Leaching of Copper, Cobalt, and Nickel from Complex Ore

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Abstract The paper focuses on leaching of complex copper–cobalt–nickel ore from Mwinilunga district in Zambia, containing 0.6% Cu, 0.21% Co, 2.6% Fe, and 0.13% Ni. Mineralogical examination of the ore using scanning electron microscope (SEM) showed that copper, cobalt, and nickel exist in fine particles of heterogenite and limonite mineral phases. The effects of leaching temperature, pH, and sodium metabisulphate (SMBS) addition were studied. The optimal conditions were found as follows: leaching temperature of 65–75 °C, leaching time of 1 h, and SMBS addition at 0.6 wt%. Copper, cobalt, and nickel were recovered from the leach solution via precipitation with sodium sulphide and magnesium oxide. Sodium sulphide was more selective than magnesium oxide.

Keywords Heterogenite · Copper · Cobalt · Nickel and leaching

Introduction

Copper, cobalt, and nickel have wider applications [1–3]. Worldwide demand for these metallic components is increasing with the rising demand for high temperature applications, digital devices, and built environment and increasing focus on decarbonisation of the global economy [1–3]. Nickel and cobalt are used for production of high temperature super alloys. Nickel is used in batteries, including rechargeable nickel–cadmium batteries and nickel–metal hydride batteries used in hybrid vehicles [4]. On the other hand, cobalt is used for making strong magnets, energy storage devices, e.g. lithium–cobalt oxide batteries [5, 6].

The copper–cobalt ore deposits in Mwinilunga district of the North Western province of Zambia contain nickel in the range of 0.05–0.3 wt%. Owing to the high demand for nickel, it is important to recover it alongside copper and cobalt.

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The common method of treating low grade oxide ores is via leaching in which the base metal(s) is selectively dissolved in acidic media [7]. The dissolution of the base metal requires that the matrix of host phase is broken during leaching. For example, leaching of copper and cobalt which is chemically combined with nickel, iron, manganese, will lead to dissolution of all these elements in solution. Copper and cobalt are chemically combined with nickel, manganese, aluminium, and silica, in the Mwinilunga deposits. Therefore, two problems might be encountered during hydrometallurgical treatment of this ore:

i. High acid consumption owing to dissolution of other elements (Ni, Fe, Mn, Al, and Mg) which are chemically combined with copper and cobalt.
ii. Produces a contaminated leach solution due to the presence of other dissolved elements.

Recovery of Cu, Co, and Ni from Leach Solution

Precipitation is the cheapest method of recovering copper, cobalt, and nickel from the leach solution. At commercial scale, selective precipitation is achieved by controlling pH as the respective compounds precipitate out at different pH values. The common reagents which are used to precipitate out copper, cobalt, and nickel are alkaline salts (MgO, CaO, NaOH, Na_2CO_3) [1, 2]. In essence, iron is first removed from the leach solution as it precipitates out at a lower pH than copper, cobalt, and nickel, and hence, it could contaminate these elements. Nonetheless, some cobalt is lost out as it co-precipitates with iron [8]. In addition to loss of cobalt via co-precipitation with iron, more serious problems might be encountered when the leach solution contains aluminium and magnesium sulphate, such as (i) high consumption of alkaline salts and, (ii) contamination of copper precipitate with aluminium as they precipitate in the similar pH range.

Precipitation with Sodium Sulphide

Sodium sulphate (Na_2SO_4) is more stable than copper, cobalt, nickel, and iron sulphates. On the other hand, copper, cobalt, nickel, and iron sulphides are more stable than sodium sulphide (Na_2S). This means that when sodium sulphide is reacted with copper, cobalt, nickel, and iron sulphates, an exchange reaction will occur as represented by Eq. 1 where M represents Cu, Co, Ni, Fe, etc.

$$MSO_4 + Na_2S = MS + Na_2SO_4 \tag{1}$$

The plot of Gibbs free energy changes against temperature for the precipitation of Cu, Co, Ni, Fe, and Mn with sodium sulphide via Eq. 1 shown in Fig. 1. One

