Reductive Dissolution of Cu and Co from an Oxide Ore from DRC in H_2SO_4 using $(NH_4)_2S_2O_3$ as a Reducing Agent

Noella M. Mbuyi and Antoine F. Mulaba–Bafubiandi

Mineral Processing and Technology Research Centre, University of Johannesburg, South Africa

Corresponding author: mbuyinm@gmail.com

An investigation of the selective dissolution of Cu and Co from their oxide ores was conducted at a laboratory scale in two stages using H_2SO_4 and $(NH_4)_2S_2O_3$ as electrolytes. The ore was first leached in H_2SO_4 then the residue was subjected to a mixture of H_2SO_4 and $(NH_4)_2S_2O_3$ at room temperature and atmospheric pressure. Thereafter, the inverse process was applied to the same ore, starting with the mixture of H_2SO_4 and $(NH_4)_2S_2O_3$ and then leaching with H_2SO_4 to compare and assess the most efficient processing route. The concentrations of H_2SO_4 and $(NH_4)_2S_2O_3$ were varied as well as the leach time. The optimum concentrations for Route 1 were 0.5 M H_2SO_4 and 0.4 M $(NH_4)_2S_2O_3$, giving a cumulative recovery of 77.2 % Cu and 31.7 % Co after an hour. During Route 2 dissolution, cumulative recoveries of 99.9 % of Cu and 82.6 % Co after 2 hours were obtained at 0.5 M H_2SO_4 and 0.35 M $(NH_4)_2S_2O_3$. To evaluate the selectivity of the process, the co-leached Ni and Fe were also assessed: it was found that 51.4 % and 4.6% leaching of Ni and Fe were obtained, respectively.

INTRODUCTION

Copper (Cu) and cobalt (Co) are strategic metals which are widely used in the manufacturing industry due to their exceptional properties. Copper is used for electrical equipment such as industrial heat exchangers and electrical wiring due to its high conductivity for electricity and heat. It is also used in piping when it is alloyed, owing to its ability to withstand corrosion. Cobalt is mostly used in steel-making to form alloys and super-alloys because of its high temperature resistance. It is also widely used as a catalyst in the petrochemical and plastics industries and in the manufacturing of rechargeable batteries. Cobalt salts are used as driers in paint and ink manufacturing (Stuurman et al., 2014). Due to the high global demand for Cu and Co metals, mining companies are obliged to develop new techniques in order to process lower-grade ores

The Democratic Republic of Congo (DRC) has the world's largest economic reserve of Cu–Co ore bodies located in its strategic Copperbelt. It is estimated to contain more than 150 million tons of Cu and 8 million tons of Co (Dewaele et al., 2006), which has a significant influence in both the worldwide supply and demand for Cu and Co on the international market. The country has become attractive for international mining investment and exploitation (Lydall & Auchterlonie, 2011).

The Copperbelt is characterized by complex mineralogy dominated by heterogenite ($CoO.2Co_2O_3.6H_2O$), chrysocolla ($CuOSiO_2.2H_2O$) and malachite ($CuCO_3.Cu(OH)_2$) with disseminated minor amounts of copper silicates and carbonates, such as dioptase ($CuSiO_3.H_2O$), katangite ($CuS_{13}O_9.nH_2O$), and azurite ($Cu_3(OH)_2(CO_3)_2$ (Crundwell et al., 2011).

Several researchers are trying to develop more efficient and economic methods for the selective extraction of Cu and Co while leaving Mg, Fe, As and other unwanted metals in the residue. The conventional acid-leaching process applied to extract Cu and Co from their oxide ores in the DRC has presented some deficiencies due to the fact that sulfuric acid (H_2SO_4) in the presence of heterogenite (in which Co occurs in both divalent and trivalent state) leaches Co(II) while the Co(III) remains in the residue (Mwema et al., 2002). The use of a reducing agent becomes essential to leach the Co(III) species. Several reducing agents, including ferrous ions, sulfur dioxide, metallic copper powder and sodium metabisulfite, either alone or in combination, have been used at the metallurgical plants in Katanga while treating these ores (Mwema et al., 2002). Mulaba-Bafubiandi et al. (2007) investigated the dissolution of Cu and Co from oxide ore using microwaves in the presence sulfur dioxide (SO_2) as a reducing agent and obtained higher yield of Co (85–95 %). Apua and Mulaba (2011) investigated the dissolution of Cu and Co in hydrochloric acid (HCl) in the presence of ferrous chloride ($FeCl_2$) and obtained a Co yield of 95%. Seo et al. (2012) examined the possibility of improving the rate of dissolution of low-grade Cu–Co oxide ore using H_2SO_4 in the presence of hydrogen peroxide (H_2O_2) and obtained excellent Co recovery (90%) at low lixiviant concentrations. Despite the wide use of all cited reducing agents, iron (Fe) is still a concern as it reports to the leach liquor. Therefore to prevent interference in the downstream processes, supplementary action is required to discard the co-leached Fe from the pregnant leach solution.

