

Article

Recovery of Cobalt as Cobalt Oxalate from Cobalt Tailings Using Moderately Thermophilic Bioleaching Technology and Selective Sequential Extraction

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Abstract: Cobalt is a very important metal which is widely applied in various critical areas, however, it is difficult to recover cobalt from minerals since there is a lack of independent cobalt deposits in nature. This work is to provide a complete process to recover cobalt from cobalt tailings using the moderately thermophilic bioleaching technology and selective sequential extraction. It is found that 96.51% Co and 26.32% Cu were extracted after bioleaching for four days at 10% pulp density. The mean compositions of the leach solutions contain $0.98 \text{ g} \cdot \text{L}^{-1}$ of Co, $6.52 \text{ g} \cdot \text{L}^{-1}$ of Cu, and $24.57 \text{ g} \cdot \text{L}^{-1}$ of Fe (III). The copper ion was then recovered by a solvent extraction process and the ferric ions were selectively removed by applying a goethite deironization process. The technological conditions of the above purification procedures were deliberately discussed. Over 98.6% of copper and 99.9% of ferric ions were eliminated from the leaching liquor. Cobalt was finally produced as cobalt oxalate and its overall recovery during the whole process was greater than 95%. The present bioleaching process of cobalt is worth using for reference to deal with low-grade cobalt ores.

Keywords: Carrollite (CoCu_2S_4); moderately thermophilic bioleaching; solvent extraction; goethite

1. Introduction

Cobalt is one kind of important basic material for industrial production. It can be processed into many different products, such as magnetic material, high-temperature alloys, etc. In addition to the metal itself, cobalt compounds—for instance, cobalt oxalate, cobalt oxide, cobalt chloride, and cobalt sulfate—also have extensive industrial application [1–3]. It is well known that cobalt is widely used as a Li-ion battery material. The demand for cobalt is growing, quickly fueled by the growth of the electronics industry and the needs of emerging green energy. However, it is not easy to recover cobalt since there is a lack of independent cobalt deposits. Instead, cobalt is always associated with other metal minerals—for example, chalcopyrite, pyrite, carrollite, pentlandite, and so on [4]. The grade of cobalt ore is always very low and quite difficult to recover. At present, it is often extracted as a by-product for mineral or metallurgical processes, especially for froth flotation and smelting processes of copper, iron, and nickel.

Due to the low grade, applying the traditional pyrogenic process will cause high energy consumption and serious air pollution. Additionally, cobalt accompanies other metals since it has similar properties to others and can lead to high loss. The beneficiation process also cannot separate cobalt adequately for a similar reason [5]. At present, only a small amount of cobalt ores are produced from the extraction of the low-grade by-product ores. The discarded cobalt ore not only causes huge economic loss but also induces environmental problems, such as forming acidic mine drainage or heavy metal pollution. Thus, it is significant to develop a new recovery process to extract cobalt from low-grade associated resources.

Compared to the conventional methods, biohydrometallurgy contains enormous merits, including low capital and operating cost, relative simplicity, short construction period, and less pollution. Therefore, it is very appropriate for the low-grade ore [6,7]. Kasese Cobalt, located in Uganda, was the first commercial plant for cobalt recovery using bioleaching technology. It mainly deals with Co-bearing pyrite. A cobaltiferous pyrite concentrate, grading 1.38% cobalt, has been used as the raw material for the bioleaching [8]. Additionally, previous research by our group revealed that cobalt can be leached from carrollite via bacteria [9]. Furthermore, it is found that during the bioleaching tests, the recovery of cobalt can increase to above 90% with the addition of a catalyst. Additionally, the leaching time can also be reduced with an activated carbon catalyst [10].

In the present study, cobalt was recovered from cobalt tailings using moderately thermophilic bioleaching technology and finally produced as cobalt oxalate after selective sequential extraction processes. The ore materials came from the Luanshya Mine, which is located along the Zaire–Zambia Copper belt and is part of the Central African Copper belt. The mine is one of the most important Cu-Co deposits in Zambia [11]. The cobalt in the mine mostly occurs as carrollite. Cobalt is not effectively extracted with the traditional pyrometallurgical and hydrometallurgical processes. Thus, patented bacteria [12] have been used in the recovery process, which contain the mixed leaching bacteria.

