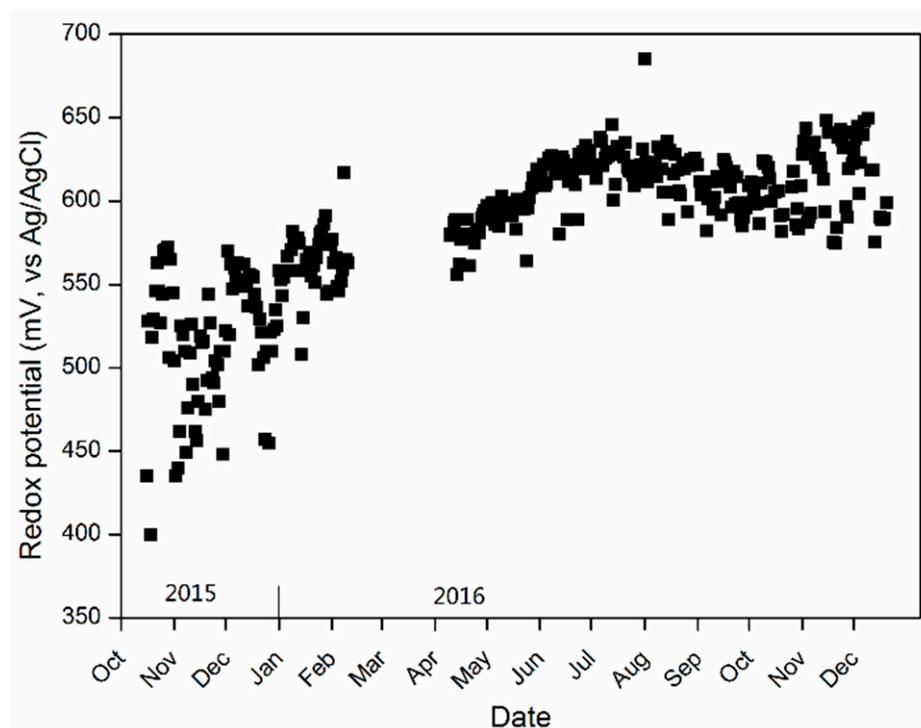
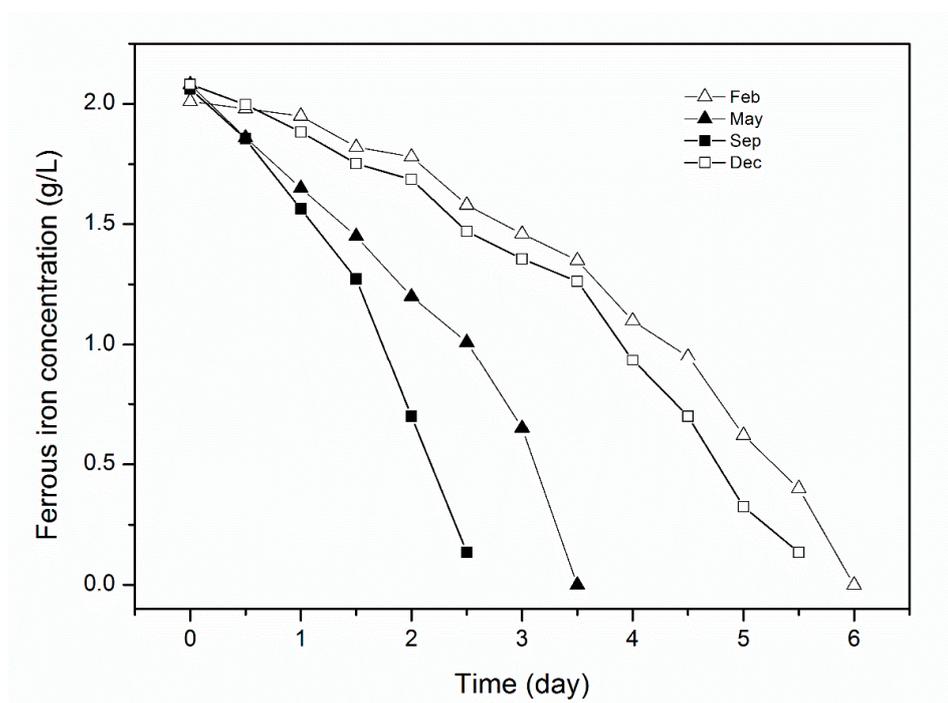


Figure 5. Redox potential of the leachate from cell P3C6.

