Metal recovery from the copper sulfide tailing with leaching and fractional precipitation technology

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Abstract
A study was conducted for metal recovery from low-grade copper sulfide tailings using the leaching and fractional precipitation methodology. Mineralogical characterization of the materials shows that the primary weight proportions of pyrite minerals, silicate minerals, and quartz in tailing are 31.50%, 38.85%, and 15.06%, respectively. Based on the optimum conditions, the achieved leaching efficiencies for Cu, Zn, Mn, and Fe are 98.45%, 21.41%, 56.13%, and 17.25%, respectively. Fractional precipitation technology was then employed for the Fe, Cu, Zn, and Mn recovery from the leachate. Sludge generated in sequential step contained 49.13% Fe, 19.53% Cu, 33.48% Zn, and 14.10% Mn. These results show how the metals can be recycled for environmentally friendly disposal of tailings and reveal their resource value.

1. Introduction
Copper sulfide tailings (Cu–S tailings) present a serious environmental problem in many regions worldwide (Ardau et al., 2009; Lu and Wang, 2012). When exposed to natural weathering and chemical percolation, heavy metals, including Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn, become more soluble and mobile (Anju and Banerjee, 2010; García et al., 2005). Once leached, heavy metals would become the major sources of contamination, which seriously damage not only stream water and groundwater, but also the soil environment (Kim et al., 2013; Zhao et al., 2012; Zhuang et al., 2009). Meanwhile, the large amount of tailings presents a significant metal resource. In order to solve these problems, metal recovery through the separation method has been studied, the separation depends on independent mineral features, such as magnetism (Li et al., 2010; Yang et al., 2011), gravity (Sriwastava and Pathak, 2000), and floatability (Alam and Shang, 2012). However, it is impossible to achieve a comprehensive recovery. On the other hand, with leaching methodology, metals such as Cu, Zn, Fe, Ni, and Mg could be recycled and the recovery efficiencies were much higher than that for the separation process. Although methods of hydrometallurgical leaching for sulfide ores (Gok and Anderson, 2013; Vračar et al., 2003), as well as for some wastes, such as batteries (Rabah et al., 2008), have been reported, few studies have been reported of its application for the Cu–S tailing. Recycled metals using the leaching process have to be purified for further reuse. It has been reported that the precipitation was an effective method for it is operationally simple and economical. With the precipitation process, the metals were enriched as a mixture in the sludge, while the metal content of the sludge was too low for reuse (Xie et al., 2005). However, the metal content of the sludge would be promoted by the fractional precipitation process (Innocenzi and Vegliò, 2012). Thus, an effective leaching with a fractional precipitation method for recovery of valuable metals from Cu–S tailing is still highly desired. As a typical poly-metallic mine in Southern China, the Dabaoshan Mine region is one of the largest open-cast copper mining bases. The amount of Cu–S tailing generated is approximately 480,000 tons per year, and the amount of tailings stored in the tailing reservoir is approximately 800 million tons. The reservoir becomes a source of acid mine drainage (AMD), contaminating the well water around the Dabaoshan Mine region (Chen et al., 2007). Therefore, a comprehensive reuse of the tailing would improve economic efficiency and lessen environmental damage as well. Such comprehensive reuse could be promoted by the leaching process. The objective of this work is to recovery Cu, Fe, Zn, and Mn from low-grade Cu–S tailing effectively using an environment-friendly and economical leaching method.

2. Experimental
2.1. Materials and analysis method
The source of the Cu–S tailing used in this study is from the Dabaoshan Mine region, and the tailings are obtained during the end of the flotation process. To determine metal contents, the solid samples were digested by microwave digestion equipment (WX-8000, EU Microwave Chemistry Technology Co., Ltd.) according to method 3052 (US EPA, 1996). Major metals are determined using an AAS (Shimadzu AA6300, made in Japan), whereas minor metals at significantly low concentrations were determined through ICP-MS (Agilent 7500, made in Japan).
The discovery efficiencies of the targeted elements through the addition of standard materials were between 95% and 108%. All given results are the averages of three repetitions of all experiments. The mineral composition was investigated by SEM–EDX and was analyzed through the SIP system of QEMSCAN. The bound moisture content was determined through the method of specific gravity.