2. Experimental

2.1. Mineral Sample Preparation

The cobalt tailings sample were picked up from the Luanshya Mine and delivered to the lab. The elemental analyses of the ore were conducted and the results are listed in Table 1. Analysis of mineralogy indicates that the dominant sulfide minerals in the cobalt tailings are carrollite (CoCu_2S_4) (the main cobalt-bearing mineral), chalcopyrite, chalcocite, bornite, covellite, and pyrite. It has been controversial for several years that the formal oxidation states regarding the constituent elements in the mineral carrollite CuCo_2S_4 , and there is still no clear consensus between $\text{Cu}^{\text{I}}\text{Co}^{\text{III}}\text{Co}^{\text{IV}}\text{S}^{-\text{II}}_4$, $\text{Cu}^{\text{I}}\text{Co}^{\text{III}}_2\text{S}^{-\text{II}}_3\text{S}^{-\text{I}}$, and $\text{Cu}^{\text{II}}\text{Co}^{\text{III}}_2\text{S}^{-\text{II}}_4$ [13]. The particles experienced fine grinding in ball mills, and the final size of 38 μm was reached before bioleaching.

Table 1. Chemical composition of cobalt ore (mass, %).

Fe	Cu	Co	S	SiO ₂	CaO	MgO
27.79	18.82	1.06	33.06	10.21	2.96	2.82

2.2. Bacterial Strain and Growth Conditions

In the whole bioleaching process, the patented bacteria were applied and labeled as HQ0211. They were screened for a long time in our lab and mixed with leaching bacteria *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, and *Leptospirillum ferrooxidans*. Before the studies were conducted, the bacteria were adapted to the conditions, such as high cobalt solution, for a period of time. The 9K medium (pH = 1.8) was used as an energy and nutrition source for the culture, and was composed of 3.00 g·L^{−1} (NH₄)₂SO₄, 0.01 g·L^{−1} Ca(NO₃)₂, 0.50 g·L^{−1} MgSO₄·7H₂O, 0.50 g·L^{−1} K₂HPO₄, 0.10 g·L^{−1} KCl, and 44.30 g·L^{−1} FeSO₄·7H₂O. The quantity of the cells were expanded for two days by shaking at a stable temperature (200 rpm and 45 °C). The solution containing the cells became red, finally, and was separated from jarosite sediments by way of centrifugation. The supernatant fraction was applied as an inoculation solution. The culture were adapted to the ore-leaching environment three times using the above procedure and, eventually, the bacterial strain could survive in a high concentration of cobalt ions (30 g·L^{−1}) after the domestication process.

2.3. Bioleaching Process

First, 20 mL of HQ0211 bacterial strain and 180 mL of 9K medium were mixed in a 500-mL conical flask. The bacteria were then kept at 45 °C in a rotary shaker at a constant speed of 180 rpm. The cell concentration rose to 2.5×10^9 cells·mL⁻¹ after incubating for 36 h and the redox potentials of the bacterial solution were about 650 mV (vs. Hg/Hg₂Cl₂). The cobalt ore was subsequently put in the liquid at an appropriate proportion. The initial pH of the slurry was controlled at 1.5. The sterilized distilled water was added occasionally to compensate the water loss by evaporation. The fresh, sterilized medium also was used to adjust the solution due to sampling. A pH meter (pHS-25) was applied to test the pH changes during the bioleaching process. The redox potential (Eh) was also measured with a Pt electrode as a counter electrode and a calomel electrode (Hg/Hg₂Cl₂) as a reference electrode.

2.4. Selective Sequential Extraction Procedure

The multi-metal solution was obtained after bioleaching process, containing mainly cobalt, iron, and copper ions. The selective sequential extraction procedure was applied to recover metals as follows.

(1) Copper extraction

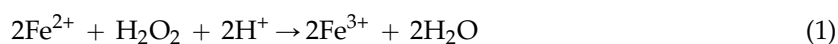
Currently, there is no highly-efficient solvent extraction agent for cobalt, but there is for copper. Thus, solvent extraction can be used to recover copper directly from bioleaching solutions. The commercial product Lix 984N is used as an extractant in the experiments. To get the optimal extraction conditions, three important factors (pH, LIX 984N concentration, and the contact time) are discussed in detail.

(2) De-ironization

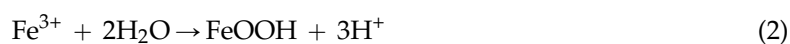
From the previous report, the goethite and jarosite precipitation can be used to remove the soluble iron at atmospheric pressure [14]. Compared to the jarosite precipitation process, iron removal by the goethite method shows an advantage of low volume, no additional alkalis required, and is more environmentally friendly. Therefore, in the current study, the dissolved iron in the bioleaching solution were removed by using the goethite precipitation method.

