

Sulphuric Acid Bake-Leach Process for the Treatment of Mixed Copper-Cobalt Oxide Ores

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Abstract

A sulphuric acid bake-leach method for the treatment of mixed copper-cobalt oxide minerals was investigated as an alternative to the reductive leaching method. Sulphuric acid bake-leach process of the mixed copper-cobalt oxide ore was carried out by mixing the sample with sulphuric acid followed by baking of the mixture in a muffle furnace. Baking tests were conducted at different conditions such as temperature, time, and varying amounts of acid. The reacted samples were then subjected to water leaching at room temperature to determine the leachability of copper and cobalt from the baked material. The dissolutions of copper and cobalt were dependent on acid concentration with cobalt showing more sensitivity to the amount of acid. Both copper and cobalt were extracted from the baked material within short leaching times and without the addition of reducing agents. The outcome of this work has shown that the sulphuric acid bake-leach process is a possible alternative to the reductive leaching method for copper-cobalt oxide ores.

Keywords

Democratic Republic of Congo (DRC), Mixed Copper-Cobalt Oxide, Sulphuric Acid Baking, Sulphate, Reducing Agent, Metal Dissolution

1. Introduction

The Central African Copperbelt region of the Democratic Republic of Congo (DRC) and Zambia accounts for more than 50% of the world's cobalt (Co) reserves and one tenth of the world's copper (Cu) reserves [1] [2]. In the oxidised deposits of the DRC, the main cobalt oxide minerals are cobalt carbonate and cobalt (III) oxide. Cobalt carbonate readily dissolves in acid while trivalent co-

balt (Co^{3+}) is insoluble in acid and requires a reducing agent to convert it to divalent cobalt (Co^{2+}) [3] [4] [5]. Cobalt (III) is the major form in which cobalt exists and from which most of the cobalt is produced [3] [4]. The common cobalt (III) minerals exist either in crystalline state as Stainierite ($\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$) or in amorphous state as heterogenite ($\text{CoO} \cdot 2\text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) [3] [6]. Malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) and chrysocolla ($\text{CuOSiO}_2 \cdot 2\text{H}_2\text{O}$) are some of the copper oxide minerals found in the oxidised deposits of the DRC. **Table 1** shows the main copper and cobalt oxide minerals from the Central African Copperbelt region of Zambia and the DRC. The main gangue minerals include dolomite ($\text{CaMg}(\text{CO}_3)_2$) and quartz (SiO_2) [1] [7].

The hydrometallurgical processing of copper-cobalt oxide minerals from the DRC involves leaching the ore/concentrate in sulphuric acid (H_2SO_4). While most copper oxide and cobalt (II) oxide minerals dissolve in sulphuric acid, Co^{3+} does not dissolve in acid during the direct acid leaching. As already stated, reducing agents are added to the leaching system in order to convert the acid insoluble Co^{3+} to soluble Co^{2+} for easy leaching. Commonly used reducing agents for Co^{3+} minerals include sulphur dioxide (SO_2), sodium metabisulphite (SMBS), ferrous ions and hydrogen peroxide (H_2O_2) [1] [3] [5] [6] [8]. A typical reaction for the dissolution of Co^{3+} using SO_2 as the reducing agent is represented by Equation (1) [4]. The leaching of the copper-cobalt ores from the DRC normally takes 2 hours but in some cases, the leaching time can go up to 8 hours [1].



Although the reductive leaching method has been well established in many metallurgical plants of the DRC and Zambia, the leaching time of 8 hours in some hydrometallurgical plants in the DRC is undesirable. Additionally, reducing agents used for Co^{3+} minerals increase the operating cost. Authors [8] and [9] stated that the high consumption of reducing agents during leaching makes the production of cobalt an expensive process. For example, at Shituru Plant in the DRC, reducing agents accounted for 47% of the total operating cost per tonne of cobalt metal produced [8]. Reducing agents, such as SO_2 , are not only

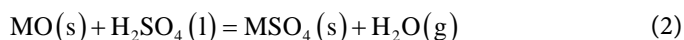
Table 1. Common copper and cobalt minerals found in central African Copperbelt region [1] [6] [7].

