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Development of copper recovery process from flotation tailings by a combined method of high–pressure leaching–solvent extraction

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ABSTRACT

Sulfide copper mineral, typically Chalcopyrite ($CuFeS_2$), is one of the most common minerals for producing metallic copper via the pyrometallurgical process. Generally, flotation tailings are produced as a byproduct of flotation and still consist of un–recovered copper. In addition, it is expected that more tailings will be produced in the coming years due to the increased exploration of low–grade copper ores. Therefore, this research aims to develop a copper recovery process from flotation tailings using high–pressure leaching (HPL) followed by solvent extraction. Over 94.4% copper was dissolved from the sample ($CuFeS_2$ as main copper mineral) by HPL in a H_2O media in the presence of pyrite, whereas the iron was co–dissolved with copper according to an equation given as $C_{Cu} = 38.40 \times C_{Fe}$. To avoid co–dissolved iron giving a negative effect on the subsequent process of electrowinning, solvent extraction was conducted on the pregnant leach solution for improving copper concentration. The result showed that 91.3% copper was recovered in a stripped solution and 98.6% iron was removed under the optimal extraction conditions. As a result, 86.2% of copper was recovered from the concentrate of flotation tailings by a proposed HPL–solvent extraction process.

1. Introduction

Copper is one of the most important base metals and widely used as wire and conductors. In the earth's crust, copper is most commonly present as copper–iron–sulfide and copper–sulfide minerals, such as chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S) [1,2]. About 80% of the world's copper ores originate in Cu–Fe–S minerals, especially chalcopyrite, which is the most refractory minerals and not easily dissolved in aqueous solutions [1–3]. For that reason, the vast majority of copper extracted from these copper minerals is usually by pyrometallurgical processes, i.e., flotation followed by smelting and refining [2,4,5]. Generally, the flotation tailings are produced as a byproduct during the beneficiation of copper ore, namely froth flotation before the pyrometallurgical processes. According to the literature data, about 90–95% of the plant general tailings, i.e. flotation tailings and cleaning tailings, are produced from flotation process and represented as flotation tailings [6,7]. They are treated by methods including cross valley or hillside dams, raised embankments/impoundments, dry–stacking of thickened tailings on land, backfilling into abandoned open pit mines or underground mines, and direct disposal into rivers, lakes and the ocean (ocean surface and submarine tailings disposal) [8,9]. In addition, the tailings containing metal sulfides present particular challenges for responsible waste management due to the formation of acid mine drainage (AMD) and dispersion of metals into the environment as a result of the exposure of these tailings to atmospheric oxygen, bacteria, and water, which can cause severe degradation of water quality in both subsurface and surface systems, and soil in their vicinities [8–17]. Due to increased exploration of copper ores and the discovery of more low–grade deposits, it can be expected that more flotation tailings will be produced in the coming years, which might cause more environmental problems and challenges. The total copper recovered from its ore through flotation process is about 56% [6,18], which indicates that the flotation tailings still contain valuable copper components such as chalcopyrite. In addition, old flotation tailings sometimes have a higher

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copper grade (0.2–0.4%) than that of low–grade ores (0.2–0.3%). These copper grades of the old flotation tailings are similar to the world average grade of about 0.4% Cu for copper-bearing ores [19–21]. Considering the current price of copper in stock market and predictions that the copper demand will increase, flotation tailings and low-grade copper ores constitute a potential future copper resource [6]. However, due to impurities such as clay minerals and pyrite, the flotation tailings become more complex and low–grade, which causes an increase in the consumption of flotation reagents and reduction in the production of high–grade copper concentrate. Therefore, it is not efficient to treat these flotation tailings using traditional pyrometallurgical technologies which require about 30% copper in concentrate [22]. Compared with the pyrometallurgical route, hydrometallurgical process offers great potential for treating complex and low–graded sulfide ores and concentrates, with a resulting increase in metal recoveries and reduction in air–pollution hazards [22]. In recent years, research and development in the hydrometallurgical process has intensified as an alternative to the pyrometallurgical route [23–25]. Some researchers have investigated the possibility of copper recovery from the tailings using bioleaching and atmospheric leaching [6,26–28]. Since the bioleaching process is very slow and sometimes produces toxic chemicals [28,29], most studies are focused on atmospheric leaching. The results showed that the dissolution percentage of copper from the tailings is quite low (lower than 55%) and the pregnant leach solution (PLS) has a lower copper concentration. These limitations impacted the further recovery of copper from the copper leach liquor using solvent extraction and electrowinning. The purpose of this study was to develop an effective copper recovery process by a hydrometallurgical route that will contribute to the utilization of flotation tailings as a potential copper source.

The copper concentrate obtained from the flotation of tailings [30] was used as feed sample in this study. To achieve an excellent copper dissolution from the concentrate of flotation tailings, which consist of chalcopyrite as the major copper component, high–pressure leaching (HPL) was conducted using an autoclave under a variety of sulfuric acid concentration (0–0.5 M), total pressure (0.8–2.0 MPa), temperature (140–180 °C) and pulp density (100–400 g/L). Then, the solvent extraction of copper from the PLS that was obtained by HPL was carried out under various conditions such as pH (0.1–2.0) and at the different sulfuric acid concentrations (0.5–1.5 M), for producing the Cu–rich solution. As a result of this research, an efficient method has been proposed to recovering substantial amounts of copper from flotation tailings and reducing the environmental impact of flotation tailings by a combined hydrometallurgical process of HPL–solvent extraction.