Since the pyrite contained in the cobalt tailings can be easily oxidized to Fe (III) by biological oxidation, excess sulfur dioxide was passed through the solution to reduce the ferric iron at ambient temperature, firstly. After that, the solution was warmed and the oxidant hydrogen peroxide was dropped slowly to form the goethite [15]. The reactions that lead to goethite precipitation are briefly summarized as follows (Equations (1)–(3)):

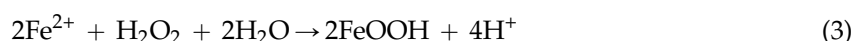
Ferrous ion oxidation:



Ferric ion hydrolysis:



Total reaction:



According to these reactions, the pH value of bioleaching solution will decrease with the formation of goethite precipitates. Hence, a neutralizing agent was added to promote the reactions. Since the acidity of the solution affects the oxidation rate of the ferrous ion and the cobalt loss in the sediment, it is important to examine the effect of pH on the iron removal rate and cobalt loss in detail. Other parameters, such as the precipitation temperature and the soaking time, also need investigating.

(3) Preparation of CoC_2O_4 powder by the precipitation process

After the de-ironization process, the cobalt was precipitated to form cobalt oxalate from the liquor by adding an excess of sodium oxalate. The consumption of sodium oxalate was studied. The cobalt oxalate product was filtered at first, and washed several times with distilled water. The morphology and composition of the cobalt oxalate were examined with scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The experimental flow diagram for the process are shown in Figure 1.

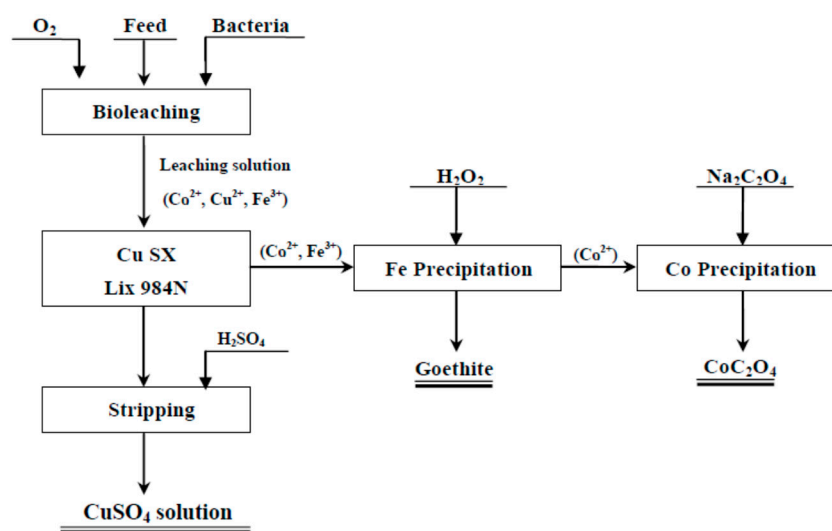


Figure 1. Flow sheet for the recovery of cobalt from cobalt tailings using the bioleaching method and selective sequential extraction technologies.

2.5. Analytical Method

Atomic absorption spectroscopy (AAS) was applied to measure the content of metal ions, such as cobalt, iron, and copper, in the bioleaching solution. The goethite precipitate and final product cobalt oxalate were analyzed by XRD and SEM. The particle size of the cobalt tailings was measured by a laser scattering particle analyzer.

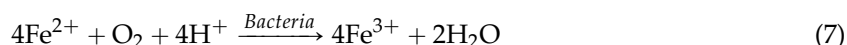
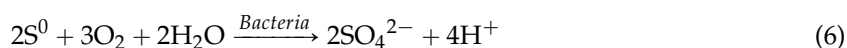
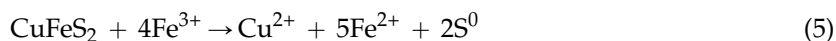
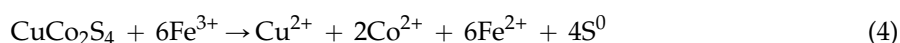
3. Results and Discussion

3.1. Bioleaching Results of Cobalt Tailings

The results of the mineralogical composition of the cobalt tailings show that the main cobalt-bearing mineral in the ore sample is carrollite. The occurrence state of copper in the cobalt tailings contains mainly chalcopyrite and chalcocite. Table 2 shows the bioleaching results of the ores. According to the Table 2, it is found that the recovery of copper and cobalt varied and the cobalt can be leached easier via bacteria. Extraction of cobalt and copper can reach 96.51% and 26.32%, respectively, after direct bioleaching for four days at 10% pulp density. The copper is also found enriched in the residue after the bioleaching process. The copper grade in the leaching residue is above 20%, thus it can be returned to the smelting process to recover remaining copper.