	Mineral	Formula
Oxides of copper	Malachite	$\text{Cu}_2\text{CO}_3(\text{OH})_2$
	Pseudomalachite	$\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$
	Cornetite	$\text{Cu}_2(\text{PO}_4)(\text{OH})_3$
	Tenorite	CuO
	Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	Chrysocolla	$\text{CuOSiO}_2 \cdot 2\text{H}_2\text{O}$
Oxides of cobalt	Heterogenite	$\text{Co}_2\text{O}_3 \cdot \text{CuO} \cdot \text{H}_2\text{O}$
	Kolwezite	$(\text{Cu}, \text{Co})_2(\text{CO}_3)(\text{OH})_2$
	Stainierite	$\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	Amorphous heterogenite	$\text{CoO}_2 \cdot \text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$

expensive, but they also cause major environmental problems, and when used in large quantities, SO₂ has an impact on copper recovery [10].

Because of the aforementioned difficulties with the reductive leaching method, it is critical to develop a process that can recover copper and cobalt in a short period of time without the use of reducing agents. Such a process will lower the operating cost of cobalt production as it will eliminate the need of reducing agents. Furthermore, developing such a process will add to the corpus of knowledge on the processing of copper-cobalt oxide ores that already exists.

Therefore, the purpose of this study was to investigate the possibility of recovering copper and cobalt from oxide ores using the sulphuric acid bake-leach process as an alternative to the reductive leaching method. The sulphuric acid baking process is a sulphation process which involves baking of a material with sulphuric acid at a low temperature (<400°C) in order to convert the minerals (oxides or sulphides) to sulphates [11]-[17]. The resulting metal sulphate can then be dissolved in water or mild acid. A typical reaction representing the sulphation of metal oxides is given by Equation (2) where M represents a metal such as copper, cobalt or iron.



2. Experimental

2.1. Materials

A copper-cobalt ore was obtained from Chambishi Metals Plc on the Copperbelt province in Zambia. Chambishi Metals obtained this material from the DRC. Sulphuric acid used in this study was 98% by mass analytical grade. **Table 2** shows the total copper (TCu), total cobalt (TCo), acid soluble copper (ASCu) and acid soluble cobalt (ASCo) as analyzed by atomic absorption spectroscopy (AAS). The chemical composition indicates that the sample contained over 90% acid soluble copper and 43% acid soluble cobalt.

2.2. Acid Baking Experiments

A 20 g copper-cobalt ore sample was mixed with sulphuric acid (*i.e.* 15% to 50% H₂SO₄) in a porcelain crucible. All baking tests were carried out at an acid:ore ratio of 1 to 1 (volume/mass). The crucible containing the mixture was transferred to the muffle furnace (Carbolite RHF 1600) preheated to the desired temperature for baking. The samples were baked at different temperatures (*i.e.* 100°C to 350°C) and times (*i.e.* 30 to 120 minutes) in order to understand the effect of baking temperature and baking time on metal dissolution. After baking the sample for the desired time, the crucible was removed from the furnace and

Table 2. AAS analysis of the as-received copper-cobalt oxide ore.

TCu (%)	ASCu (%)	TCo (%)	ASCo (%)
11.30	10.60	6.39	2.76

those reported by [1] and [7].

Further characterization of the copper-cobalt oxide sample was carried out using scanning electron microscopy (SEM). As seen in **Figure 2**, the scanned area (Spectrum 1) contains strong cobalt, oxygen, and copper peaks. This could indicate the presence of heterogenite, a cobalt oxide mineral. As seen in **Table 1**, heterogenite is a common cobalt oxide mineral found in oxidized deposits of the Central African Copperbelt region [4] [6] [7].

The minor peaks of phosphorus suggest the presence of phosphate minerals such as pseudomalachite or cornetite. The peaks of aluminium and silicon in the point scan indicate the presence of aluminium silicates in association with cobalt and copper oxides.