To date, no study has been done on the recovery of Cu and Co from Cu–Co oxide ores from the DRC using $(NH_4)_2S_2O_3$ as a reducing agent. The present study was conducted to analyse the efficiency of $(NH_4)_2S_2O_3$ as a reducing agent in the presence of H_2SO_4 whereby a simultaneous dissolution using H_2SO_4 combined with $(NH_4)_2S_2O_3$ was applied using two routes methods consisting of two stages each.

MATERIALS AND METHODS

Materials

Ore Sample

The ore samples used in this study were Cu–Co oxidized ores from Katanga province in the DRC. The ore was crushed, milled and then sieved to the size of –75 µm.

Chemicals

High-grade purity H_2SO_4 (98% v/v, Sigma Aldrich) and $(NH_4)_2S_2O_3$ (Merck) were used. Distilled water was used for the preparation of lixiviant and washing of residues.

Characterization of the Sample

X-ray fluorescence (XRF; Rigaku ZSX Primus II) with a scintillation counter and flow-proportional counter was used for chemical composition determination. The mineralogy of the sample was determined by X-ray diffraction analysis (XRD; Rigaku Ultima IV) with powder diffraction X-ray logical (PDXL) analyser software equipped with the International Center for Diffraction Data (ICDD) card.

Method

The experimental work was conducted using two routes with two stages each.

- Route 1: leaching of Cu and Co with H_2SO_4 (stage 1) followed by the leaching of the residue in the mixture of H_2SO_4–$(NH_4)_2S_2O_3$ (stage 2).
- Route 2: leaching of Cu and Co in the mixture of H_2SO_4–$(NH_4)_2S_2O_3$ (stage 1) followed by leaching of the residue with H_2SO_4 (stage 2).

In both routes, the optimal concentration of the lixiviants was determined by maintaining one condition constant and varying the other. Residues from each stage were washed, dried and analysed by XRF. The dissolved metals of interest were analysed using atomic absorption spectroscopy (AAS).

For leaching in both routes, 10 g of the sample was used in stage 1 while 5 g of the residue was used in stage 2. All parameters were kept constant (solid–liquid ratio of 1:20; temperature of 25 °C; stirring rate avoiding vortex formation; particle size of –75 µm and atmospheric pressure). Leaching was conducted by varying the concentration of $(NH_4)_2S_2O_3$ (0.28–0.47 M) while keeping H_2SO_4 constant at 0.5 M for all stages involving mixture dissolution. For stages involving acid dissolution only, the concentration of H_2SO_4 varied within this range (0.2–0.6 M). The sample was analysed for Co, Cu, Ni and Fe using AAS.

The recovery of the dissolved metal in the solution was calculated with respect to the grade of the feed (Equation 1; Chen et al., 2009).

$$\eta_{Me} = [\frac{[C_{Me} \times V]}{[m \times C^{o}_{Me}]} \times 1000 \quad [1]$$

where η_{Me} is the recovery (%), C_{Me} (g/L) is the concentration of metals in the leach liquor; V (L) is the total volume used during leaching, m (g) is the mass of ore used and $C^{o}_{M}e$ (%) is the grade of metal in the feed as determined by XRF.

RESULTS AND DISCUSSION

The chemical composition of the feed (Table I) shows that sample contained 4.5 % of Co with 12.2 % Cu. As expected, XRD analysis shows the presence of quartz, malachite and heterogenite (Table II).

Table I. Chemical composition of the Cu–Co oxide ores.

Components	Cu	Ni	Co	Mg	Al	Si	Mn	Fe
Composition (% mass)	12.2	1.4	4.5	6.8	3.2	19.7	0.8	5.7

Table II. Mineralogical phases present in the as "received "Cu-Co oxidized ore.

Phase	Chemical formula	Content (%)
Heterogenite	$(Co_2O_3.CuO)H_2O$	8.2
Malachite	$Cu_2CO_3(OH)_2$	6.3
Cobalt oxide	Co_3O_4	3.3
Quartz	SiO_2	62.5
Cuprite	Cu_2O	4.7
Iron oxide	Fe_3O_4	12.6
Cobalt silicate	Co_2SiO_4	2.4

Leaching Process

Based on the stochiometry of reactions [2–5], the reagent concentrations were determined.

$$Cu^{2+} + S_2O_3^{2-} \leftrightarrow 6H + 3e^- + Cu(SO_3)_2^{3-} \quad [2]$$

$$Co^{3+} + S_2O_3^{2-} \leftrightarrow 5H^+ + 3e^- + CoSO_4 \quad [3]$$

$$Cu^{2+} + SO_4^{2-} + e^- \leftrightarrow CuSO_4 \quad [4]$$

$$Co^{3+} + SO_4^{3-} + e^- \leftrightarrow CoSO_4 \quad [5]$$

Route 1: Leaching of Cu and Co with H_2SO_4 (stage 1) followed by the leaching of residue with the mixture of H_2SO_4–$(NH_4)_2S_2O_3$ (stage 2)

