

Laboratory-scale sulphation roasting testwork for copper and cobalt production

P. Sithole, X.C. Goso, and H. Lagendijk

Mintek, Randburg

Laboratory scale sulphation roasting testwork was conducted to study the sulphation efficiency and recovery of cobalt and copper from synthetic and natural raw materials. The sulphation roasting efficiency was studied in terms of mass change, phase chemical compositions, and leaching characteristics. In agreement with literature, the results showed that the sulphation of cobalt and copper oxides is fairly feasible. In addition, the sulphation kinetics of copper oxide are superior to those of their sulphide counterparts. The relatively low sulphation efficiencies of the copper sulphides was attributed to the fact that the mechanism of the sulphation roasting operates via the sulphation of copper oxide – this means the sulphides are essentially converted to oxides before sulphation. In the cases where copper was sulphated in the presence of iron in synthetic $\text{CuO-Fe}_2\text{O}_3$ and natural chalcopyrite materials, the selectivity of sulphation was initially for copper at low reaction times of 8 hours, while the sulphation of iron species became significant after 16 hours. The sulphation roasting approach appears to be quite selective in terms of the sulphation of copper, and likely cobalt. However, the kinetics of the sulphation roasting process are generally inferior.

INTRODUCTION

Roasting of sulphide concentrates, in particular copper and cobalt concentrates from central Africa, is a well-established unit operation in the extraction flowsheet of these elements. In a typical copper-cobalt production flowsheet shown in Figure 1, the purpose of roasting is to selectively convert the copper and cobalt sulphides into sulphates that are readily leachable in water or dilute mineral acid, while the undesirable iron forms oxides that are insoluble under these leaching conditions (Guntner & Hammerschmidt, 2012; Palperi & Aaltonen, 1971). Fluid bed roasters are typically used to react wet concentrate with air in an autothermal manner. Developments in fluidized bed techniques have made it possible to firmly control process conditions such as temperature, material distribution and reaction gas atmosphere (Guntner & Hammerschmidt, 2012). Under these controlled conditions, cobalt and copper occur primarily as sulphates which are subsequently leached, while iron compounds form oxides that are insoluble under mild leaching conditions. The recovery of cobalt and copper from the pregnant leach liquor is typically achieved by solvent extraction (SX) followed by electrowinning (EW). The sulphation roasting off gas is generally used for the production of sulphuric acid. This technology is well established for processing cobalt and copper concentrates and has been in operation throughout the world for many decades. The sulphation roasting operations are generally uncomplicated and profitable at low capacities (Guntner & Hammerschmidt, 2012).

The sulphation roasting technology has been demonstrated in many parts of the world in a continuous configuration in both pilot-plant scale testwork and large scale plant operations. It has also been practised in the presence of Na₂SO₄ to intensify the sulphation reaction (Guntner & Hammerschmidt, 2012). Sulphation roasting is however difficult to simulate in a laboratory scale setup. Laboratory scale testwork would offer a cost effective approach for testing a wide range of parameters for the intensification of the sulphation roasting technology in terms of the improvement of metallurgical process throughput and overall economics. This paper describes the experience gained on the laboratory scale processing of various cobalt and copper materials through the sulphation roasting technology.