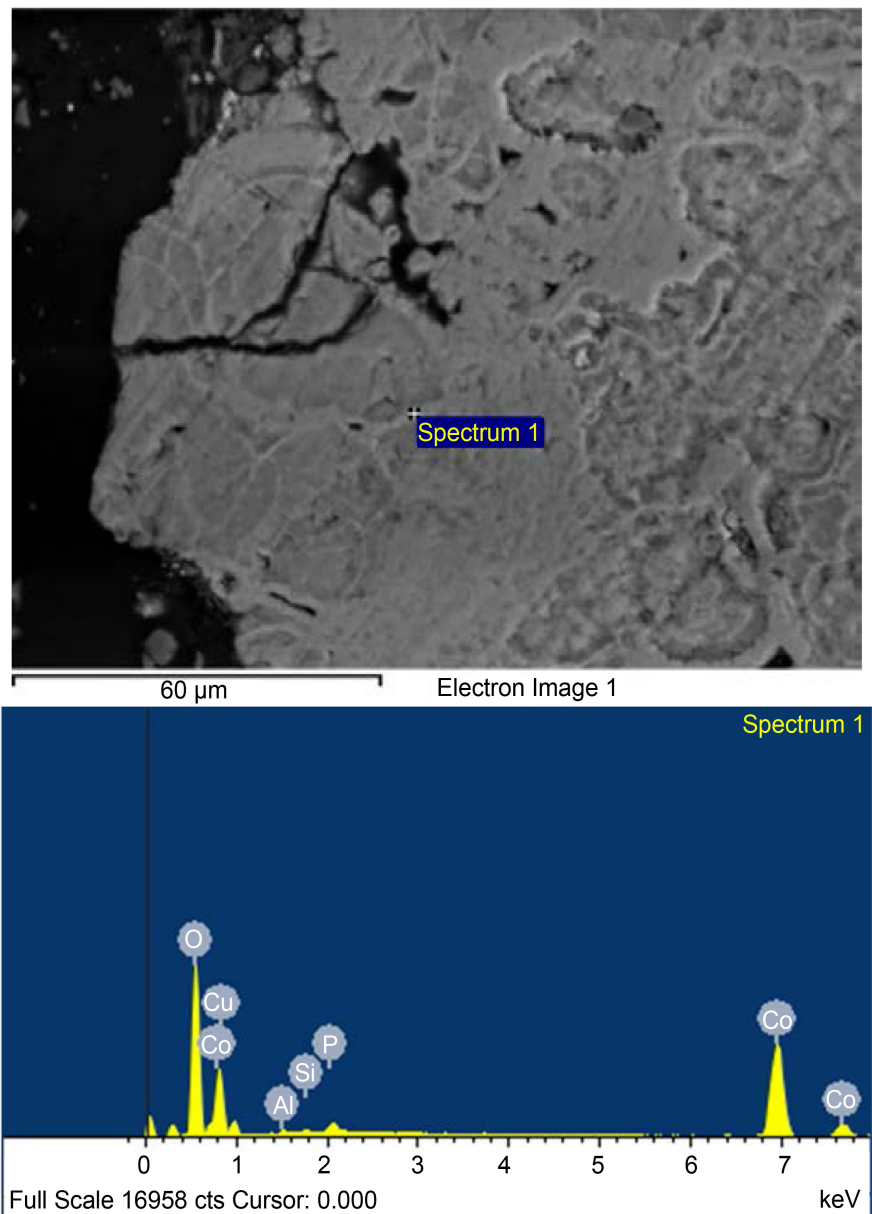


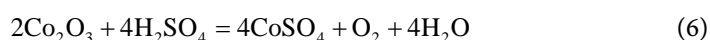
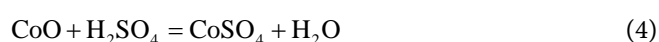
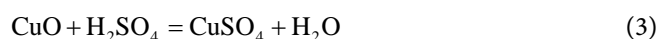
Figure 2. SEM point scan of the copper-cobalt oxide ore.