During heap bioleaching, leachate in February, May, September, and October were collected, respectively. Solutions were added with 2 g/L  $\text{Fe}^{2+}$  and cultured in an oscillator (35°C) in laboratory to test the microbial iron oxidizing activity. The iron oxidizing activity was higher in May and September so that the  $\text{Fe}^{2+}$  were oxidized in about 3.5 and 2.5 days, respectively (Figure 6). While in February, the microbes continued to grow after inoculated to heaps ( $\text{Fe}^{2+}$  were oxidized in about 6 days); and in December ( $\text{Fe}^{2+}$  were oxidized in about 5.5 days); the low pH and accumulated ions (total dissolved solids at 80.2 g/L at December, 2016) in solution may start inhibiting the microbial activities.



**Figure 6.** Ferrous iron oxidation activity of the microbes from the leachate of P3C6 collected at different time during heap bioleaching.

#### 4.3. Sulfuric Acid and Iron Concentration in the Leachate

Sulfuric acid concentration and iron concentration continuously increased during heap bioleaching. However, they increased slowly until April 2016, and then increased quickly. Although pyrite was continuously oxidized, the sulfuric acid consumption of the gangue minerals was usually at the beginning stage of the heap leaching, so only after acid consumption by the gangue minerals would the sulfuric acid gradually accumulate in the solution. Besides, the heap was an inhomogeneous environment; iron was easily precipitated in some region with higher sulfuric acid consumption, even though the leachate pH was already below 2.0. Additionally, the acidified solution from the first six cells were preferentially fed to other new cells, and when in May 2016, about 15 cells were already acidified, the cells for acid generation was sufficient enough, then the acid accumulation grew quicker.

Ferric ion is confirmed to be a more effective oxidant than oxygen at all pH values [34,35], and an increase in pyrite dissolution is achieved with increasing the concentration of ferric ions. By May 2016, a quick increase in the acid and iron concentration were observed to about 9 g/L and 7.5 g/L of sulfuric acid and iron concentration, respectively (Figures 7 and 8). It was usually reported that acid and iron concentration at this level was enough for the chalcocite leaching [36]. At the same time, elevated acidity and iron concentration will later impact microbial activity [12,37]; the inhibition effect on iron oxidizing activity was already shown in December 2016 (Figure 6). The net evaporation capacity in the Monywa region is much higher than rainfall capacity, so all solutions cycled in the heap bioleaching-solvent extraction system without pumping out. The free acid was increased and then reached a stable level at about 12–14 g/L, and total iron concentration at about 35 g/L by the end of 2020 (data not shown) in the whole leaching system. The increasing acid and iron concentration resulted in the decrease in redox potential from 850 mV (vs. SHE) at 2016 to about 700 mV (vs. SHE) at 2019–2020, and a slower down pyrite oxidation and reduced increase in acid and iron concentration in the heap leaching system (data not shown).