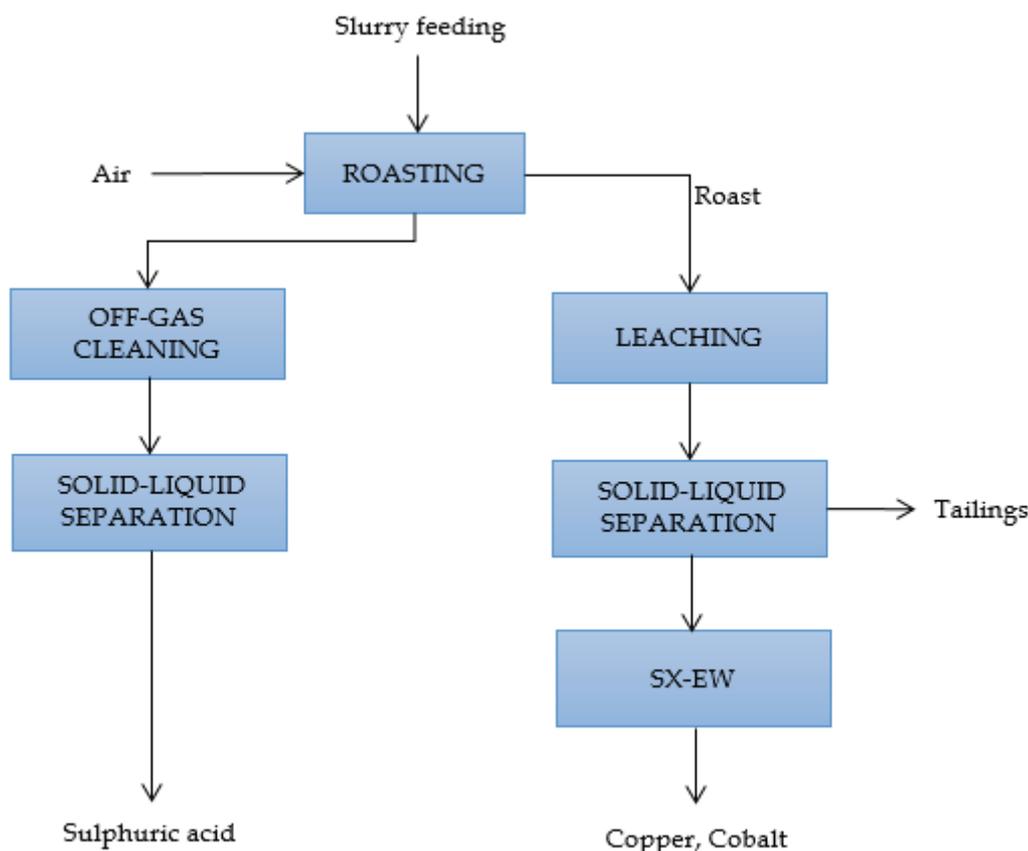


Figure 1. Simplified typical flow diagram for the production of cobalt and copper (Guntner & Hammerschmidt, 2012)

Sulphation Roasting process

Sulphation roasting refers to the process of converting valuable metal oxides and sulphides into metal sulphates. The process is applicable to the treatment of minerals that produce sulphates that are readily leachable in water or dilute mineral acids. The sulphation roasting process is usually achieved by heating the raw material with sulphur trioxide (SO₃), a stoichiometric mixture of SO₂ and O₂, in a bubbling fluid bed furnace (Guntner & Hammerschmidt, 2012).

Chemical reactions and kinetics

The sulphation roasting of cobalt and copper sulphides and oxides can be presented in the reaction steps shown in Equation [1] to [4] (Palperi & Aaltonen, 1971).



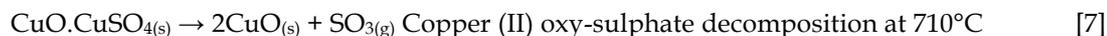
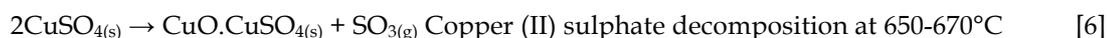
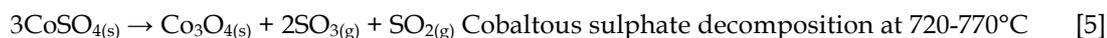


'Me' represents Co (II) or Cu (II). In reaction [1], the metal sulphide is converted to metal oxide. This reaction can be very rapid for some sulphidic concentrates. Reaction [2] shows the reaction of SO₂ and O₂ to produce SO₃. This reaction is known to be slow at the typical process conditions, however, it is generally catalysed by copper and iron present in the concentrate to enhance the overall reaction rate. The products of reaction [1] and [2], i.e. metal oxide and sulphur trioxide, further react to produce the readily leachable metal sulphates and oxy-sulphates as shown in reaction [3] and [4], respectively. Cobalt generally does not form the oxy-sulphate intermediate product. Cobalt sulphate, copper sulphate, and copper oxy-sulphates are generally soluble in mild leaching conditions. In the overall sulphation process, some excess oxygen is required in order to shift the reactions towards the formation of the metal sulphates and oxy-sulphates. The off gas may contain oxygen at 5-8 volume%. In addition, high concentrations of SO₂ are required to produce more sulphates. However, in the processing of sulphide minerals, the SO₂ content depends on the sulphur content of the feed material. Notwithstanding the above, the ratio of SO₂ to O₂ in the sulphation roasting reactor is typically 2:1 (Guntner & Hammerschmidt, 2012).

Thermochemistry

Temperature is an important parameter that is generally controlled within a narrow range in order to avoid decomposition of the formed sulphates. The typical working temperature range for the sulphation roasting of cobalt and copper minerals is between 650° and 700°C. The sulphate compounds of the detrimental iron decompose to hematite in this temperature range. At 680°C the sulphation efficiency of copper is generally high at 93%, and that of cobalt, which is less sensitive to temperature increase, is 90% even when the temperature is increased to about 720°C. The predominance phase diagram of the Cu-O-S system at 680°C is shown in Figure 2 (Guntner & Hammerschmidt, 2012).

The thermal stability of different sulphates varies in a wide temperature range. It is possible to predict the decomposition temperature of sulphates using available thermodynamic data (Palperi & Aaltonen, 1971). The decomposition vapour pressure of some metal sulphates measured as a function of time is shown in Figure 3. When heated to excessive temperatures, most metal sulphates decompose directly to metal oxides while some metal sulphates first produce intermediate oxy-sulphates prior to the formation of the oxides. The decomposition of cobalt and copper sulphates over the typical working temperature range is illustrated by Equation [5] to [7] for demonstrating the direct and intermediate type decomposition of sulphates to form the metal oxides (Kellogg, 1964).