3.2. Effect of Acid Concentration on Metal Dissolution

Figure 3 shows the results of the influence of acid concentration on metal dissolution from which it can be seen that both copper and cobalt dissolution increased as the acid concentration increased.

More than 80% copper was recovered from the sample at 15% H₂SO₄, whereas only 5.6% cobalt dissolved at the same acid concentration. Increasing the acid concentration to 50% H₂SO₄ resulted in 93 percent and 76 percent dissolution for copper and cobalt, respectively. This rise in cobalt extraction can be due to the fact that, according to [4] and [6], the acid concentration is a key parameter on which cobalt dissolution depends.

It is noteworthy that the sulphuric acid baking process results in transformation of metal oxides to metal sulphates which are soluble in water and mild acid. The suggested reactions for copper and cobalt oxides during the sulphuric acid baking process are represented by Equations (3) to (6). It can be noticed from Equations (5) and (6) that for heterogenite, both Co (II) and Co (III) are converted to cobalt sulphate during sulphuric acid baking process.



Furthermore, the sulphuric acid bake-leach process achieves acceptable levels of copper and cobalt in the pregnant leach solution (PLS). The PLS obtained from a sample baked with 50% H₂SO₄ at 200 °C and 1 hour then leached in water at room temperature for 1 hour contained 33.1 and 13.9 grams per litre (g/L) of copper and cobalt respectively. The concentrations of copper and cobalt in the PLS obtained from the sulphuric acid bake-leach process in this study at the aforementioned conditions are even higher than those obtained from some industrial plants as shown in **Table 3**.

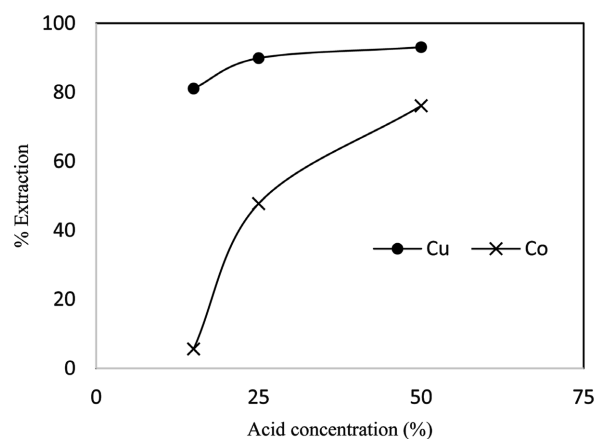


Figure 3. Effect of acid concentration on metal dissolution at baking temperature of 200 °C, 1 hour baking time and 1 hour leaching time.

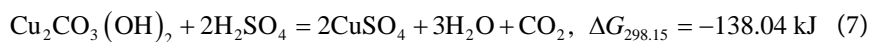
Table 3. Typical content in gram per liter (g/L) of copper and cobalt in the PLS from industrial plants [1] [18].

	Content (g/L)	
	Copper	Cobalt
Oxides	2 - 12	-
Sulphides	12 - 25	7

3.3. Effect of Baking Temperature on Metal Dissolution

It can be observed from **Figure 4** that increasing the baking temperature had a corresponding rise in the dissolution of both copper and cobalt.

As shown from the results, 88% copper was extracted from the material at the baking temperature of 100°C. The mineralogy analysis presented earlier, showed that over 90% of the copper in the sample was acid soluble, predominantly malachite. Previous studies [18] [19] [20] [21] have indicated that copper oxides dissolve in sulphuric acid under atmospheric leaching conditions. Thermodynamically, the dissolution of malachite in sulphuric acid is feasible at room temperature because of the negative value of the Gibbs free energy (ΔG), *i.e.* $\Delta G_{298.15} = -138.04$ kJ calculated using HSC Chemistry 6.0 [22] as presented by Equation (7). Since temperature increases the rate of diffusion, the baking temperature of 100°C accelerated the sulphation of the copper oxides thereby enhancing metal dissolution.