Figure 2 shows the changes of microscopic characteristics of the chalcopyrite/carrollite mineral pair during the bioleaching process. From the left picture, carrollite mineral presents as smooth, ivory-colored, and encapsuled in the chalcopyrite. After 120 h of biological oxidation, the surface color of carrollite turns to brown. The oxidation effects of carrollite by the bacteria can be obviously revealed from the distinct color variation. Comparatively, it is noted that the surface of chalcopyrite have a less pronounced change, which indicates the lesser corrosion effects on chalcopyrite by the cells.

The reaction occurring on the minerals carrollite and chalcopryrite during the bioleaching process are listed as follows (Equations (4)–(7)):



It is clear that carrollite dissolution was faster than chalcopryrite dissolution from microscopic characteristics of the chalcopryrite/carrollite mineral pair (Figure 2) during the bioleaching process.

Table 2. Bioleaching results of cobalt tailings.

Pulp Density/%	Cell Density/mL ^{−1}	Time/Day	Recovery of Co/%	Recovery of Cu/%	Co Content in Residue/%	Cu Content in Residue/%
5	10 ⁹	2	97.23	30.21	0.078	24.58
10	10 ⁹	4	96.51	26.32	0.087	21.26
15	10 ⁹	4	92.59	35.12	0.11	22.17
18	10 ⁹	5	90.86	30.29	0.12	23.05

From the results of the bioleaching process, iron, cobalt and copper are dissolved. The bioleaching experiments were also performed in a small scale (5 L) under the following operating conditions: pulp density of 10%, and a reaction time of 4 day at 40 °C. The obtained leaching liquor contains 0.98 g·L^{−1} of Co, 6.52 g·L^{−1} of Cu, and 24.57 g·L^{−1} of Fe (III). It was found that the bioleaching solution contains not only low content of cobalt ions, but also a high content of copper and ferric ions, which need follow-up selective recovery processes.

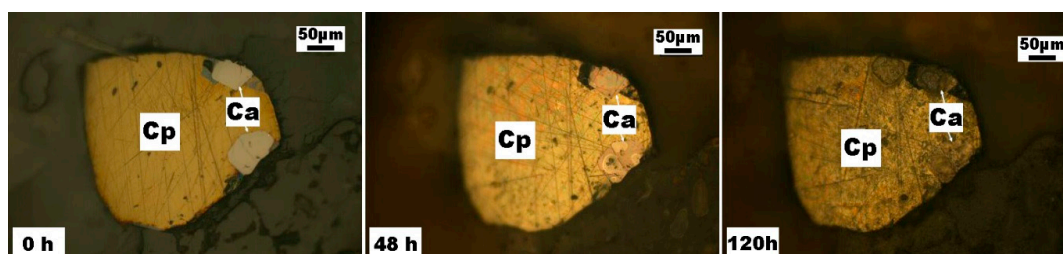


Figure 2. Microscopic characteristics of bio-oxidizing chalcopryrite (Cp)/carrollite (Ca) mineral pair.

3.2. Copper Extraction Process from Bioleaching Solutions

3.2.1. Effect of Equilibrium pH

The effects of the equilibrium pH on the recovery of copper, cobalt, and iron are shown in Figure 3a. It is observed that when the pH increased from 0.25 to 1.25, the recovery of copper has a rapid increase from 45.4% to 98.6%. However, there is only a slight increase in the copper recovery when the pH was further increased to 2.00. It is beneficial for the extractant LIX 984N to ionize at a higher pH value. It can promote the extraction reaction of copper and enhance the recovery efficiency of copper. For the case of cobalt and iron, their recovery are both lower than 4% when the pH is lower than 1.25. This is helpful for the separation of copper from cobalt and iron. While the recovery of Co and Fe increase if the pH is higher than 1.25, it can be confirmed by Figure 3b that the separation rate of both Cu/Co and Cu/Fe first increase, and then decrease. The largest separation rate of Cu/Co and Cu/Fe obtained 16,646 at pH 1.25 and 3610 at 1.50 respectively. Therefore, the optimum pH of copper extraction was at 1.25.