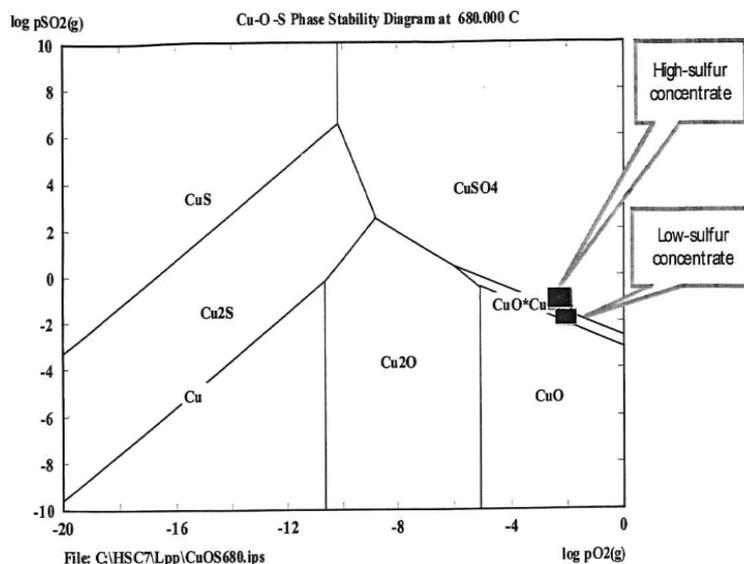


Figure 2. Predominance phase diagram for Cu-O-S system at 680°C (Guntner & Hammerschmidt, 2012)

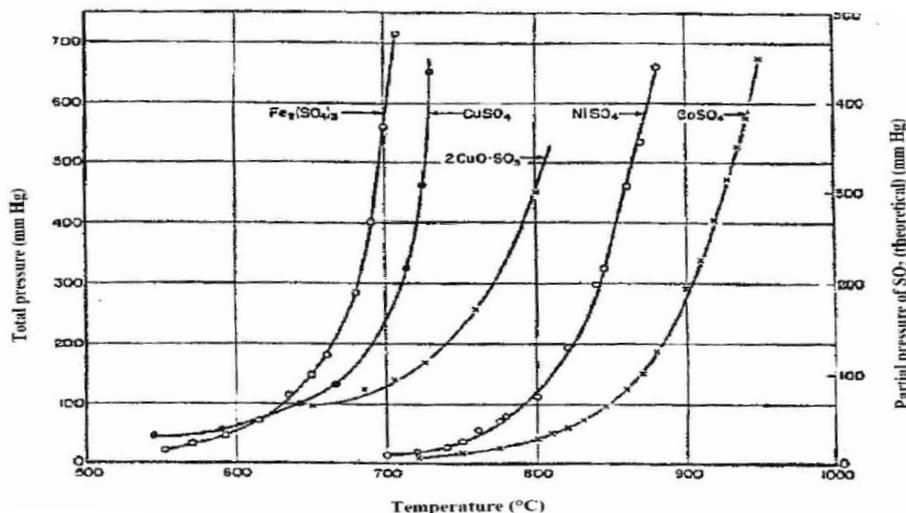


Figure 3. Decomposition vapour pressure of some metal sulphates plotted as a function of temperature (Palperi & Aaltonen, 1971)

EXPERIMENTAL

Material and equipment

All chemicals and reagents used in the testwork were of analytical grade. A summary of the chemical reagents used to make synthetic materials is given in Table I. CuS was prepared by mixing stoichiometric masses of Cu metal and Sulphur powder, followed by burning the mixture using an open flame – the successful production of CuS was confirmed by X-Ray Diffraction (XRD) analysis. The chalcopyrite sample was supplied by a client of Mintek. The chemical and phase compositions of the chalcopyrite are given in Table II and Table III, respectively.

The chemical analyses of head and processed samples were conducted by inductively coupled plasma optical emission spectrometer (ICP-OES), a 'SPECTRO CITROS VISION' model. The phase chemical compositions of sulphated materials were determined by a Bruker D8 advanced X-ray diffractometer (XRD).

A schematic representation of the horizontal tube furnace that was used in the testwork is shown in Figure 4. The reactor is made up of a 30 mm diameter quartz tube which is heated to a set temperature in a resistance-type tube furnace. A K-type thermocouple was placed next to the sample inside the furnace reactor to monitor the sample temperature throughout the test. The furnace controller was connected to the sample thermocouple for automatic regulation of the furnace resistance to control the temperature.