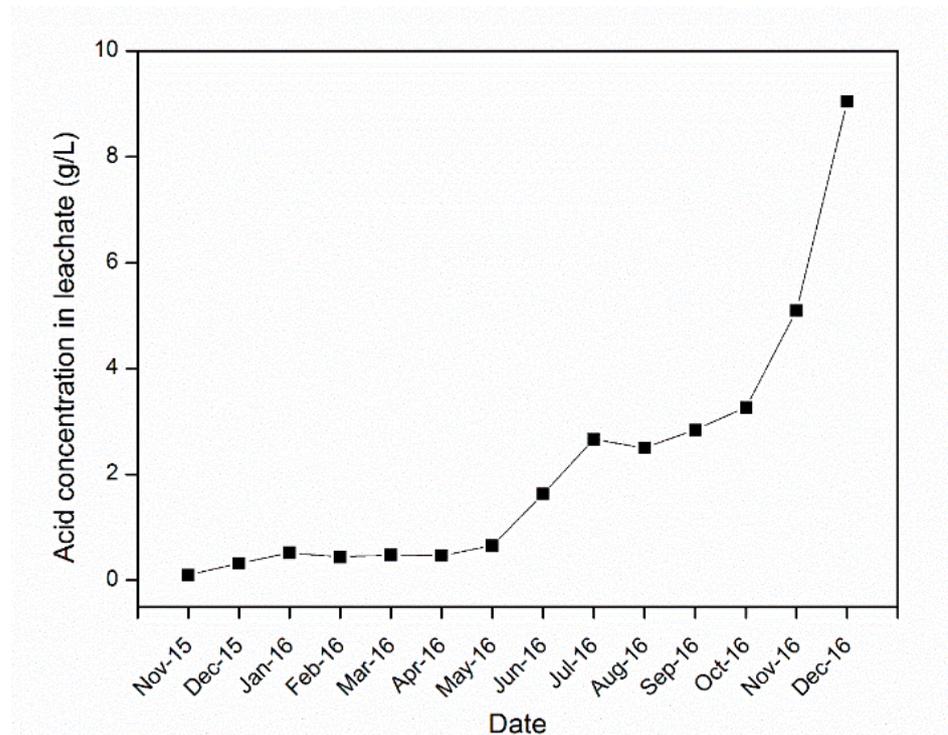


Figure 7. Sulfuric acid concentration of the leachate during the heap bioleaching of P3C6.

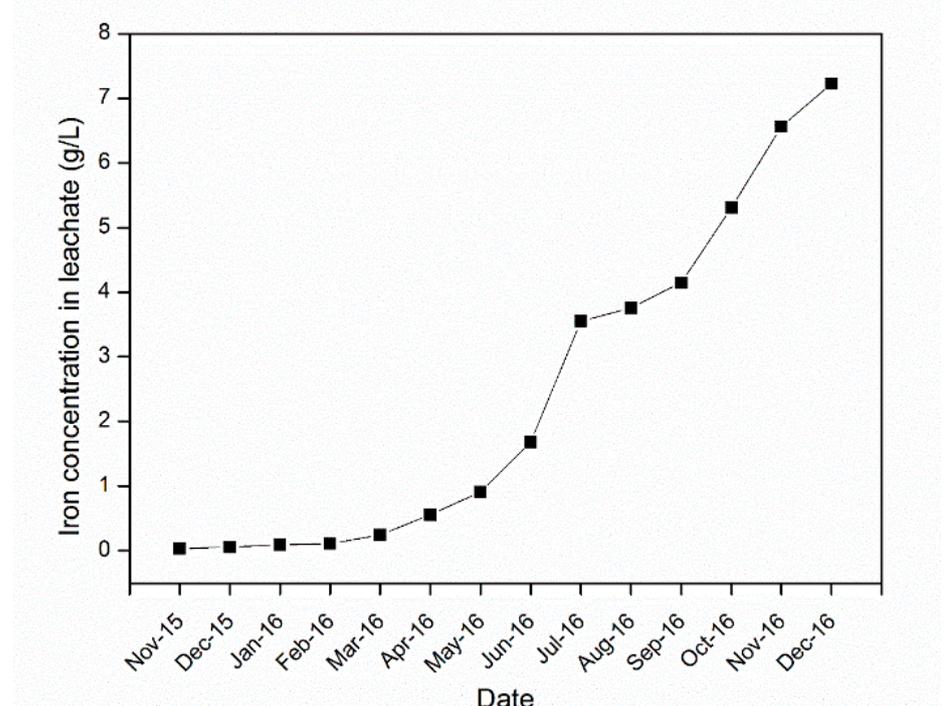
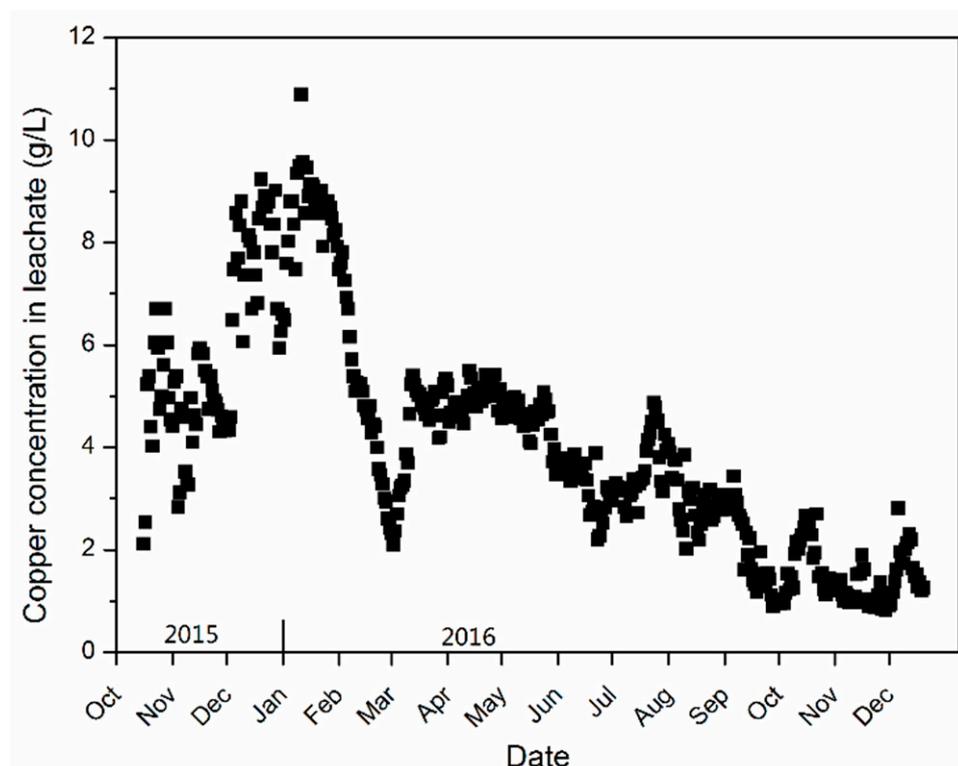


