

Processing of Oxidised and Sulphide Copper Ore Mixtures: Preliminary study

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Abstract. The Many investigations on leaching of different copper sulphide ores from different countries have been conducted and optima working conditions recommended. This work is a preliminary study of leaching of a mixture of sulphides and oxides copper ores from the Democratic Republic of Congo. With the mine deepening a mixture of oxides and sulphides copper is mined. The leaching of the mixture becoming more difficult, thus the need to find new avenues of leaching. Three categories of leaching tests were conducted. In category A, oxide and sulphide ores were separately leached with sulphuric acid where particle size influence was investigated and the best size identified as well as the optimum pH value. Category B, the sulphide ore was leached with sulphuric acid in conjunction with hydrogen peroxide. An improvement in copper and cobalt dissolution was noticeable. In category C, a mixture of oxide and sulphide ores was dissolved with sulphuric acid with hydrogen peroxide. The best mixture was found and optimum pH value identified with pH varied from 1.5 to 2.5.

Keywords: Oxide and sulphide copper ore, processing, mixtures.

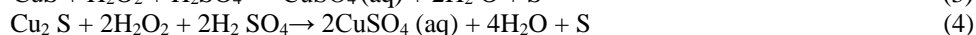
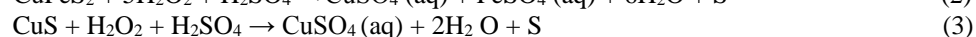
1 Introduction

This The leaching of a copper oxide and sulphide copper ores have been largely reported. Many investigations on the leachability on different copper sulphide ores from different countries have been conducted and optima working conditions recommended. The present work present is a preliminary study on a mixture of sulphides and oxides copper ores from Kamoto mine in the Katanga province in the Democratic Republic of Congo which is located central Africa in the copper belt region. Many investigation son different sulphides copper ores have been conducted using different oxidizing agents. Investigations on leaching of copper (I) sulphide using sulfuric acid with addition of sodium nitrate have been conducted [1]. It was found that the quantity of copper dissolved was increasing with growth of the values of all the parameters namely temperature, concentration of NaNO_3 and H_2SO_4 . Also, the influence of ferric ion on the leaching of chalcopyrite was investigated [2]. It was found that ferric iron plays two important roles in the leaching of chalcopyrite namely as a mineral oxidizing agent and as the agent responsible for chalcopyrite passivation. Further, investigations on the effect of redox potential on the leaching of chalcopyrite was conducted. It was found that although ferric iron is responsible for the oxidation of chalcopyrite, whilst ferrous ion also plays an important role because it was found that it controls precipitation and nucleation of jarosites, which ultimately causes passivation of the sulphide. Same researchers also found that Chalcopyrite dissolves

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through the formation of an intermediary product covellite (CuS) that ferric ion oxidises later, releasing Cu²⁺ ions [3]. Furthermore, the same authors investigated the influence of adding silver as catalyst on the redox potential and found that the surface of chalcopyrite was transformed into copper-rich sulphides such as covellite and geerite [4]. Moreover, many other works have investigated the role of redox potential in the presence of some bacteria have concluded that some microorganisms may lead to solution being overoxidised. Hydrogen peroxide is one of the strong oxidizing agents and it promotes the oxidation of the ore body and leaching potential of sulphuric acid or the leaching medium used. Among the advantages of hydrogen peroxide besides its high oxidizing potential, it is easier to handle than gas oxidants. Investigations on the kinetics and mechanisms of dissolution of the major base metal sulphide minerals, pyrite, chalcopyrite, galena and sphalerite in acidic (chloride) have found that there is a development of a sulphur-rich surface during galvanically-promoted dissolution [5]. Other authors suggested that amongst the mineral sulfides, the most well studied is chalcopyrite and that for this mineral several different passivating species have been suggested more specially elemental sulfur, polysulfides, metal-deficient sulfides, jarosite and jarosite-like compounds [6]. Additional investigations have provided an overview on the mineralogy and geochemistry of sulphide minerals [7] and also provided mechanisms and rate of oxidation of sulphides due to acid mine drainage [8].