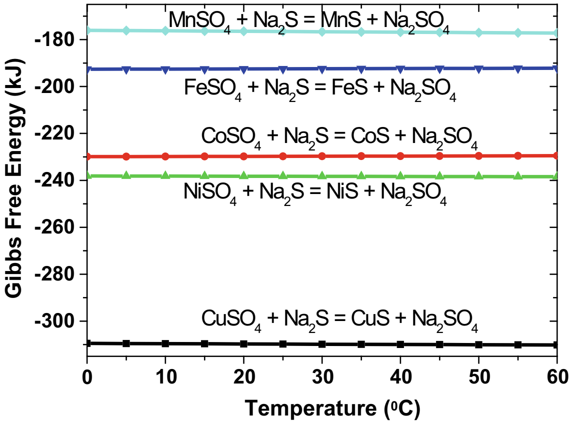

Fig. 1 Plot of Gibbs free energy against temperature for the precipitation of Cu, Co, Ni, Fe, and Mn with sodium sulphide [9]

important feature which can be observed from Fig. 1 is that selective precipitation can be achieved owing to the difference in the stability of the respective sulphides. The following observations can be made from Fig. 1:

1. There is a wide window between the precipitation of CuS and NiS, and hence, the former can be selectively precipitated.
2. There is a narrow window between the precipitation of CoS and NiS such that a mixture of CoS and NiS can be obtained during precipitation.
3. There is a wide window between the precipitation of CoS and FeS such that it is possible to selectively precipitate out CuS, CoS, and NiS, and hence, the former can easily be selectively precipitated.

There are no studies that have been carried out on Mwinilunga copper–cobalt ore, and hence, this paper focuses on processing of this ore.

Experimental Procedure

The sample was collected from Mwinilunga district of the North Western province of Zambia. The as-received sample was crushed in a laboratory jaw crusher and ground down to particle size of less than 150 µm. The full analysis of the sample is shown in Table 1 from which it can be observed that the sample contains 0.57 wt% copper,

Table 1 Analysis of the as-received sample

Cu	Co	Fe	Mn	Ni	Ca	Si	Mg	Al	F
0.57	0.20	2.41	0.42	0.13	1.39	23.48	14.94	4.99	0.89

0.2 wt% cobalt, and 0.13 wt% nickel. It is worth noting that no studies have been conducted on such material.

Leaching Experiments

A representative portion of the sample was collected and placed in a Pyrex glass. The weight of the sample in each experiment was 500 g. All samples were leached at 33% solids. The following parameters were varied during experiments in order to study their effects: temperature, pH, and quantities of sodium metabisulphite (SMBS). SMBS was added in powder form after the experiment had reached the set pH. A constant pH of the solution was maintained throughout the experiment.

Precipitation of Copper, Cobalt, and Nickel

Copper, cobalt, and iron were precipitated with magnesium oxide or sodium sulphide (Na_2S). Both magnesium oxide and sodium sulphide were added in slurry form at strength of 10% in order to minimise localised precipitation. The precipitation of copper, cobalt, and nickel hydroxide is dependent on pH, and hence, these experiments were carried out at fixed pH for a period of 1.5 h. Precipitation of copper was carried out at pH of 5.5, whereas cobalt and nickel were precipitated at pH of 8.5. Iron has a tendency of precipitating alongside cobalt and nickel, and hence, iron removal stage prior to precipitation of copper was carried out. For precipitation of copper, cobalt, and nickel with sodium sulphide, a stoichiometric amount was added by following Eq. 1.

Analysis of the Sample

As-received and reacted (after experiments) were all analysed and examined by atomic absorption spectroscope (AAS) and scanning electron microscope, respectively. The SEM machine is equipped with energy dispersive X-ray fluorescence spectroscopy (EDX) which allows both overall and phase quantification of the sample.