Figure 8. Iron concentration of the leachate during the heap bioleaching of P3C6.

Since the Letpadaung ore leaching was net acid generation at the final stage, if the sulfuric acid was added to the irrigation solution at the beginning, the latter may then need to be neutralized. Starting the heap leaching with water will not only save the cost in acid addition but will also save the cost in future possible acid neutralization with lime. The higher microbial activity (bacteria seeds adapted at the higher pH) in the beginning and lower activity later helped the fast acid and iron generation launch the heap bioleaching, and also prevented too much acid and iron generation in the long run.

#### 4.4. Copper Leaching

Based on the industrial practice of Letpadaung mine, it was easy for the ore to drop to a pH lower than 4 after the ore mining, transportation and stacking on heaps (about 2 month). Then, under water irrigation, Cu directly leached out from the acidified heaps. The hydrolysis pH was about 4.7 of  $\text{Cu}^{2+}$ , thus  $\text{Cu}^{2+}$  was dissolved to the solution after the pH dropped to about 3.5. Chalcocite oxidation occurred under neutral or slightly acidified conditions by both oxygen and ferric [38], and was accelerated with the microbial activity under acidified condition. After the pH of the ore dropped down, and  $\text{Cu}^{2+}$  concentration in the leachate gradually increased. The Cu concentration reached as high as 10 g/L only with the water irrigation, far higher than the concentration need of the solvent extraction (Figure 9). Then, after the SX-EW plant was ready,  $\text{Cu}^{2+}$  in the leachate was extracted, and the  $\text{H}^+$  was generated to raffinate during the reverse extraction process. The raffinate was then used as the irrigation solution, preferentially to other new cells, and the pH of all cells continuously dropped down. The copper dissolution rate was not slow in the beginning of the water irrigation stage, and finally reached about 75% under a leaching period of 450 days (Figure 10).



**Figure 9.** Copper concentration in the leachate during the heap leaching. Before December 2015, open cycle irrigation with river water; then the leachate solution was cycling used as irrigation solution not only in this cell, and also was pumped to other new cells; and then after March 2016, the solvent extraction and electro-winning started, the raffinate was also used as the irrigation solution.