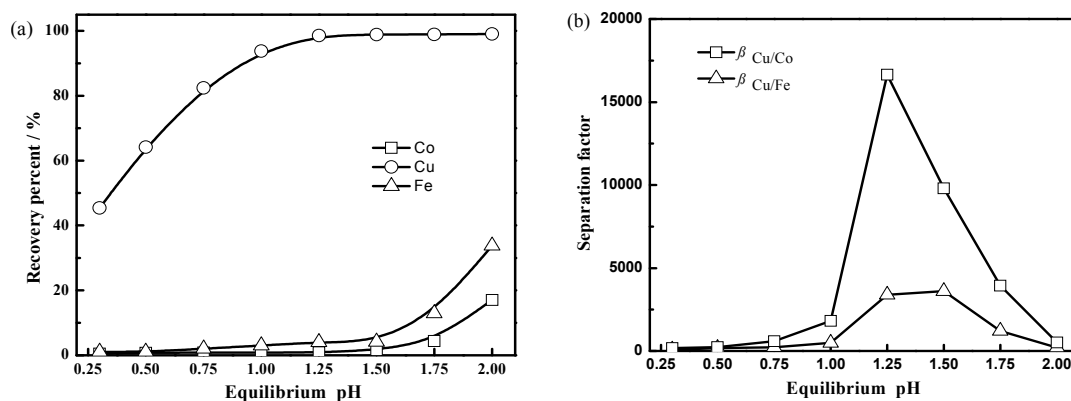


Figure 3. Effect of equilibrium pH on the recoveries of copper, cobalt, and iron (a) and separation factor (b) (A/O phase ratio = 1/1, LIX 984N concentration = 25% (v/v), contact time = 20 min, temperature = 25 °C).

3.2.2. Effect of LIX 984N Concentration

The influence of LIX 984N concentration on the recovery of copper from the bioleaching solution was studied. The concentrations of LIX 984N varied from 5% to 20% (v). Recoveries of the copper, cobalt, and iron ions versus LIX 984N concentration are shown in Figure 4a. It is noted that the recovery of copper enhanced remarkably with the increase of the extractant concentration from 5% (v) to 15% (v) and it remained nearly the same when the extractant concentration was further increased to 30% (v). The recoveries of cobalt and iron showed a lesser increase (no more than 8% for both cobalt and iron) when the LIX 984N concentration rose from 5% (v) to 20% (v). The significant gap in the recoveries and the high separation factor (Figure 4b) state that it is a proper method to separate copper from cobalt and iron by using an appropriate pH range and LIX 984N concentration.

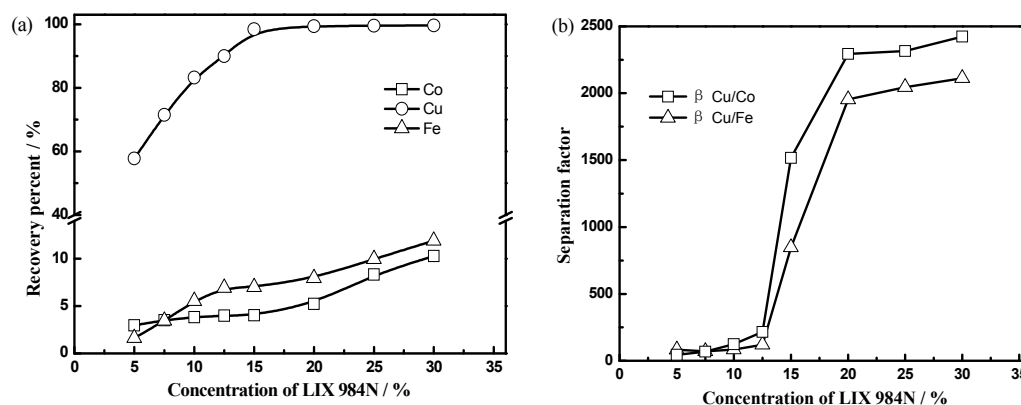


Figure 4. Effect of concentration of LIX 984N on the recoveries of copper, cobalt, and iron (a) and separation factor (b) (A/O phase ratio = 1/1, pH = 1.25, contact time = 20 min, temperature = 25 °C).

3.2.3. Effect of Contact Time

The effect of phase contact time on the recoveries of cobalt, iron, and copper has been studied. An A/O phase ratio was fixed at 1/1 and 20% LIX 984N was applied. Figure 5 shows the test results and it is found that the recovery of copper can reach the maximum within 5 min. When the phase contact time increases from 0.5 min to 5.0 min, the recovery of cobalt and iron were increases from 0.26% to 0.90% and from 2.89% to 4.21%, respectively. Thereafter, there is no obvious change for the three metal ions. It is inferred that the necessary contact time for achieving the recovery equilibrium for copper is 5 min, and this contact time is useful for the separation of copper from other metal ions.