Table I. Summary of the reagent grades and suppliers

Reagent	Grade (%)	Supplier
Fe ₂ O ₃ (s)	97	ACE
Co ₃ O ₄ (s)	96.7	Merck
Cu metal(s)	99.9	ACE
CuO(s)	99.0	Merck
S(s)	99.5	ACE
SO ₂ (g)	99.9	AFROX
N ₂ (g)	99.9	AFROX
O ₂ (g)	99.9	AFROX
HCl(aq)	36	ACE
H ₂ SO ₄ (aq)	98	ACE

Table II. Elemental composition of the chalcopyrite sample used in the testwork (mass %)

Mg	Si	Ca	Mn	Fe	Co	Cu	S
0.26	1.90	0.07	0.52	41.1	0.12	10.5	23.0

Concentration of Al, Ti, V, Cr, Ni, and Pb < 0.05%, which is the detection limit

Table III. Phase chemical composition of the chalcopyrite material used in the experiments

Mineral Name	Chemical composition	Relative abundance
Pyrite	FeS ₂	intermediate
Chalcopyrite	CuFeS ₂	predominant
Quartz	SiO ₂	trace
Siderite	FeCO ₃	minor

<5%-trace, 5-15 %minor, 15-25% intermediate, 25-50%major, >50% predominant

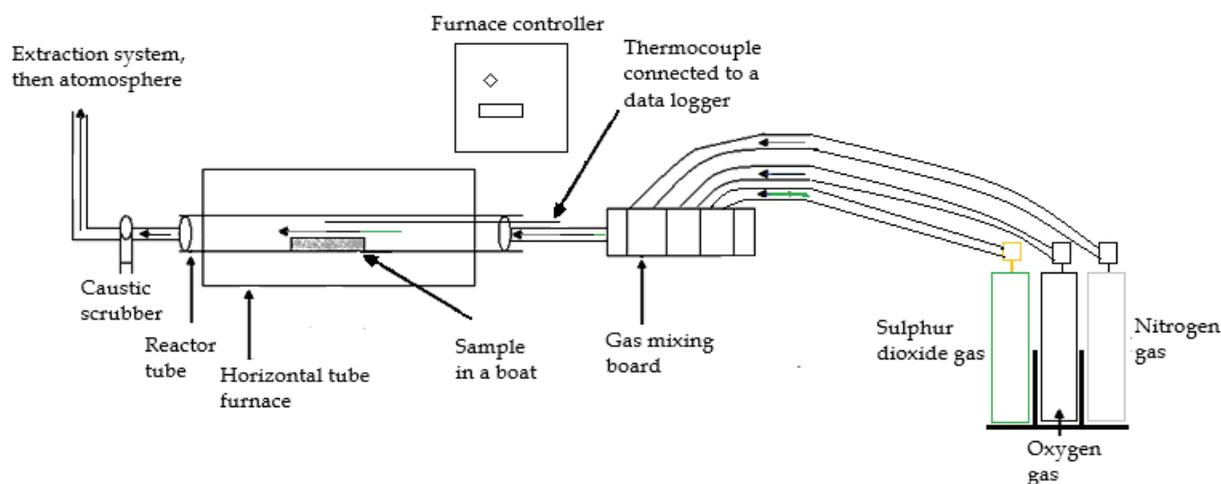


Figure 4. Schematic representation of the sulphation roasting setup

Thermochemical simulation

FactSage thermochemical software (Bale, et al., 2009) was used to calculate the predominance phase diagrams in the temperature range of 600-700°C. The objective was to use thermochemical information to predict the standard roasting conditions for acceptable levels of sulphation of cobalt and copper. As shown by the predominance phase diagrams in Figure 5 and Figure 6, the predictions concur with literature in that substantial sulphation of cobalt and copper can be achieved at a low temperature of 650°C in an atmosphere made up of SO₂ to O₂ in a ratio of 2:1 (Guntner & Hammerschmidt, 2012). In addition, the equilibrium relations in the predominance phase diagram for the Co-S-O system at 650°C show that cobalt sulphate (CoSO₄) can be produced from Co₃O₄, CoO, and CoS₂. For the Cu-S-O system at 650°C, it appears that copper sulphate (CuSO₄) can be produced from CuO, Cu₂O, Cu₂S and CuS. Hence, to complete the experimental testwork, the standard conditions were deduced to be an operational temperature of 650°C in an atmosphere of 16% O₂ and 32% SO₂ with the remaining 52% made up by an inert gas (N₂).