The dissolution of copper sulphide minerals in the presence of hydrogen peroxide is thermodynamically feasible according to the following reactions:



The present investigation is a preliminary work on a possible leaching of a mixed sulphide-oxide copper ores from Kamoto in the Democratic Republic of Congo using hydrogen peroxide as oxidising agent.

2 Methodology

2.1 Material and experimental

XRD, XRF and SEM were used to characterise the samples. To conduct the experiments, beakers of 1 litre capacity were used and were covered to avoid high evaporation and decrease of volume of the solutions. To increase the temperature, hot plats equipped with magnetic agitator were used. 10 g of ore were used in all the experiments. The agitation rate was 100 rpm. This was decided as velocity to avoid the formation of a vortex which would possibly dissolve oxygen from air and disturb the process. Time varied from 30min to 90 min with 30 min increase while the temperature was increased from 25 to 40 and 50°C. For category A, 100ml of sulfuric acid were used whereas for category B sulfuric acid was coupled with hydrogen peroxide in couples of (90,10); (80,20); (60,40) and (50,50) ml. In category C, the proportions of oxide and sulphide were coupled in (90,10); (80,20) and (70,30) while the volumes of sulfuric acid and hydrogen peroxide were 90 and 10ml respectively.

2.2 Characterisation

The experiment uses two types of Copper ore samples, copper sulphide and copper oxide ore. The two samples are from Kamoto Oliveira Virgule (KOV) mine located in Katanga province in the DRC. A representative sample was dried, screened using various screen sizes for 30 minutes, shown in tables 1 and 2 below.

From the CUM mass percentage passing it could be observed that the sulphide ores had higher CUM mass % passing than the oxide ore for the sizes -150+160 μm and -160 +75 μm . But the -75 μm the oxide ore had higher CUM mass % passing.

Table 1. Cu-Co Oxide ore screen analyses.

Aperture size(μm)	Mass (g)	Mass %	CUM mass % passing
+150	0.1	0.01	
-150 +106	164.5	27.8	99.99
-106 +75	123.5	20.9	72.19
-75	302.5	51.2	51.2
Total	591	100	

Table 2. Cu-Co Sulphide ore screen analyses

Aperture size(μm)	Mass (g)	Mass %	CUM mass % passing
+150	160.6	27.2	
-150 +106	122.3	20.7	72.8
-106 +75	123.4	20.9	52.1
-75	183.9	31.2	31.2
Total	590	100	

Table 3. XRF analyses of different particle sizes of Cu-Co sulphide and oxide ores

Aperture size(μm)	Mass (g)	Mass %	CUM mass % passing					
Particle (μm)	Mg%	Si%	S%	Ca%	Fe%	Co%	Cu%	Al%
-75 S	1.44	0.99	12.27	3.9	15.2	0.1	28.85	
O	1.32	36.63	12.01	4.09	1.8	0.46	7.53	1.32
	2.03	3.38	10.45	3.89	14.61	0.1	27.81	
+75 S	2.96	36.27	12.01	4.09	1.85	0.47	7.64	1.28
O	1.47	1.04	12.01	4.09	15.23	0.11	28.95	

Table 4. XRF chemical Analyses of Representative Ore of Cu-Co sulphide and Oxide sample.