A copper dissolution of 93% was observed in the temperature range of 200°C - 250°C beyond which increasing the baking temperature resulted in decreased copper dissolution. According to [23], there is considerable water formation with either liquid sulphuric acid ($\text{H}_2\text{SO}_{4(l)}$) or gaseous sulphuric acid ($\text{H}_2\text{SO}_{4(g)}$) at temperatures above 200°C. As the water forms during the reactions, it decreases the concentration of H_2SO_4 which results in low vapor pressure of H_2SO_4 at the same temperatures. Therefore, reactions with $\text{H}_2\text{SO}_{4(l)}$ are more likely to occur up to 200°C. Additionally, the rate of evaporation of sulphuric acid increases above 300°C (boiling point of H_2SO_4 : 337°C). Therefore, the decrease in metal extraction beyond 300°C might have been due to increased rate of evaporation of sulphuric acid which led to slow or incomplete sulphation of minerals in the concentrate [15] [16].

Cobalt dissolution increased from 54% at 100°C to 79% at 250°C indicating that temperature had great influence on the dissolution of cobalt. Author [4] listed temperature among the factors that affect the dissolution of cobalt (III). Author [6] quoting [24] stated, “the dissolution of cobalt is highly dependent on temperature”. It is well known that increase in temperature enhances the reaction kinetics of a chemical reaction. Therefore, during the acid bake-leach process of the copper-cobalt ore, increasing the temperature increased the sulphuric acid dissociation thus enhancing its ability to solubilize metals.

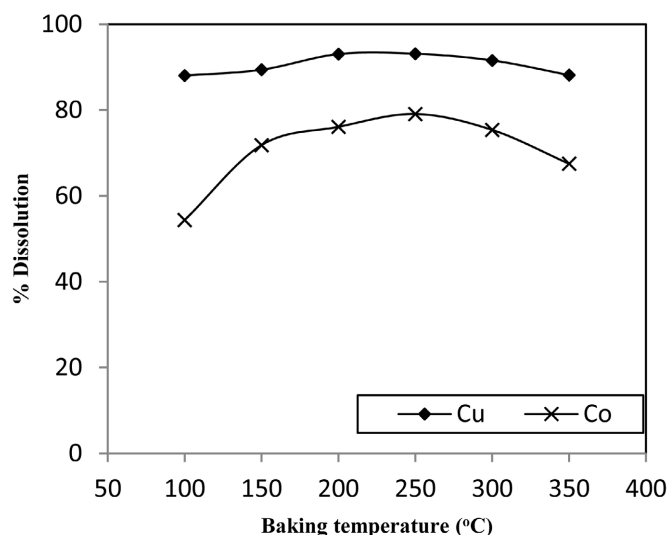


Figure 4. Effect of baking temperature on metal dissolution for material baked with 50% H₂SO₄ for 1 hour followed by room temperature leaching.

3.4. Effect of Baking Time on Metal Dissolution

The effect of baking time on the dissolution of copper and cobalt was studied by varying the baking time between 30 - 120 minutes and the results are shown in **Figure 5**. It can be observed that 30 minutes was sufficient to transform the phases of the ore which could dissolve 91% copper and 74% cobalt. Increasing the baking time to 90 minutes resulted in additional 2.5% and 7.5% extractions for copper and cobalt respectively. Beyond 90 minutes, baking temperature is not an important parameter on the dissolution of copper and cobalt.

3.5. Effect of Leaching Time on Metal Dissolution

After investigating the effects of acid concentration, baking temperature and baking time on metal dissolution, the optimum conditions of 50% H₂SO₄, 200°C baking temperature and 90 minutes baking time were selected for further study of influence of leaching time on copper and cobalt extraction and the results are graphically depicted in **Figure 6**.