2.2. Leaching and the leachate metal recovery process

Parameters affecting on the recovery efficiency, such as leaching temperature, amount of added leaching reagent, leaching time, and leaching solid-to-liquid ratio (S:L, weight to volume) were investigated. The sulfuric acid concentration is 98%. To obtain the optimal conditions for the leaching tests, the experiments were performed at a constant stirring speed of 400 r·min⁻¹ (Antonijević et al., 2008). Fractional precipitation was used for the metal separation recovery from the leachate, whose principle is the solubility discrepancy of different metals. A series of tests were conducted using the procedure shown in Fig. 1. Precipitation tests were performed within a 500 mL beaker, and the actual liquor volume was 300 mL. A homothermal magnetic stirrer (85-2, AoHua) was used for the precipitation chemical reaction, the agitation rate was 50 rpm and the temperature was controlled as 35 °C. Each precipitation test was replicated 3 times. After each precipitation step, the solution was filtered with a 0.45 μm filter membrane, and the resulting filtrate was used for the next precipitation process until the last of the targeted metals was recovered. The sludge was air dried for further disposal.

2.3. Characteristics of tailings

Analytical determination of the tailing contents is shown in Table 1. The total metal content (determined as free metal) amounts to approximately 18 wt.%. The contents of the targeted major metals, including Cu, Zn, Fe, and Mn, are 2923.15, 1638.21, 108671.20, and 590.80 g/t, respectively. The mineral composition is listed in Table 2. The tailing primarily contains pyrite minerals, silicate minerals, and quartz, with proportions of 31.50%, 38.85%, and 15.06%, respectively. The oxide of Fe is approximately 4.43%, whereas the sulfide and oxide of Cu are 31.62% and 68.34%, respectively. Meanwhile, 100% of the Zn is in the ZnS formula.

3. Results and discussion

3.1. Leaching analysis

3.1.1. Effect of leaching temperature

The main agent chosen here for tailing leaching was H₂SO₄ due to its attractive properties, including low cost and easily available. The leaching results obtained at various temperatures (30, 40, 50, 60, and 80 °C) are shown in Fig. 2 with the addition of 0.24 mL/g of concentrated H₂SO₄. The S:L was 1:2, and leaching was conducted for 2 h. As shown in Fig. 2, a negligible effect of temperature on the leaching efficiencies of the metals is noted. The leaching efficiencies at 30 °C are 97.47%, 26.56%, 54.45%, and 15.47% for Cu, Zn, Mn, and Fe, respectively. However, the lower the leaching temperature, the lower the leaching cost. Hence, leaching temperature of 30 °C could be suggested to be the best temperature in this present experiment condition. To
further investigate other experimental effect on leaching efficiencies, the leaching temperature was fixed at 30 °C.

3.1.2. Effect of different H₂SO₄ addition

The effect of the different H₂SO₄ addition was investigated under a fixed S:L of 1:2. The leaching temperature was set to 30 °C, and leaching occurred for 2 h. As presented in Fig. 3, the leaching efficiency of the metals increased gradually with an increasing amount of H₂SO₄. A nearly complete leaching efficiency of 97.75% for Cu was obtained with the addition of 0.24 mL/g of H₂SO₄. For Zn and Mn, leaching efficiencies of 27.04% and 56.25% were obtained with the addition of 0.18 mL/g of H₂SO₄. However, only 17.39% for Fe was leached when 0.29 mL/g of H₂SO₄ was added. The low amount of leached Fe may be attributed to reprecipitation, for Fe(OH)₃ precipitate emerged below a pH of 2, the pH value of the leachate with 0.29 mL/g H₂SO₄ addition was 2.18, and even with the addition of 0.40 mL/g of H₂SO₄ the pH value was 1.92. Thus, the recovery efficiency of Fe is relatively low although Fe is more apt to be leached during the H₂SO₄ leaching process.

3.1.3. Effect of leaching time

The effect of leaching time was further investigated with the addition of 0.24 mL/g concentrated H₂SO₄. S:L was 1:2, and leaching temperature was set as 30 °C. The effects of leaching time are illustrated in Fig. 4. Under the above leaching conditions, the leaching yields of Cu, Zn, and Mn increased steadily within the 2 h leaching process, that of Fe increased within 1 h. A leaching time of 2 h is found to be optimal time for reducing the amount of acid consumed and increasing the amount of metals recovered. Leaching low-grade Cu–S tailing for 2 h at ambient temperature and atmospheric pressure resulted in the effective leaching of valuable metals Cu, Zn, Mn, and Fe at 98.40%, 27.31%, 55.61%, and 17.03%, respectively.