Component	Mg	Al	Si	P	S	Ca	Fe	Co	Ni	Cu	Zn
Weight S	1,74	0,19	0,75	0,39	13,75	4,28	14,77	0,1	0,13	26,18	0,00
O	3,46	1,41	36,53	0,25	0,03	0,32	1,71	0,44	0,01	6,81	0,03

*S =sulphide *O= oxide

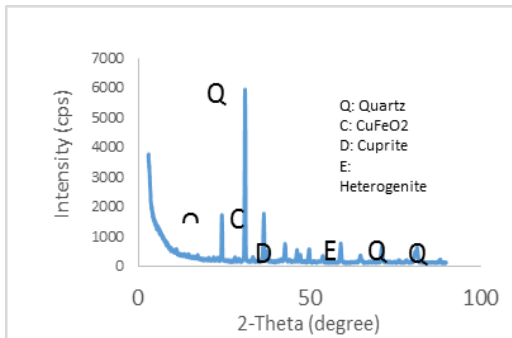


Figure 1. XRD pattern of Cu-Co oxide

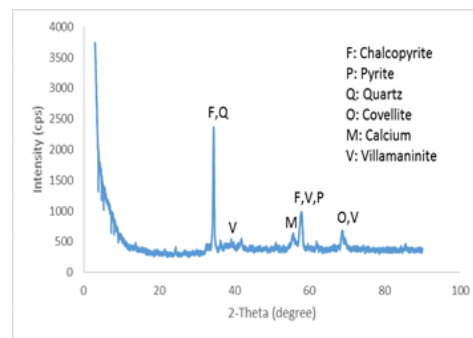
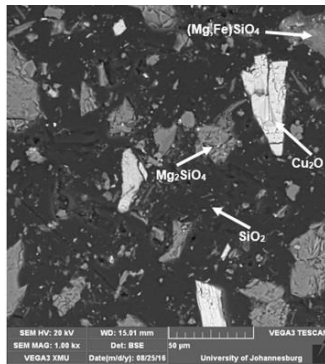
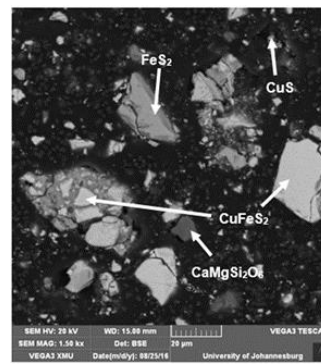


Figure 2. XRD pattern of Cu-Co sulphide



a)Oxide ore



b) sulphide ore

Figure 3: SEM micrograph of polished section of copper

Table 5: Percentage of minerals: copper oxide sample.

Element	F	Mg	Al	Si	P	Cl	Fe	Cu	O	Mineral
Weight %	0,2	0,75	0,5	0,97	1,6	0,0	0,24	72,8	22,6	Cuprite
	6		9		6	1		3	8	
	1,1	8,61	0,0	39,3	0,0	0,0	0,01	0,27	50,5	Fosterite
	5		2	7	1	2			8	e
	0,1	1,84	0,8	42,0	0,3	3,2	0,2	0,85	50,5	Quartz
	8		3	2	3	1			3	

1,6	16,0	6,7	14,0	0,4	2,7	18,4	3,72	39,3	Olivine
	7	2	3	6	8	7		6	

Table 6: Percentage of minerals: copper sulphide sample.

Element	Mg	Si	S	Cl	Ca	Ti	Mn	Fe	Cu	O	Mineral
Weight %	0,02	0	18,3	0,01	0,02	0,04	0,01	7,69	35,6	38,5	Cuprite
	10,6	26,5	0,08	0,01	16,1	0	0	1,8	0,67	44,3	Fosterit
	0,8	0,01	10,1	0,02	0,01	1,6	0,3	63,5	0,75	23	Quartz
	2,21	1,04	15,6	3,02	0,77	0,01	0,1	11,4	28,9	36,9	Olivine
									1		

3 Results and discussion

3.1 Leaching with sulphuric acid only on Cu-Co oxide and sulphide ore (Part A)

3.1.1 Effect of particle size

The effect of particle size on the dissolution of copper and cobalt was studied from Cu-Co oxide ore (figure 1A) and sulphide ore (figure 1B). The experiment was done using different particle sizes of 100 % passing 75 μ m (<75) ,+106-75 (>75) and +150-106 μ m (>106).