The leaching time of 30 minutes resulted in 93% and 83% extractions for copper and cobalt respectively. Increasing the leaching time from 30 minutes to 3 hours resulted in an additional 3% extraction for copper and 9% extraction for cobalt. The fast leaching of copper and cobalt from the baked material can be attributed to the fact that the sulphuric acid baking process transforms the mineral phases of the ore into metal sulphates that readily dissolve in water or mild acid. This observation is consistent with previous studies on the sulphuric acid baking and leaching of other materials. In the study of selective recovery of metals from spent lithium-ion batteries, [16] reported more than 50% cobalt recovery within just 5 minutes of leaching time and 80.4% cobalt recovery in 1 hour of leaching time. Author [17] also reported high copper extraction efficiencies of 92.65%

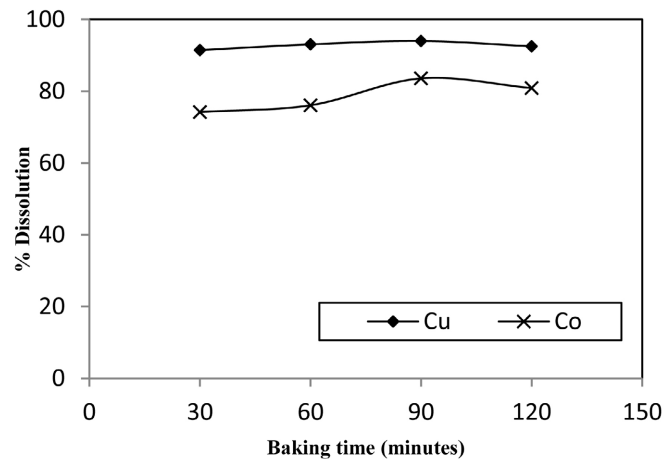


Figure 5. Effect of baking time on metal dissolution at for material baked at 200°C with 50% H₂SO₄ followed by room temperature leaching for 1 hour.

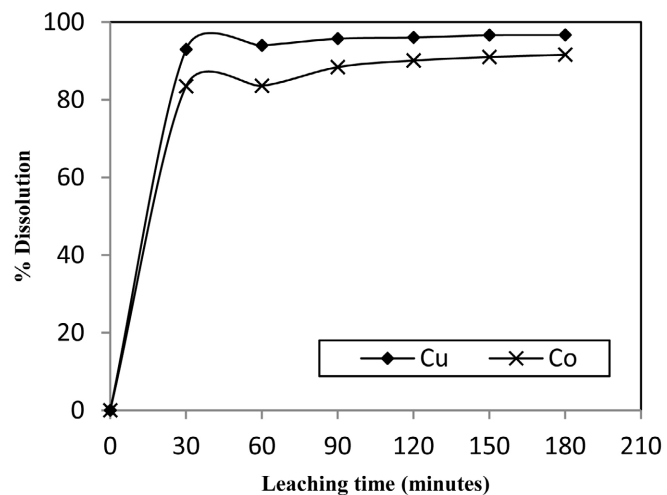


Figure 6. Effect of leaching time on metal dissolution for a material baked at 200°C and 90 minutes with 50% H₂SO₄ followed by room temperature leaching.

after 15 minutes of leaching a roasted calcine during the study of copper recovery from smelting slag.

4. Conclusions

The study has demonstrated that the sulphuric acid bake-leach process has considerable potential for treating mixed copper-cobalt oxide ores. According to the results, both copper and cobalt dissolution increase with increase in the acid concentration with cobalt showing more sensitivity to the amount of acid.

Copper and cobalt dissolution from the sulphuric acid baked material requires shorter leaching times compared to the conventional reductive leaching method therefore, the amount of ore treated is expected to be more. The pregnant leach solution (PLS) from the sulphuric acid bake-leach process contains acceptable

concentrations of copper and cobalt suitable for the solvent extraction process. In this study 33.12 gpl Cu and 13.86 gpl Co were obtained from an ore baked at 200°C with 50% H₂SO₄. It is noteworthy that unlike the reductive leaching method which requires the use of costly reducing agents to convert insoluble Co³⁺ to acid soluble Co²⁺, the sulphuric acid bake-leach process, as demonstrated by this study, does not require the addition of reducing agents since the metal oxides are converted to soluble sulphates during baking. Therefore, the sulphuric acid bake-leach process can be considered a possible alternative to the reductive leaching method for mixed copper-cobalt oxide ores.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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