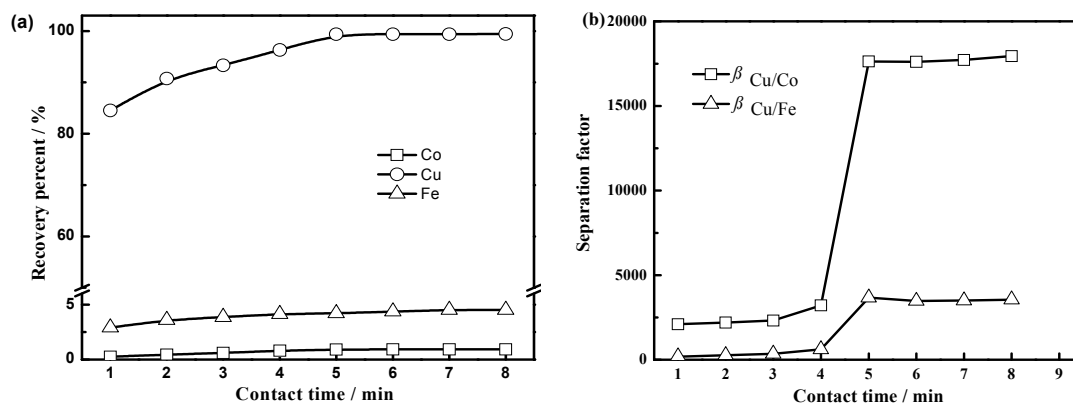


Figure 5. Effect of contact time on the recoveries of copper, cobalt, and iron (a) and separation factor (b) (A/O phase ratio = 1/1, pH = 1.25, LIX 984N concentration = 25% (v/v), temperature = 25 °C).

3.3. De-Ironization via a Precipitation Process

The remaining solution after the copper extraction process had $0.94 \text{ g} \cdot \text{L}^{-1}$ cobalt and $22.62 \text{ g} \cdot \text{L}^{-1}$ ferric ions. The goethite deironization process was then applied to remove the high content of iron. The effects of precipitation conditions, such as equilibrium pH, reaction temperature, and the soaking time, on the removal percent of Fe and Co are investigated in detail.

3.3.1. Effect of Equilibrium pH

Figure 6 shows the effect of equilibrium pH on the removal percent of iron and cobalt. The pH is one of the most critical controlling parameters in the iron removal process because hydrogen ions directly participate in the hydrolysis reaction, according to the reactions (Equations (1)–(3)). As shown in Figure 6, when the equilibrium pH increased from 1.0 to 3.0, the removal of iron was promoted rapidly. 99.46% of iron removal was obtained at pH 3.0. During the iron removal process, the loss of cobalt into the sediments was also a significant issue of concern. From Figure 6, it can also be seen that the cobalt loss increases slowly when the pH is below 3.0, however, it approaches a cobalt loss of 78.47% at pH 4.0. The loss of cobalt may be due to the fact that the goethite formed can adsorb more cobalt ions from the bioleaching solution with an increasing pH value. The precipitation pH controlled at 3.0~4.0 presents satisfactory comprehensive effects.

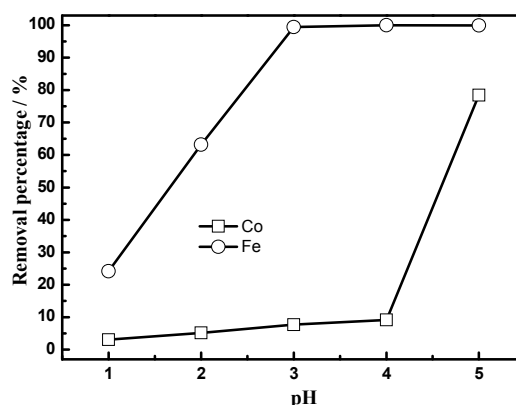


Figure 6. Effect of pH on the removal rate of iron and cobalt (soaking time = 1 h, temperature = 85 °C).

3.3.2. Effect of Temperature

Temperature can influence both the mass transfer speed of the iron removal process and goethite solubility in the leaching solution. As Figure 7 shows, it can be observed that the precipitation

temperature influences the iron removal rate more remarkably than the removal rate of cobalt. 99.08% of the iron removal rate was obtained at 70 °C, while the loss of cobalt was only 5.87%. Therefore, the suitable temperature for the precipitation process was 70 °C.