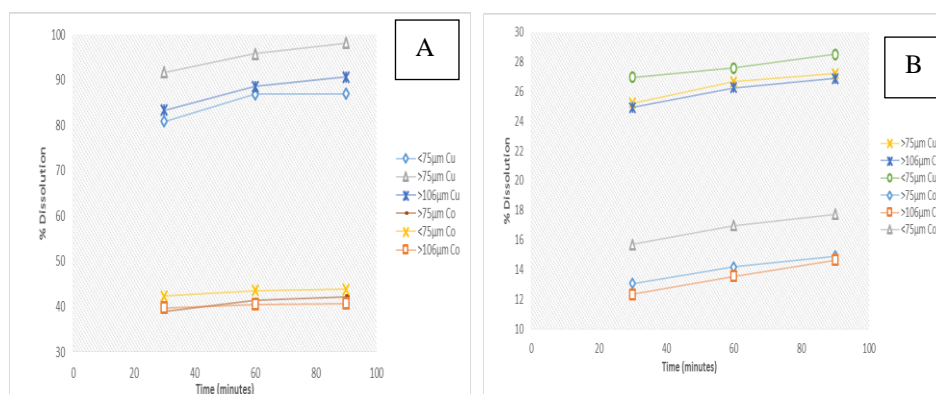


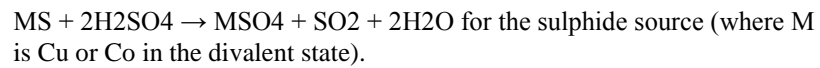
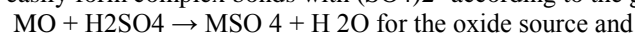
Figure 4. Effect of different particle sizes on the %dissolution of copper and cobalt in oxide (A) and sulphide (B) ore.

Results from the oxide ore referring to figure 4A show that the % dissolution of copper and cobalt increase with a decrease in particle size. This is due to the fact that there is an increase in surface area which results in exposure of the ore particles to the leaching reaction therefore increasing contact between the leaching agent and the targeted metal. The results on the oxide ore (figure 4A) show a high percentage dissolution of copper at a particle size of >75 μ m with 98.2% dissolution of copper. For cobalt the results (still on figure 4A) high percentage dissolution is obtained at a particle size of <75 μ m. It evident from the results shown in figure 4A that the smaller the size particles the higher the percentage dissolution of copper and cobalt. The percentage dissolution of copper and cobalt from the sulphide ores in comparison with their behaviour from the oxide was as well investigated. Results demonstrated (figure 4B) that the recovery of Cu and Co from the sulphide ores was far lower as compared to that from the oxide

leached at the same conditions. This is due to the fact that, despite the size reduction of particle sizes aiming to expose more particles to the leaching agent, the elementary sulphur present in the sulphide mineral render this latter refractory regarding to the H_2SO_4 .

3.1.2 Effect of pH

In this experiment the effect of different pH values on the percentage dissolution of copper and cobalt was studied on both Cu-Co oxide ore (figure 5A) and sulphide (figure 5B). The leaching investigation took place at varying pH values of 0.5; 1 and 1.5 in accordance with the thermodynamic prevision of the Eh-pH diagram. In the pH range of 0.5 to 1.5 there is a possibility of having Cu and Co in their ionic states of Cu^{2+} and Co^{2+} (as shown later on figure 8) these ions can easily form complex bonds with $(SO_4)^{2-}$ according to the general equations:



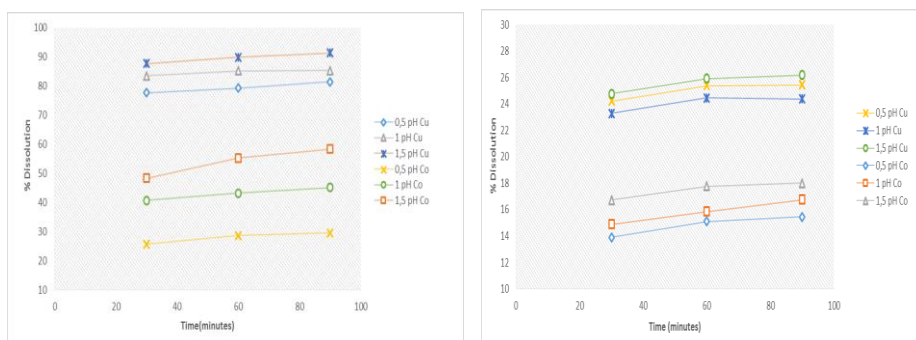


Figure 5. Effect of different pH values on the %dissolution of copper and cobalt in oxide (A) and sulphide (B) ore.

According to the results illustrated in figure 5A it is seen that after 90 min at pH 1.5, 91.4% of Cu and 58.4 % of Co were recovered from the oxide ore while from the sulphide ore shown in figure 5B which was experimented in the same conditions only 26.2 % of Cu and 18 % of Co were recovered. The low dissolution of Cu and Co from sulphide may be justified by the fact that, beside the fact that elementary S make these ores refractory, the formation of polysulphides, metal-deficient sulphides, jarosite and jarosite-like compounds during the leaching passivate Cu and Co and makes their dissolution to decrease rapidly.

In both cases, in the oxide and the sulphide ores it was noticed low dissolution of Co. Most of mineral occurring in the copper belt region contain cobalt in the form of heterogenite (shown in figure 1) where it is in 2+ and 3+ states. Because the above described situation only cobalt 2+ will pass into the solution. This requires the use of a reducing agent in order to reduce the remaining Co^{3+} to Co^{2+} .

At a higher pH (>1.5) the leaching would produce solid compound of copper (CuFeO_2) and cobalt ($\text{CoO} \cdot \text{Fe}_2\text{O}_3$) as illustrated in the Eh-pH diagram in figure 9 a) and b).

3.1.3 Effect of temperature

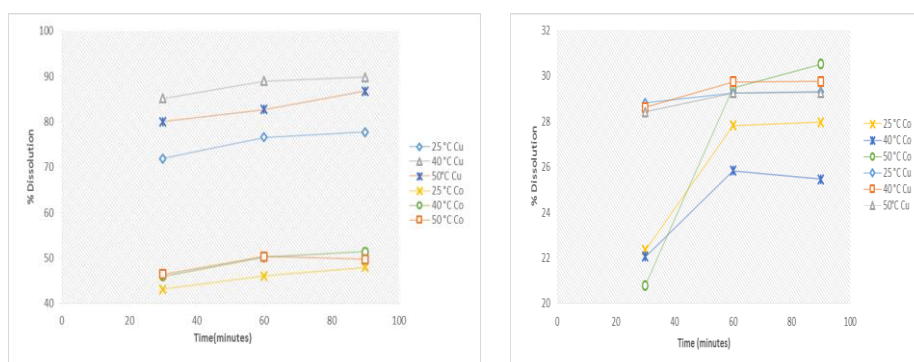


Figure 6: The effect of temperature on %dissolution of copper and cobalt oxide (A) and sulphide (B) ore.

The effect of temperature was also studied on the Cu-Co oxide ore (figure 6A) and the sulphide ore (figure 6B). The experimental temperature values that were used in the present investigation were 25, 40 and 50°C. Results shown in figure 6 both A and B reveal that the dissolution of both copper and cobalt were affected by the increase in temperature since the rate of reaction is directly linked to the increase of temperature. It is noticed that the dissolution of Cu and Co increased with the increase in temperature from 25°C to 40°C then decreased at 50°C. According to the results shown in figure 6A, after 90 minutes of leaching, it is noticed that 89.8 % of Cu and 49.7 % were recovered from the oxide ore on the other hand as shown on figure 3B after 90 minutes of leaching only 29.8 % and 25.5 % of Cu and Co were respectively recovered from the sulphide ore. The low percentage dissolution of cobalt and copper from the sulphide ore can still be justified by the fact that it is a refractory ore and it cannot be recovered by traditional (conventional) methods.