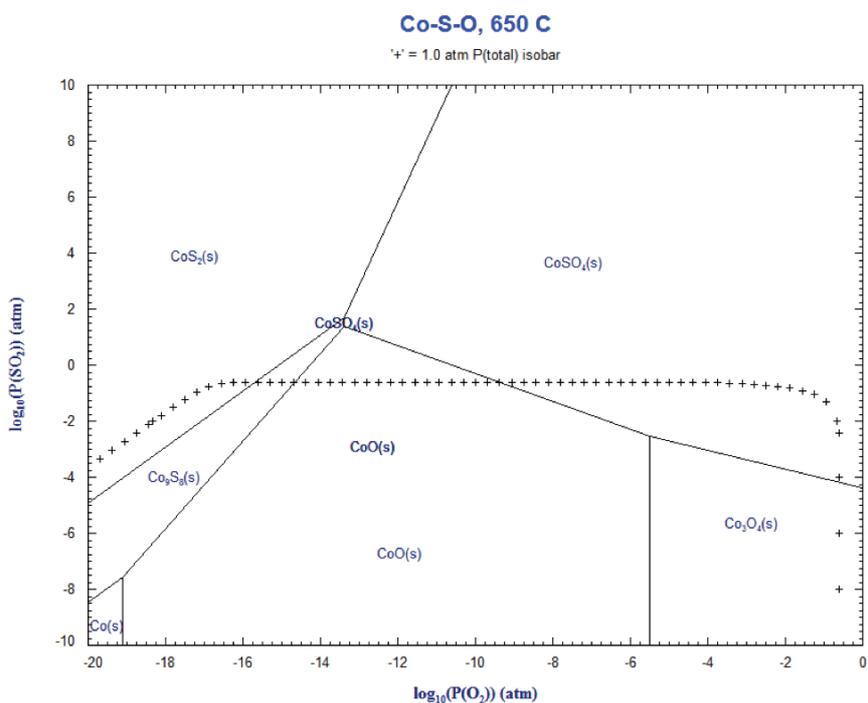


Figure 5. Predominance phase diagram for the Co-S-O system calculated at 650°C

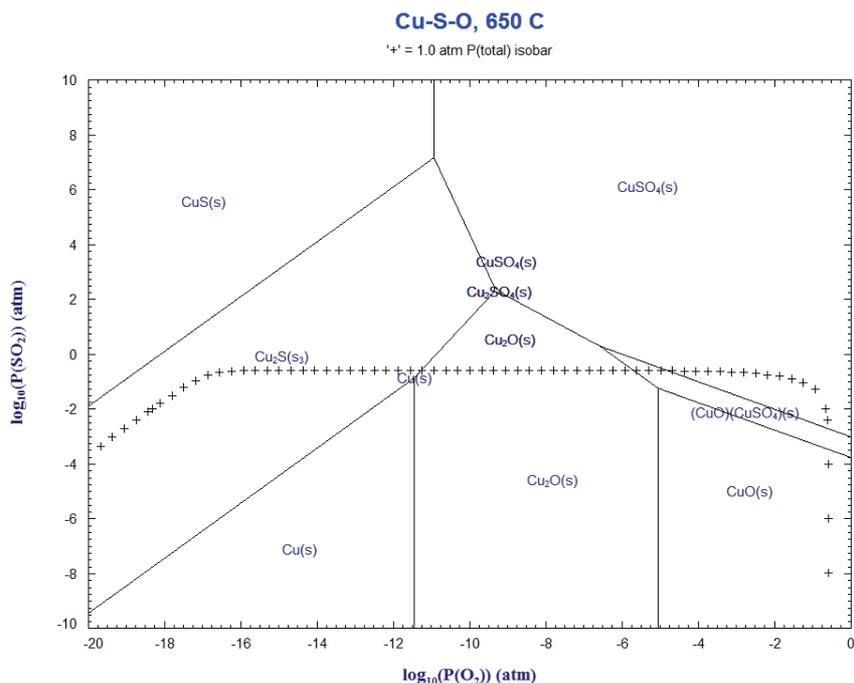


Figure 6. Predominance phase diagram for the Cu-S-O system calculated at 650°C

Sulphation roasting

To complete the sulphation roasting testwork, discrete masses of 5 g of the synthetic Co-Cu and natural chalcopyrite samples were weighed into sample boats and placed at the centre of the reactor, i.e. at the hot zone of the horizontal tube furnace. In each test run, two sample boats were processed to make a total sample of 10 g per test run. The inlet of the quartz tube was connected to a mass flow controller which was used to mix and control the amount of SO_2 , O_2 and N_2 passing through the reaction tube. The total flow of gases through the reactor was 300 Standard Cubic Centimetres per Minute (scm). The outlet of the reactor was connected to a caustic scrubber (made up of 10% NaOH solution) to absorb excess SO_2 as Na_2SO_4 and ensure that no toxic SO_2 gas was emitted directly to the atmosphere. The furnace was heated at 10°C per minute to 650°C under a flow of N_2 gas. Once at the desired operating temperature, the N_2 gas was replaced by the gas mixture of O_2 , SO_2 and N_2 which ran for the predetermined duration of the test. At the end of the test duration, the gas mixture was replaced by N_2 gas to run during the cooling of the sample to room temperature. In the testwork the main parameter was the reaction time, which was varied between 8 and 24 hours at an operational temperature of 650°C and reaction gas composition of 16% O_2 , 32% SO_2 , and 52% N_2 . A summary of the test materials and sulphation roasting times is given in Table IV.