2. Experimental

2.1. Material

A sample of flotation tailings obtained from Bor Mining, Serbia, was used in this study. The chemical compositions of the initial sample (flotation tailings) and feed sample (copper concentrate) were confirmed by inductively coupled plasma optical emission spectroscopy (ICP–OES) and X–ray fluorescence spectrometry (XRF) as shown in Table 1. The copper concentrate was first prepared by flotation under the optimal conditions obtained from the previous study, which was pH 10, pulp densities 25%, collector (PAX) dosage 100 g/t–ore, sulfurizing reagent (NaHS) dosage 1000 g/t, frother (MIBC) dosage 200 g/t–ore, and flotation time 15 min [30]. The copper grade was upgraded to 0.65 mass% from the initial 0.34 mass% under the determined conditions, whereas the recovery of copper was 78.4%. The mineral composition of the materials was identified by X–ray diffractometer (XRD, Rigaku RINT–2200V) and XRD patterns of the samples were shown in Fig. 1. The main mineralogical constituents of the flotation tailings were quartz (SiO_2), pyrite (FeS_2), and kaolinite ($Al_2Si_2O_5(OH)_4$). The copper minerals were not detected in both the flotation tailings and its concentrate by the XRD analysis due to the detection limits of the equipment. However, scanning electron microscope–energy dispersive X–ray spectroscopy (SEM–EDS) test confirmed that chalcopyrite ($CuFeS_2$) was the major copper phase of the flotation tailings (Fig. 2). In addition, to investigate the effect of FeS_2 on copper leaching efficiency and to confirm the possibility of applying the optimal conditions to another copper resource, sample A (copper ore excludes FeS_2) and sample B (copper ore consists of 0.5% FeS_2) were used in the relevant part of this paper (Table 1; Fig. 1).

Table 1
Chemical compositions of each sample.

Sample name	Grade (mass%)				
	Cu	Fe	Al	S	SiO_2
Flotation tailings	0.34	8.96	8.12	11.2	57.8
Concentrate of the flotation tailings	0.65	33.2	2.63	32.7	23.4
Sample A (copper ore excludes FeS_2)	0.45	6.19	2.39	6.13	47.7
Sample B (copper ore consists of 0.5% FeS_2)	18.4	16.4	1.08	19.4	36.6

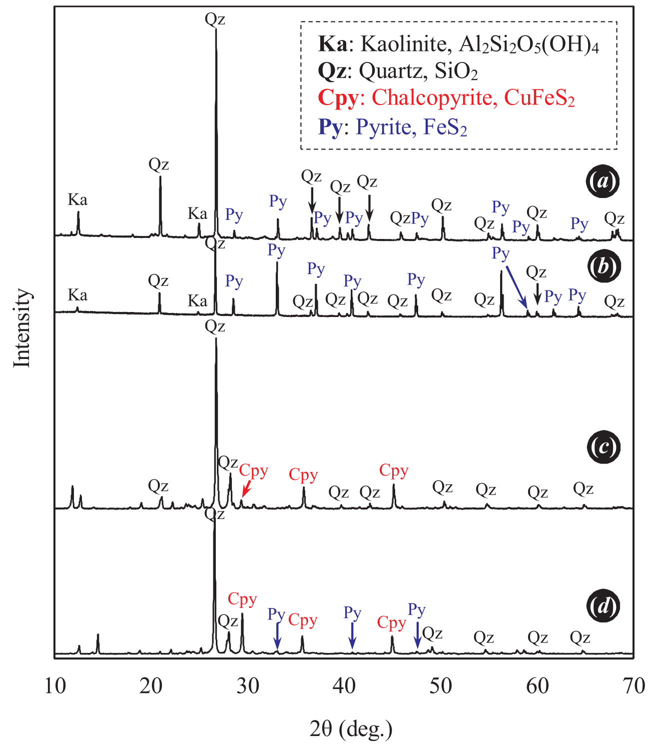

Fig. 1. The XRD patterns of (a) flotation tailings, (b) concentrate of the flotation tailings, (c) sample A, and (d) sample B.

2.2. Procedure

2.2.1. High–pressure leaching

An autoclave (Nitto Koastu, Japan) which has a 2 L of Teflon vessel was used as a leaching reactor in the HPL experiments. The slurry sample was prepared in 0.5 L distilled water or sulfuric acid solution (0.2–0.5 M) with 50–200 g concentrates of flotation tailings into a vessel for adjusting the pulp density in the range of 100–400 g/L. The vessel containing slurry was placed in the autoclave and the system was allowed to heat up to the desired setpoint temperature (140–180 °C). When the temperature reached the target value, oxygen (O_2) gas was injected to the slurry into the vessel with a controlling total pressure (0.8–2.0 MPa), and the reaction was left to proceed until the required leaching duration of 60 min. After cooling down the slurry to below