3.1 Leaching with sulphuric acid in conjunction with hydrogen peroxide of Cu-Co sulphide ore (Part B).

Leaching of copper sulphide ore only with varying H₂O₂ volumes and 1M H₂SO₄. Due to the fact that it was noticed there was low percentage dissolution of Cu and Co during the leaching of sulphide ores, the use of an oxidizing agent was compulsory to oxidise the sulphide ore making it easier to leach the targeted metal. Therefore, the effect of varying the concentration of hydrogen peroxide when leaching with sulphuric acid on Cu-Co sulphide ore was studied as shown in figure 7 below, the volume of hydrogen peroxide was varied at 10, 20, 40 and 50mL.

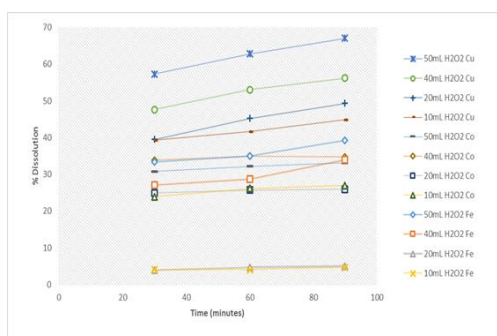


Figure 7. Effect of H₂O₂ on dissolution of copper, cobalt and iron at pH1.5

The experiment where 10 mL of hydrogen peroxide was added to the leaching system yielded 44.8% Cu and 27.0% Co. Adding 10 mL dissolved the least copper and cobalt into solution, with cobalt increasing at a steady rate and copper increasing rapidly.

When 20ml of hydrogen peroxide was added the percentage dissolution of copper was 49.3% and cobalt 27.2%. These results show that hydrogen peroxide have a significant impact on the recovery of copper and cobalt, as compared to adding 10mL of hydrogen peroxide the recovery shows an increase.

The results of adding 40mL of hydrogen peroxide yielded higher percentage dissolution as compared to adding 10 and 20mL of hydrogen peroxide. The results show that 56.1% of Cu and 34.0% of Co was recovered.

The final experiment was conducted by adding 50mL of hydrogen peroxide which yielded the highest copper and cobalt recovery at 67.0% and 34.2%. These findings reveal that with increasing volume of hydrogen peroxide added to the leaching system the greater the percentage dissolution of both copper and cobalt within the 90 minutes of leaching.

It is expected that when adding a significant amount of hydrogen peroxide the leaching potential should increase, this experiment proved this theory correct as the highest potential (mV) was obtained with adding 50mL of hydrogen peroxide, which increased from -1.52 mV to 960 mV, this is further explained in figure 9 (further below). This is because hydrogen peroxide is a strong oxidising agent thus promoting oxidation, in this case hydrogen peroxide oxidises the copper sulphide, therefore increasing the percentage dissolution of copper. As shown before, the percentage dissolution of both copper and cobalt in sulphide ore was lower when leaching without hydrogen peroxide but after the addition of hydrogen peroxide the percentage dissolution of copper and cobalt increased, this is supported further graphically in figure 8 (further below).