The mass changes due to sulphation roasting and phase chemical compositions of sulphated materials determined by XRD were used to evaluate the sulphation efficiency of the test materials. In addition, as detailed below, the sulphated materials were also subjected to scoping leaching testwork to quantify the leachable cobalt and copper from the sulphation roasting products.

Table IV. Summary of the sulphation roasting tests

Test	Test material	Reaction time (hours)
1	Co ₃ O ₄	8
2	Co ₃ O ₄	16
3	Co ₃ O ₄	24
4	CuO	8
5	CuO	16
6	CuO	24
7	*50% CuO - 50% Co ₃ O ₄	24
8	CuS	8
9	CuS	16
10	CuS	24
11	*50% CuO - 50% Fe ₂ O ₃	8
12	*50% CuO - 50% Fe ₂ O ₃	16
13	*50% CuO - 50% Fe ₂ O ₃	24
14	Chalcopyrite	8
15	Chalcopyrite	24

*the respective mixtures were made by mixing 1:1 mass of each component

Leaching of sulphated materials

Scoping leaching conditions were used to study the leaching efficiency of cobalt and copper from sulphated materials. The scoping leaching conditions were deduced from a previous test conducted at Mintek. The procedure for the leaching testwork entailed the weighing of the sulphated roast (5 g) into a beaker that was used as a reactor. The roast was then slurried by the addition of 400 mL of de-ionised water used as the lixiviant. The basis for the mixing of the roast and lixiviant was to target an average of 5 g/L of each base metal in the leachate assuming that 100% sulphation is achieved - this target was not applicable in case of chalcopyrite tests, i.e. Test 14 and Test 15, because of the relatively low copper concentration in the chalcopyrite. The reactor was placed on a magnetic stirring plate. A magnetic stirrer bar was used to effect the agitation of the slurry at 250 rpm. The pH of the slurry was adjusted and controlled to 3.5 using a 5 M H₂SO₄ solution. Each leaching test was run for a total time of 1 hour. It should be noted that the leaching tests were conducted at ambient temperature.

At the end of the test duration, the slurry was filtered using a Buchner funnel. For each test, the volume of the filtrate and the mass of the dry residue were recorded and subsequently subjected to chemical analyses by ICP-OES.

RESULTS AND DISCUSSION

Evaluation of the sulphation roasting efficiency

The efficiency of the sulphation roasting for the recovery of cobalt and copper from synthetic and natural materials was evaluated through XRD chemical phase characterisation, mass change evaluation and selective leaching.

Phase chemical characterisation and mass change evaluation

A summary of the phase chemical compositions of the sulphated roasts are included in Table V. The chemical phases in the table are listed in the order of decreasing abundance, i.e., the most abundant is recorded first. The mass changes as a consequence of the sulphation roasting are also included in this table. The positive mass change indicates an overall mass gain, which would be expected in sulphation roasting, whereas a negative mass change indicates an overall mass loss. A negative mass change show that a phenomenon occurred resulting in mass loss which was more intense than the sulphation in terms of mass change.

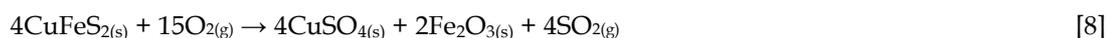
As shown by the presence of the CoSO₄ and CuSO₄ as well as the significant mass gain in Test 1 to Test 6, the sulphation of synthetic cobalt (II, III) and Cu (II) oxides appears to be substantial even in the first

eight hours of the sulphation roasting test. The sulphation of these synthetic oxides increases with increasing reaction time. For cobalt (II, III) oxide, the oxide is completely converted to a sulphate after 24 hours. However, the actual mass gain once the cobalt (II, III) oxide is converted entirely to cobalt sulphate is lower than the theoretical mass gain of 93%. The mass difference was attributed to a number of factors including the low purity of the starting Co_3O_4 reagent which was only 96.7% pure, and procedural errors due to the handling of relatively small masses of 5 g. After 24 hours, the copper oxide had formed different copper sulphate compounds which are soluble in mild leaching conditions and a copper sulphide. The formation of the copper sulphide was likely due to insufficient oxygen in the system (Guntner & Hammerschmidt, 2012). The presence of the sulphide would deteriorate the extraction efficiency of copper when mild leaching conditions are used. However, the sulphation of a synthetic 1:1 Co-Cu oxide material over 24 hours in Test 7 resulted in the conversion of the oxides to sulphates as well as oxy-sulphate in the case of copper.