3.1.4. Effect of leaching solid to liquid ratio

To shed light on the effect of S:L, the reaction process was monitored by examining the products prepared at different S:L with the addition of 0.24 mL/g of concentrated H₂SO₄. Leaching temperature was set as 30 °C, and leaching lasted for 2 h. The tailing contents in the pulp were 10%, 17%, 25%, 33%, 40%, and 50%, corresponding to S:L of 1:9, 1:5, 1:3, 1:2, 1:1.5, and 1:1, respectively, as shown in Fig. 5. Under the above leaching conditions, the leaching efficiencies of Cu and Mn increased and Fe leaching decreased slightly as the pulp density decreased. The maximum leaching efficiencies of Cu and Mn reached 98.40% and 56.85%, respectively, at an S:L of 1:2. The leaching efficiency of Zn increased with decreasing pulp density, the increased volume of leaching reagent would promote the mass transfer process of the solid–liquid interface (Aydogan et al., 2005; Zhang et al., 2005). A greater volume of leaching reagent results in lower concentrations of the metals leached from the tailings, which would affect the recovery of
The leaching S:L was 1:2. The leachate was filtered through a 0.45 μm filter membrane. The metals contained in the filtrate are illustrated in Table 3. The leaching efficiencies of Cu, Zn, Mn, and Fe were 98.45%, 21.41%, 56.13%, and 17.25%, respectively. The concentrations of Cu, Zn, Mn, and Fe were 1.45, 0.18, 0.20, and 9.31 g/L, respectively, which are significantly greater than those published in previous reports (Pepe et al., 2007). The metal recovery from the leaching filtrate was preceded by fractional precipitation with the addition of different chemical agents (Barnnitt et al., 1992; Xie et al., 2005). At first, the pH of the leaching filtrate was adjusted to 3.0 with the addition of Ca(OH)2 to recover Fe as hydroxide. Thereafter, Cu and Zn were recovered as their metal sulfides through the dropwise addition of a 0.5 wt.% aqueous Na2S solution in sequence. The pH value of the solution after Cu and Zn precipitations are 3.6 and 3.8 respectively. Finally, Mn was recovered by adjusting the pH to 9.0 in the leaching filtrate. As shown in Table 4, the recovery efficiencies of metals from the filtrate are 95.45%, 93.74%, 89.7%, and 93.29%, respectively. The sludge generated in every step contained 49.13% Fe, 19.53% Cu, 33.48% Zn, and 14.10% Mn (Table 5). With the UV conversion of the Fe sludge, magnetite particles could be obtained and it can be applied for the paint industry (Silva et al., 2012), while the Fe2O3 content of the magnetite particles should be higher than 75%. It has been found that mostly Cu and Zn sludges and those generated in the sulfide precipitation process were covellite and sphalerite (Sampaio et al., 2010), and those could be refined and sold to smelters to recover the metals (Cibati et al., 2013). Generally, the Cu and Zn contents of the sludge were 19.5% and 33.5% respectively. The metal contents of the sludge are higher than these specifications, therefore, the sludge could be refined with the flotation process. Furthermore, Cu and Zn could be obtained through the flotation process of the flotation concentrates. The Mn sludge can be used as cement material and the leaching of heavy metals from the solidified blocks would be negligible (Petal and Pandy, 2012).

3.3. Mass balance analysis and the preliminary economic analysis

The mass balance of the metal recovery process was illustrated in Fig. 6, with 1 kg tailing disposed, about 0.84 kg leaching residue was left and the yield of the Fe sludge, Cu sludge, and Zn sludge are about 23.4 g, 7.15 g, and 0.95 g respectively. The leaching residue could be recycled as the cement materials. The metals contained in the filtrate after the fractional precipitation process would meet the Chinese integrated wastewater discharge standard.

![Fig. 6. Mass balance of the metal recovery process.](image-url)
4. Conclusions

Fe, Cu, Zn, and Mn from the low grade Cu-S tailing are successfully recycled via a H$_2$SO$_4$ leaching and subsequent fractional precipitation technology. Based on the mineral composition analysis results, leaching temperature, the amount of H$_2$SO$_4$ added, leaching time, and S:L have been evaluated for the leaching efficiencies. The amount of H$_2$SO$_4$ added and S:L have strongly influenced the leaching efficiencies. Under the optimum conditions of ambient temperature and atmospheric pressure, 0.24 mL/g of H$_2$SO$_4$, S:L of 1:2, stirring speed of 400 rpm, and leaching time of 2 h, leaching efficiencies achieved for Cu, Zn, Mn, and Fe are 98.45%, 21.41%, 56.13%, and 17.25%, respectively. With the fractional precipitation process, Fe and Mn were enriched as hydroxide, whereas Cu and Zn were enriched as sulfides. The sludge generated in every step contained 49.13% Fe, 19.53% Cu, 33.48% Zn, and 14.10% Mn; the recovery efficiencies of these metals from the filtrate are 95.45%, 93.74%, 89.7%, and 93.29%, respectively. The Fe, Cu, and Zn sludges could be further refined and sold to the paint industry or the smelters to recover the metals, and with the recycle disposal, the environment problems caused by the tailing could be mitigated. While the leaching residue reuse needs further consideration for its environment impact.

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