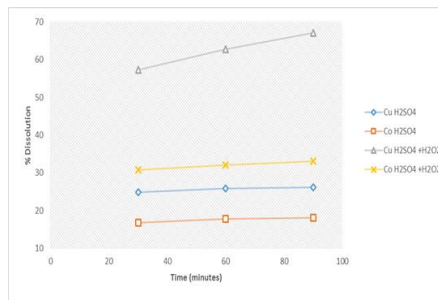


Figure 8. leaching with sulphuric acid (1M) only and leaching with sulphuric acid in conjunction with hydrogen peroxide (50mL) of Cu-Co sulphide ore at 1.5 pH

The results in figure 8 illustrate the comparison of leaching with sulphuric acid only and leaching with sulphuric acid mixed with hydrogen peroxide, these experiments are performed using Cu-Co sulphide ore. The objective of this experiment is to justify the efficiency of hydrogen peroxide on the percentage dissolution of copper and cobalt which is evident looking at that copper increased from 26.2% without adding hydrogen peroxide to 67.1% when adding (50mL) hydrogen peroxide. As for cobalt it was also seen to increase from 18% to 33.1% when leaching in conjunction with hydrogen peroxide.

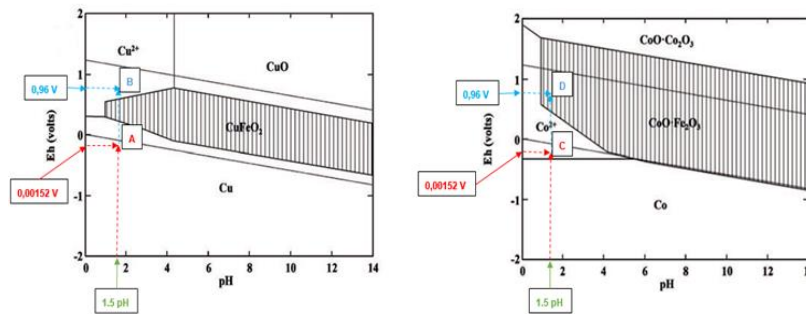


Figure 9. Eh-pH diagrams for Cu system (A) and Co system (B) showing the effect of adding hydrogen peroxide on the leaching potential

Hydrogen peroxide plays an important role in this leaching experiment, the above figure is still based on the leaching with and without hydrogen peroxide experiment which shows the effect of hydrogen peroxide thermodynamically. Leaching of Cu-Co sulphide ore with sulphuric acid only at 1.5 pH measured a potential of 0.00152V but when hydrogen peroxide was added the potential measured 0.96V which causes a shift in the positioning of the aqueous electrochemical system, seeing figure 9A for copper the aqueous system was repositioned to Cu^{2+} ionic boundary from a Cu stable state boundary. According to figure 9B the results show that for cobalt the aqueous system repositioned from stable Co to $\text{CoO.Fe}_2\text{O}_3$ ionic boundary after the addition of hydrogen peroxide. This experiment proves that the hydrogen peroxide (oxidizing agent) did increase the leaching potential (Eh) of the system thus increasing percentage dissolution for both copper and cobalt.

3.2 Leaching with sulphuric acid in conjunction with hydrogen peroxide of mixed Cu-Co oxide and sulphide ore (Part C).

The effect of varying the ratios of oxide and sulphide copper ore while adding 10mL of H_2O_2 was studied, varying oxide: sulphide ore at 90:10, 80:20 and 70:30. The results shown in figure 10 showed that when mixing oxide and sulphide ores at a ratio of 70:30; 62.0% of Cu and 26.0% of Co were recovered. This was the lowest percentage dissolution when compared to the other experiments that were conducted.

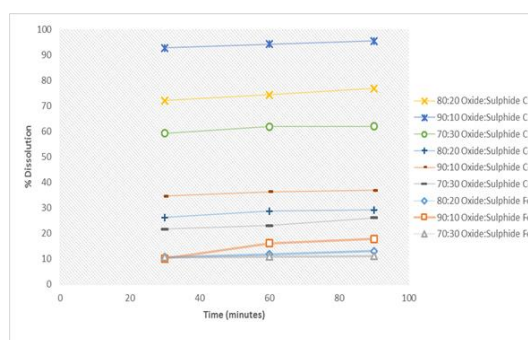


Figure 10. Effect of ratio of oxide and sulphide Cu-Co ore on the %dissolution of copper, cobalt and iron

The experiment where the ore ratio of 80:20 was used yielded a higher recovery than the 70:30 ore ratio in both metals. The percentage dissolution of the metals in this experiment was 76.8% Cu and 29.1% Co.