The phase chemical compositions after sulphation roasting of a synthetic copper (II) sulphide material, i.e. Test 8 to Test 10, include anhydrous and hydrated copper sulphates, copper oxides, and sulphides at all reaction times. Though the mass gain in the tests increases with increasing reaction time, the mass gain quantities are significantly lower than those achieved in the sulphation roasting of copper oxide. The consistent presence of the oxides and sulphides in the sulphated products and relatively low mass gain quantities suggest that the sulphation of the copper sulphide is not as fast as that of copper oxide. According to the reaction mechanism presented in Equation [1] to [4], the sulphation of a copper sulphide entails the formation of copper oxide as an intermediate product before the formation of the desired copper sulphate (Guntner & Hammerschmidt, 2012). Hence, it is not unusual that the sulphation extent of copper sulphide is inferior to that of the copper oxide. In addition, these results have also shown that the rate limiting step for the sulphation roasting of sulphidic copper concentrate is the conversion of copper sulphite to copper oxide.

In studying the selectivity of the sulphation of copper oxide in an iron oxide rich matrix, Test 11 to Test 13 were conducted. In the first eight hours of the test, it appears that only copper oxide is sulphated. However, after 16 hours minor iron (III) sulphates formed. In addition, copper and iron combined with the sulphur to form a synthetic chalcopyrite (CuFeS_2) phase – this was probably due to a deficiency of oxygen in the sulphation roaster. The chalcopyrite was reacted further within 24 hours to make more copper sulphate and oxide as well as iron (III) sulphates and oxides. The sulphation roasting of copper in an iron rich matrix at 650°C in a 2:1 ratio of SO_2 to O_2 seems to be selective at reaction times below 8 hours. In addition, the mass gain in these tests increased with increasing reaction time without reaching a saturation point. From these results, it appears that the sulphation kinetics of Cu-Fe oxide are relatively poor. The sulphation kinetics of a Cu-Fe sulphide, like the chalcopyrite would likely be worse compared to the Cu-Fe oxide as a consequence of the need for the conversion of the sulphide to oxide and subsequently to the sulphate.

The sulphation roasting behaviour of a natural Cu-Fe-S concentrate, i.e. chalcopyrite (CuFeS_2), was evaluated in Test 14 and Test 15. The sulphation roasting of chalcopyrite was anticipated to follow the reaction shown in Equation [8] (Stephens, 1958). The phase compositions in the test results show that the sulphation of natural chalcopyrite concentrate resulted in the formation of copper sulphate after 8 hours with no sulphation of iron species. These results concur with what was observed in the synthetic Cu-Fe-O system above. After 24 hours, as observed above, the anhydrous and hydrated copper sulphates occurred together with iron (III) sulphates. In addition, at this extended time there are no copper oxide phases in the roast – this suggests that all the copper is in the leachable sulphate phases.



The sulphation roasting of natural chalcopyrite resulted in a negative mass change overall. The mass loss increased with increasing reaction time. The significant mass loss was attributed to several factors including the loss of volatile matter and procedural errors due to the handling of relatively small masses of 5 g. In both tests, the mass lost is larger than the mass gained due to the sulphation process.

Table V. Summary of the phase chemical compositions and mass changes of sulphated materials

Test	Phase composition	Mass change (%)
1	CoSO ₄ , Co ₃ O ₄	72.33
2	CoSO ₄ , Co ₃ O ₄ , CoO	83.75
3	CoSO ₄	84.21
4	CuSO ₄ , Cu ₂ O(SO ₄), CuO	61.62
5	CuSO ₄ , Cu ₂ O(SO ₄), CuSO ₄ .3H ₂ O, Cu ₉ S ₅ , CuO	71.97
6	CuSO ₄ , Cu ₂ O(SO ₄), CuSO ₄ .3H ₂ O, CuSO ₄ .5H ₂ O, Cu ₉ S ₅	83.09
7	CoSO ₄ , CuSO ₄ , Cu ₂ O(SO ₄)	91.78
8	CuSO ₄ , Cu ₂ S, CuSO ₄ .5H ₂ O, CuSO ₄ .3H ₂ O, CuO, Cu ₉ S ₅	1.95
9	CuSO ₄ , Cu ₂ O(SO ₄), CuSO ₄ .3H ₂ O, CuO, CuS	19.03
10	CuSO ₄ , Cu ₂ O(SO ₄), CuSO ₄ .3H ₂ O, CuSO ₄ .5H ₂ O, CuO	24.51
11	Fe ₂ O ₃ , CuSO ₄ , CuO, CuSO ₄ .3H ₂ O, Cu ₂ O(SO ₄)	15.84
12	CuSO ₄ , Fe ₂ O ₃ , CuSO ₄ .3H ₂ O, Fe ₂ (SO ₄) ₃ , CuFeS ₂	57.72
13	CuSO ₄ , Fe ₂ O ₃ , CuSO ₄ .3H ₂ O, Fe ₂ (SO ₄) ₃ , CuO	60.15
14	Fe ₂ O ₃ , CuSO ₄ , CuSO ₄ .3H ₂ O, SiO ₂	-1.34
15	Fe ₂ O ₃ , CuSO ₄ .3H ₂ O, CuSO ₄ .5H ₂ O, CuSO ₄ , SiO ₂ , Talc, Fe ₂ (SO ₄) ₃	-14.22