Results and Discussion

Scanning electron microscope image of the as-received sample is shown in Fig. 2. The phases were examined by analysing the individual particles in the sample. The

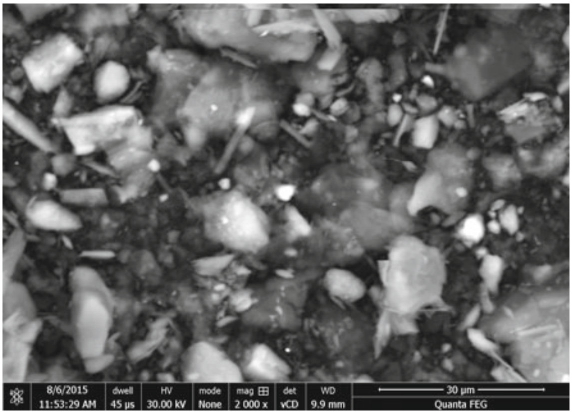

Fig. 2 Scanning electron microscope image under backscattered electron imaging of the as-received sample. The bright areas are the Cu–Co bearing particles

main gangue minerals were enstatite ($MgSiO_3$), pyrope ($Mg_3Al_2(SiO_4)_3$), and humite group ($(Mg,Fe)_7(SiO_4)_3(F,OH)_2$). On the other hand, the major Cu–Co–Ni bearing minerals are malachite, heterogenite, limonite, and complex magnesium aluminium silicate.

Leaching

The results showing effects of leaching pH and temperature are shown in Table 2 from which the following can be observed:

Table 2 Leach test results showing effect of pH and temperature on % recovery. Samples leached at 70 °C in (a) and at 25 °C in (b)

pH	SMBS (wt%)	% Recovery				Acid consumption (kg/ton ore)
		Cu	Co	Fe	Ni	
(a)						
pH = 1.4	1.0	81.58	88.57	36.10	70.00	138
pH = 1.6	1.0	74.91	88.57	20.75	58.46	106
pH = 1.8	1.0	70.18	81.90	14.11	58.46	67
pH = 2.0	1.0	74.21	81.90	17.84	61.54	40
(b)						
pH = 1.4	1.0	55.92	71.82	1.754	29.23	74
pH = 1.6	1.0	58.78	73.00	0.439	31.54	72
pH = 1.8	1.0	53.06	77.27	4.825	30.77	69
pH = 2.0	1.0	51.84	85.91	0.877	34.62	39

i. The recoveries of Cu, Co, Fe, and Ni are decreasing with increase in pH for the sample that was leached out at 70 °C.
ii. The consumption of sulphuric acid was decreasing with increase in pH for the sample that was leached out at 70 °C.
iii. There was minimal change in the recoveries of Cu and Ni, whereas that of co increased with increase in pH for the sample that leached out at 25 °C.
iv. The recovery of iron is lower at all pH range for the samples that were leached out at 25 °C compared to 70 °C.
v. Acid consumption is much higher at pH of 1.4 and 1.6 for the samples that were leached out 70 °C than at ambient temperature. However, acid consumptions were similar at pH of 1.8 and 2.0.

From the above observations, it can be concluded that high recoveries can be achieved when the sample is leached out at high temperature (70 °C). Nonetheless, pH should be 1.8 and above in order to have less acid consumption. High recoveries were obtained at high temperature because the complex copper–cobalt–nickel–magnesium–silicate matrix is broken down.

The results showing effect of SMBS addition and quantities is shown in Table 3 from which it can be observed that the recoveries of Cu, Co, and Ni were extremely poor in the absence of SMBS at both 25 and 70 °C. On the other hand, recoveries of Cu, Co, and Ni all increased when 0.6 wt% SMBS was added. However, there was minimal increase in recoveries of Cu, Co, and Ni when SMBS was added beyond 0.6%. Based on the results in Table 3, it can be concluded that the optimum SMBS addition is 0.6 weight %. By comparison, better recoveries were obtained at 70 °C than at 25 °C.