The ratio of 90:10 showed a high percentage dissolution of copper at 95.4%. This finding is reasonable because most of the copper was in oxide form ("90") than in sulphide ("10") and it has been proven in experiments discussed earlier that Cu-Co oxide ore respond to leaching very well with or without an oxidizing agent. Still referring to figure 10 the percentage dissolution of cobalt was also affected by the varying ratios of the oxide and sulphide ore. Amongst the ratios again 90:10 showed higher percentage dissolution of just 36.8%, this finding was the same for the percentage dissolution of iron which was higher at a ratio of 90:10 at a recovery of 17.7%.

4 Conclusions

The effects of leaching with sulphuric acid only and leaching with sulphuric acid in conjunction with hydrogen peroxide were investigated. The following was observed:

Part A: Leaching the oxide ore and sulphide ore separately with sulphuric acid only.

The recovery of copper and cobalt increased by employing the most efficient conditions of the leaching parameters which are particle size, pH and temperature.

The particle sizes -75 and +75 μm were found to be more efficient yielding higher percentage dissolutions than other particle sizes (+106 μm) used in the study. The results showed that the highest percentage dissolution was 96.2% Cu and 43.9% Co when leaching oxide ore and for sulphide ore 28.5% Cu and 17.7% Co was obtained. At at 1.5 pH higher percentage dissolution of copper and cobalt were obtained than when leaching at 0.5 and 1 pH. The highest percentage dissolution was found to be 91.4% Cu and 58.4% Co in oxide ore and for sulphide ore it was found to be 26.2% Cu and 18.0% Co.

The influence of the temperature showed that the percentage of copper and cobalt dissolved increased when the temperature increased. The highest percentage dissolution obtained was 89.8% Cu and 51.4% Co in oxide ore and 29.3% Cu and 30.4% Co for sulphide ores.

Part B: Leaching the sulphide ore with sulphuric acid in conjunction with hydrogen peroxide.

As observed earlier, leaching the sulphide ores with sulphuric acid only yielded very low copper and cobalt, which was not satisfactory thus a need for an oxidizing agent.

The effect of varying the concentration of hydrogen peroxide when leaching with sulphuric acid on sulphide ores showed that adding 50mL of hydrogen peroxide was more efficient than 10, 20 and 40 mL. The results showed that copper increased from 26.2% to 67.1% when adding (50mL) hydrogen peroxide.

The cobalt increased from 18% to 33.1% when leaching in conjunction with hydrogen peroxide.

Part C: Leaching the mixed oxide and sulphide ore with sulphuric acid mixed with hydrogen peroxide.

Finally in this study the behavior of mixed ores was closely observed. Oxide and sulphide copper ore ratios were varied while adding 10mL of hydrogen peroxide. From the results it was noticed that higher percentage of dissolution was obtained at a ratio of 90:10 with copper at 95.4% and cobalt at 36.8%.

A final experiment was conducted using the optimum ore ratio of 90:10 (oxide: sulphide) and adding 50mL of hydrogen peroxide working at pH 1.5 and 2.5. It was found that at pH 1.5 higher percentage dissolution of copper, cobalt and iron was obtained. This finding was also supported thermodynamically that when leaching at pH 1.5 it is more likely to position the Co/Cu/Fe aqueous system in an ionic boundary where copper, cobalt and iron are dissolving into solution. This study shows the significance of leaching at different pH values and how it affect the dissolution of copper and cobalt. The behavior of ferric iron should be well investigated to understand its influence on the leaching under this work conditions.

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