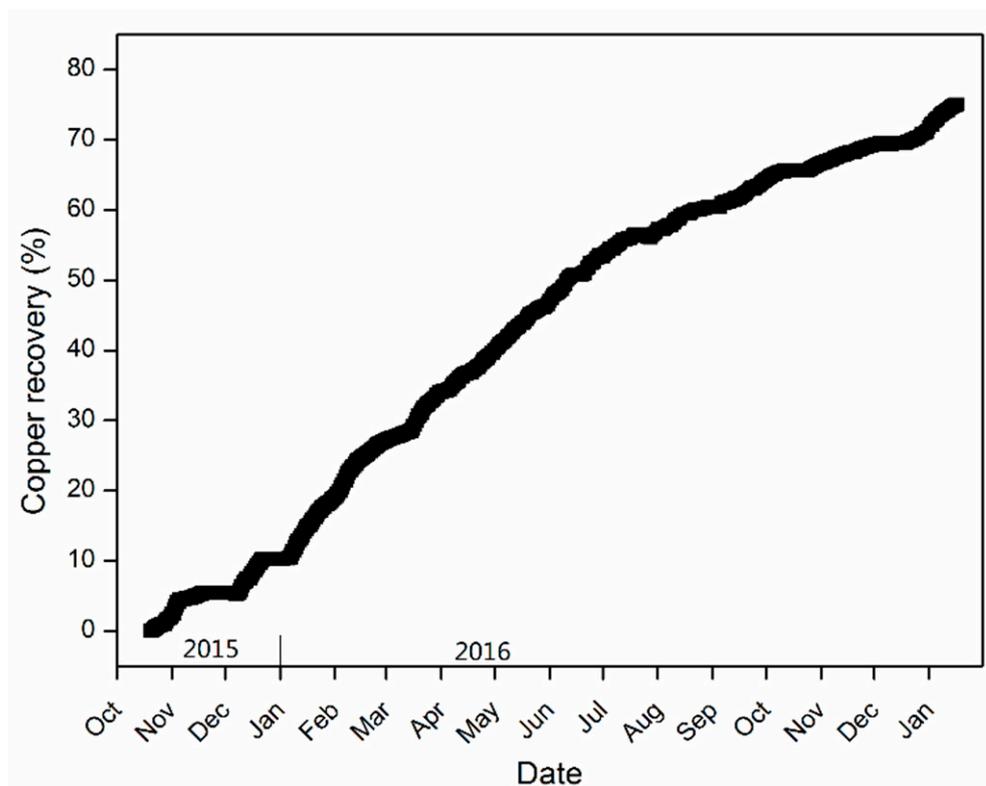


Figure 10. Copper recovery of the P3C6 cell during heap bioleaching.

## 5. Conclusions

When starting a heap bioleaching plant, quite a lot of sulfuric acid is usually needed for ore wetting and solution cycling, and for neutralization of the gangue mineral acid consumption and copper dissolution. Oxidation of pyrite can provide the essential sulfuric acid and oxidant  $\text{Fe}^{3+}$  for copper sulfide dissolution during heap bioleaching of copper sulfides. So, if the ore contains enough pyrite, it is possible to apply water-initiated heap bioleaching to reduce the cost for sulfuric acid, as introduced in this manuscript.

This procedure of Letpadaung heap bioleaching practice was summarized as below. (1) The mineral composition and the batches of laboratory tests were carried out to prove the possibility of starting heap bioleaching with only water. (2) During the ore mining, transportation and stacking period (about two months), wet ore became acidified to about pH 3.5, but did not acidify enough to maintain the ferric ion in the solution. (3) It was lucky that the hydrolysis pH of  $\text{Cu}^{2+}$  was quite high and this guaranteed the  $\text{Cu}^{2+}$  dissolution in solution rather than precipitated in heaps at slightly acidified heaps. (4) Additionally, the suitable microbial communities were quite important to match the low nutrient and low acidity environment. When the pH dropped down to 3.0, microbes and nutrients were added to the irrigation solution. Pyrite oxidation, together with Cu solvent extraction generated acid, further accelerated the acidifying of the heap. Under this condition, the Cu, Fe, acid concentration and microbial activity in the leaching solution gradually increased.

These processes take full advantage of the oxygen oxidation, ferric oxidation, and microbial oxidation of the sulfides (copper sulfides and pyrite) under different pH condition, to solve the demands of the huge acid and iron in the process of the initiation of heap bioleaching of copper sulfides, and achieve the fast Cu production, using only water as the irrigation solution without sulfuric addition. Letpadaung heap bioleaching achieved sulfuric acid and iron concentration in leachate at about 9 g/L and 7.5 g/L in about one year without sulfuric acid addition to the heap leaching system, and a copper recovery of about 75% under a leaching period of 450 days. Even if the water-start heap bioleaching could not be realized in some other plants, the promotion of pyrite oxidation in heap bioleaching can still reduce the amount of acid addition. The application of this invention in industrial

heap bioleaching plants will reduce the operation cost, and also make it easier to maintain the acid balance. Additionally, the decrease in sulfuric acid addition and reduction of acid neutralization by lime made the heap bioleaching technology more environmental friendly.

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