Table 3 Leach test results showing the effect of SMBS addition. Samples leached at 70 °C in (a) and at 25 °C in (b)

pH	SMBS wt%	% Recovery				Acid consumption (kg/ton ore)
		Cu	Co	Fe	Ni	
(a)						
pH = 1.8	0	27.52	16.32	6.93	12.04	36
pH = 1.8	0.6	74.74	80.48	15.77	65.38	84
pH = 1.8	1.0	70.18	81.90	14.11	58.46	67
pH = 1.8	1.5	77.89	87.62	30.29	63.85	69
pH = 1.8	2.0	76.32	86.67	34.44	66.15	74
(b)						
pH = 1.8	0	21.83	13.29	0.94	8.34	18
pH = 1.8	0.6	56.33	61.82	1.75	38.46	32
pH = 1.8	1.0	53.06	77.27	4.82	30.77	69
pH = 1.8	1.5	56.33	70.45	4.83	43.08	44
pH = 1.8	2.0	59.18	78.64	7.02	36.92	32

Analysis of the Leach Solution

The contents of the leach solution were determined by analysing the dried solids which were obtained by evaporating leach liquor, and the results are shown in Table 4. Apart from the usual Cu, Co, Ni, Fe, and Mn, the leach solutions contain Al, Mg, Si, and Na. The presence of Al, Mg, and Si is due to dissolution of complex nickel silicate phases. The dissolution of Al, Mg, and Si explains why acid consumption is extremely high for the material.

Precipitation of Copper, Cobalt, and Nickel with Magnesium Oxide

The results in Table 3 have shown high recoveries for the sample that was leached at 70 °C, and hence, precipitation test works were carried out on this material. pH of the solution was slowly raised to 3.8, 5.5, and 8.5 in order to allow selective precipitation of iron, copper, and cobalt hydroxide, respectively. The first precipitate at pH of 3.8 had 30.9 wt% Fe and very less Cu, Co, and Ni as shown in Table 5. The high selectivity in the precipitation of iron is because Cu, Co, and Ni are highly soluble at pH of 3.8.

The precipitate at pH of 5.5 only had 10.6 wt% Cu, and this was due to co-precipitation of aluminium and silica. In other words, precipitated aluminium hydroxide and silica decreased the grade of Cu in the precipitate. In addition, part of Co and Ni, co-precipitate such that the precipitate had 2 wt% Co and 1 wt% Ni. As such, it can be concluded that the co-precipitation of Co, Ni, silica, and aluminium hydroxide adversely affects the quality of copper precipitate at pH of 5.5.

The pH of the solution was further increased to 8.5, and the final precipitate had 3.42 wt% Co and 2.4 wt% Ni. In fact, the final precipitate demonstrates a possibility of producing a Co–Ni alloy which has wider applications.

Precipitation of Copper, Cobalt, and Nickel with Sodium Sulphide

The results showing the precipitation of copper, cobalt, and nickel with sodium sulphide are presented in Table 6. The first precipitate which was produced with 1.1 times stoichiometric amount for the formation of CuS has 58.13 wt% copper. A small amount of cobalt, iron, and nickel were also precipitated, and this might be due to the excess addition of sodium sulphide. In the second experiment (experiment B), only the stoichiometric amount of sodium sulphide was added and the grade of copper increased to 63 wt%.

Table 4 Chemical analysis in weight % of the dry solids obtained by evaporating the leach liquor

Conditions	Cu	Co	Fe	Ni	Mn	Al	S	Ca	Si	Mg	Na
pH = 1.4, 25 °C, 1% SMBS	2.49	0.67	1.14	0.23	1.32	1.95	16.9	0.02	1.85	2.22	8.52
pH = 1.4, 70 °C, 1% SMBS	2.08	0.39	3.03	0.41	0.96	2.54	22.3	0.03	0.55	1.74	2.80
pH = 2.0, 70 °C, 1.0% SMBS	3.85	1.67	3.22	0.69	2.91	3.55	16.9	0.08	1.53	1.92	3.98
pH = 2.0, 70 °C, 1.5% SMBS	2.83	1.19	3.53	0.52	1.97	3.24	16.2		0.98	1.72	5.22

Table 5 Chemical analysis in weight % for the precipitate that was obtained via precipitation with magnesium oxide