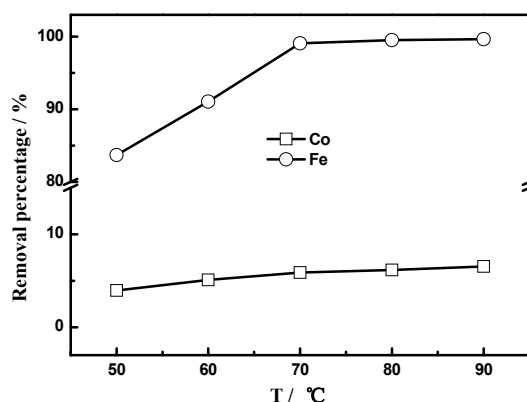


Figure 7. Effect of temperature on the removal rate of iron and cobalt (soaking time = 1 h, equilibrium pH = 3.5).

3.3.3. Effect of Soaking Time

The soaking time of the iron removal process was also studied. As shown in Figure 8, it is found that the soaking time influences the removal rate of iron and cobalt slightly. This means that the iron was removed mainly via forming goethite precipitates and the adsorption of iron and cobalt by the formed precipitates occurred in lesser amounts.

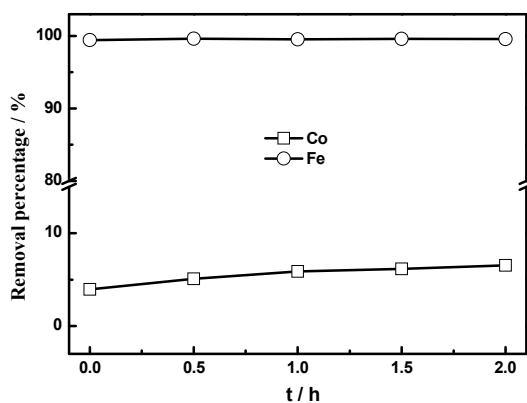


Figure 8. Effect of soaking time on the removal rate of iron and cobalt (temperature = 85 °C, equilibrium pH = 3.5).

From the above, the optimized conditions were obtained. If controlling the experimental conditions of pH value at 4.0, the oxidation temperature at 70 °C, and soaking time at 1 h, then the iron removal rate achieved 99.9% while the loss of cobalt was only 0.5%. The goethite precipitation residue had a very good filterability (Figure 9b). The XRD pattern in Figure 9a confirmed that the precipitate was goethite.

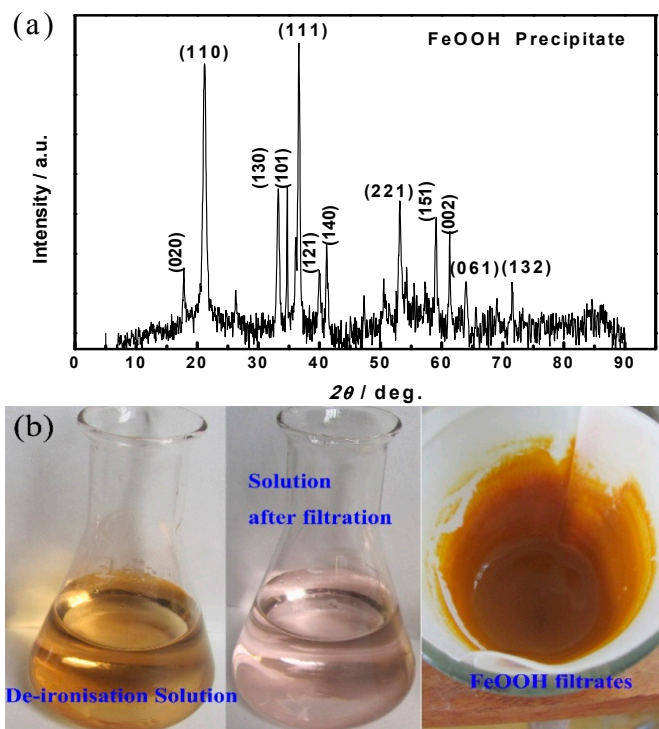


Figure 9. (a) XRD patterns of precipitates; and (b) photographs of the goethite precipitates.

3.4. Preparation of Cobalt Oxalate

After extraction of copper, iron, and the goethite deironization process, Co (II) ions were precipitated as Co (II) oxalate at room temperature immediately. The solid Co (II) oxalate formed here was separated easily by filtration and washed with excess deionized water, then dried in an oven. There was no Co remaining in the filtrate.