Leaching characteristics of sulphation roasting products

The objective of the leaching testwork was to determine the leaching efficiency of cobalt and copper from the respective synthetic and natural base metal bearing feed materials subsequent to sulphation. The efficiency of the extraction of these base metals, i.e. Co and Cu, was calculated as shown in Equation [9].

$$\% \text{ base metal extraction} = \frac{\text{Mass of base metal in leachate}}{\text{Mass of base metal in the feed}} \times 100 \quad [9]$$

The results of the extraction efficiencies of cobalt and copper from different synthetic and natural materials are plotted as a function of time and shown in Figure 6. The extraction efficiency results agree with the phase chemical and mass change results reported above in that the sulphation roasting is best when the feed is in oxide form for both cobalt and copper. After 24 hours of sulphation reaction time, both the cobalt (II, III) oxide and copper (II) achieve 100% leaching, i.e. 100% sulphation under the test conditions. The cobalt and copper extraction from Co₃O₄-CuO after 24 hours of sulphation reaction time is 95% and 84% respectively. Cobalt oxide appears to be converted to sulphate faster than copper oxide. This was attributed to the fact that the sulphation of cobalt oxide results in the direct formation of a cobalt sulphate, whereas that of copper oxide forms an intermediate copper oxy-sulphate (which is likely less soluble than copper sulphate because of the presence of the oxide) before the formation of the highly soluble copper sulphate.

As shown in Figure 6, the extraction of copper from a sulphated copper (II) sulphide material increases from 52% after eight hours of sulphation to 72% after 24 hours of sulphation. The copper extraction from a synthetic CuO-Fe₂O₃ system increases from 33% after eight hours of sulphation to a saturation point of 77% after 16 hours of sulphation reaction time. The extraction of copper from a sulphated natural chalcopyrite increases from 46% after 8 hours sulphation reaction time to 63% after 24 hours sulphation reaction time. The low extraction of copper is in contrast with the phase chemical composition results which showed that all the copper in the sulphated natural chalcopyrite was in copper sulphate form which is highly soluble. The low leaching extraction efficiency of copper from the sulphated chalcopyrite was attributed to possible low solubility kinetics of copper sulphate in a chalcopyrite matrix.

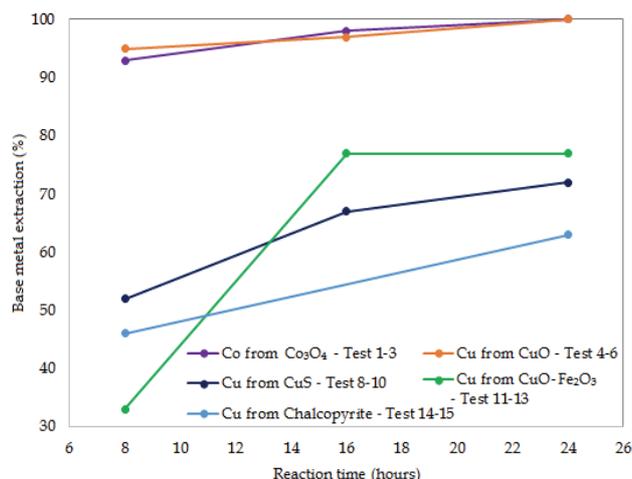


Figure 6. Extraction of cobalt and copper from various synthetic and natural materials plotted as a function of time

CONCLUSIONS AND RECOMMENDATIONS

Sulphation roasting tests were conducted on synthetic and natural cobalt and copper bearing materials. The sulphation results showed that the sulphation of cobalt and copper is fairly feasible – this is in agreement with literature (Guntner & Hammerschmidt, 2012). The sulphation kinetics of copper oxides are superior to those of their sulphide counterparts. When copper was sulphated in the presence of iron, i.e. in synthetic CuO-Fe₂O₃ and natural chalcopyrite, the selectivity of sulphation was such that copper was sulphated first at low reaction times of 8 hours while the sulphation of iron species became significant after 16 hours. The sulphation roasting proved to be more selective in terms of the sulphation of copper, and likely also cobalt. However the sulphation roasting reaction kinetics were observed to be poor in general. Further testwork is recommended for the assessment of the current relatively mild sulphation roasting conditions on the extraction of base metals from various natural base metal concentrates. More aggressive conditions may be investigated to ensure the best recovery of base metals from the respective concentrates by the sulphation roasting coupled with leaching process, although techno-economic studies would need to determine the viability of using such conditions industrially.

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