Conditions	Cu	Co	Fe	Ni	Mn
Precipitated at pH 3.8	0.21	0.13	30.88	0.01	0.02
Precipitated at pH 3.8 then 5.6	10.63	2.08	13.69	1.00	0.29
Precipitated at pH = 3.8, secondly at pH = 5.6, and finally ay pH = 8.5	0.76	3.42	0.67	2.40	1.93

Table 6 Chemical analysis in weight % for the precipitate that was obtained via precipitation with sodium sulphide

Addition of Na_2S	Cu	Co	Fe	Ni	Mn
Experiment A					
1.1 Times stoichiometric amount of Na_2S for formation of CuS	58.13	1.31	1.41	0.53	0.33
1.2 Times stoichiometric amount of Na_2S for formation of CoS, NiS, and FeS	0.10	9.59	14.91	4.58	0.58
Experiment B					
1.1 Stoichiometric amount of Na_2S for formation of CuS	63.01	1.08	0.55	0.55	–
1.2 Stoichiometric amount of Na_2S for formation of CoS, NiS, and FeS	2.78	12.18	5.37	7.42	–

Even though the amount of iron decreased to 0.55 wt%, the first precipitate had 1.01 wt% cobalt. The presence of a smaller amount cobalt and nickel might be due to localised precipitation. Thermodynamically, nickel, cobalt, and iron can only precipitate out when all copper is depleted but localised concentration might occur as the sodium sulphide solution comes in contact with the leach liquor.

The fact that the first precipitates are mainly rich in copper whereas the second precipitates are rich in cobalt and nickel confirms that there is broad agreement between the experimental results and thermodynamic prediction.

Conclusions

1. Addition of SMBS is important for dissolution of Cu, Co, and Ni during leaching as shown in Table 2. However, increasing the quantity of SMBS above 0.6% weight is not necessary as the recovery does not improve further as shown in Table 3.
2. There is broad agreement between the experimental results and thermodynamic prediction. Preferential precipitation of copper sulphide was achieved where a

solution containing copper, cobalt, nickel, iron, manganese, aluminium, silica, and magnesium was reacted with sodium sulphide.

3. The material must be leached out at a higher temperature (70 °C) for high recoveries for Cu, Co, and Ni. Nonetheless, pH should be 1.8 and above in order to have less acid consumption.
4. Some cobalt and nickel co-precipitate with copper during precipitation with magnesium oxide (MgO) at pH of 5.5 (see Table 5).
5. Use of Na_2S resulted in selective precipitation of a high-grade Cu_2S precipitate and second precipitate rich in cobalt and nickel sulphides.

References

1. Cobalt Monograph (1960) Cobalt monograph. Centre d'Information du Cobalt, Brussels, Belgium, p 515
2. Betteridge W (ed) (1982) Cobalt and its alloys. In: Industrial metals, 1st edn. Chichester, Ellis Horwood, pp 43–48
3. Davis JR (2001) Copper and copper alloys. ASM specialty handbook. A.S.M. International
4. Schmidt T et al (2016) Investigation of the primary production routes of nickel and cobalt products used for Li-ion batteries. Resour Conserv Recycl 112:107–122
5. Vijayakumar G et al (2011) Development and testing of PM flowmeter with samarium cobalt magnet assembly. Energy Procedia 7:630–637
6. Zhou X et al (2019) Validated model of thermochemical energy storage based on cobalt oxides. Appl Therm Eng 159
7. Davenport WGL et al (2002) Extractive metallurgy of copper. In: Chemical, petrochemical & process, 4th edn. Elsevier, pp 1–452
8. Dyer L et al (2012) Cobalt loss due to iron precipitation in ammoniacal carbonate solutions. Hydrometallurgy 125–126:144–147
9. Roine A (2002) HSC Chemistry 5.1. Outokumpu research oy, Finland
10. Li J et al (2009) Effect of pre-roasting on leaching of laterite. Hydrometallurgy 99:84–88. https://doi.org/10.1016/j.hydromet.2009.07.00