In order to figure out the effect of the dosage of sodium oxalate on the formation of CoC_2O_4 powders, the ratio of oxalate and Co (II) was controlled from 0.5 to 4. As seen from Figure 10, it is noted that when the $n(\text{C}_2\text{O}_4^{2-})/n(\text{Co}^{2+})$ was controlled at 2, the highest cobalt recovery rate 99.84% can be achieved and the content of iron impurity in the cobalt oxalate was the lowest.

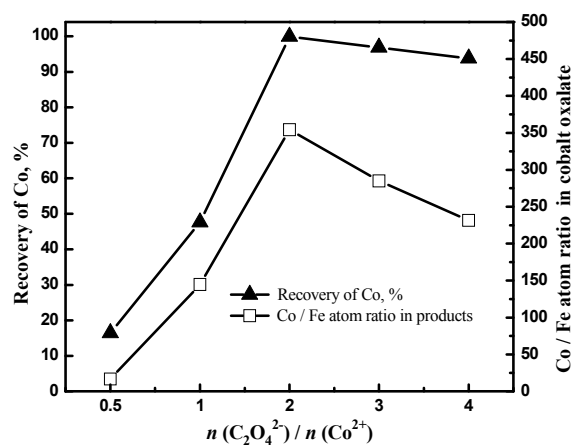


Figure 10. Effect of dosage of sodium oxalate on preparation of cobalt oxalate product in a low concentration solution.

Figure 11 shows the SEM and XRD patterns of cobalt oxalate product. The shape of the powders was rod-like and the XRD pattern of solid residues was confirmed to be well-crystallized orthorhombically-structured Co (II) oxalate with a space group of Cccm (JCPDS file: 25-0250) [16].

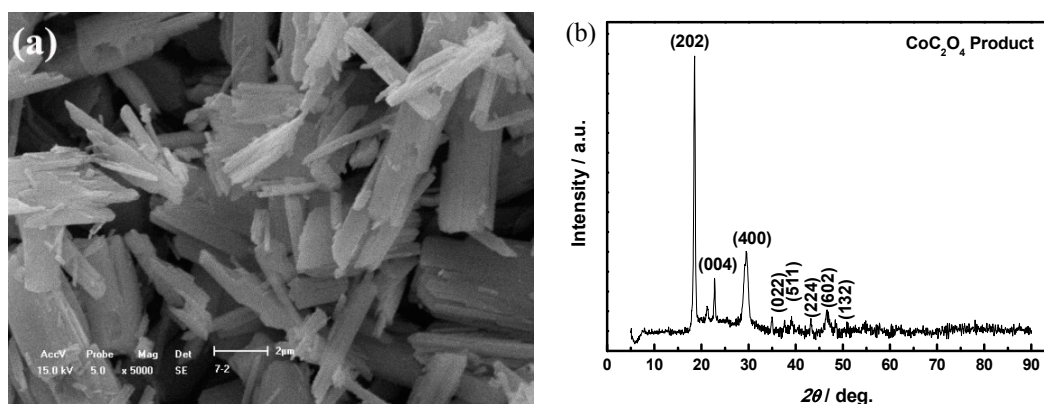


Figure 11. SEM (a) and XRD patterns (b) of cobalt oxalate product in a low concentration of cobalt solution.

4. Conclusions

A hydrometallurgical route for the recovery of Co from cobalt tailings was developed based on the bioleaching and selective sequential extraction technologies. It is found that 96.51% Co and 26.32% Cu can be selectively extracted from the cobalt tailings at 10% pulp density after direct bioleaching for four days. The leaching residue can be sent to a smelter for copper recovery and, from the leaching solution, cobalt can be recovered via selective sequential extraction processes. Copper can be extracted by solvent extraction. When the pH value was fixed at 4.0, oxidation temperature was 70 °C, and soaking time was 1 h, 99.9% of iron can be removed from the solution by the goethite precipitation method. Cobalt oxalate can be finally prepared with sodium oxalate. The total recovery of cobalt during the entire recovery process obtained more than 95%. The successful recovery of cobalt confirms the feasibility of applying a moderately thermophilic bioleaching technique to the recovery of low-grade cobalt ores.

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Author Contributions: Guobao Chen and Hongying Yang conceived and designed the experiments; Guobao Chen and Haijun Li performed the experiments; Guobao Chen and Haijun Li analyzed the data; Linlin Tong contributed materials; Guobao Chen wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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