During stage 1 leaching an optimum H_2SO_4 concentration of 0.5 M was obtained (Figure 1A) with recoveries of 60.9 % Cu and 1.9 % Co. At this concentration, 7.9 % Ni and 0.8 % Fe co-leached. It is assumed that the low dissolution of Co is because of the presence of Co^{3+} in the sample which is not soluble in H_2SO_4 media alone (Ndalamo et al., 2011). As noticed from Table III, after H_2SO_4 leaching, the residue still contained a relatively high amount of Co (4.7 %). The use of $(NH_4)_2S_2O_3$ as a reducing agent was thus essential to reduce Co^{3+} to Co^{2+} for efficient dissolution. Thus stage 2 leaching was conducted which led to a slight increase in Co recovery (29.8 %) at 0.4 M of $(NH_4)_2S_2O_3$ with 10.1 %, 3.1 % and 39.1 % of Cu, Fe and Ni, respectively (Figure 2B).

The overall recovery is represented in Figure 2C, where the optimal conditions were selected for low recovery of Fe. These conditions gave 75.8 %, 31.7 %, 45.8 % and 3.8 % of Cu, Co, Ni and Fe, respectively at 0.5 M of H_2SO_4 and 0.4 M of $(NH_4)_2S_2O_3$. It is argued that this poor improvement on the recovery might be associated with the presence of high quartz content in the ore sample because SiO_2 is a gangue mineral which consumes acid and produces a gel-like substance that inhibits metal dissolution. In order to appreciate the efficiency of these processes, residues were analysed, as shown in Table III. The amounts of retained metals in the residues (Cu 0.33 %; Co 0.26 %; Ni 0.34 %) were considerable. This led researchers to reverse the process for further investigation.

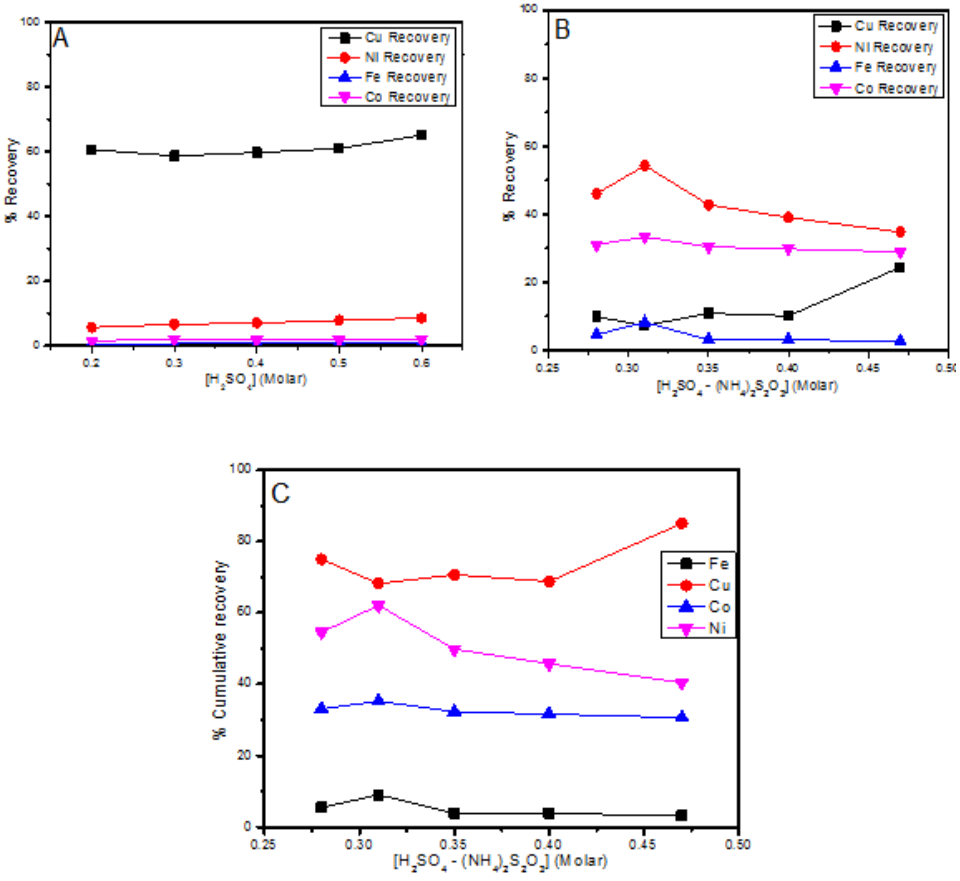

Figure 1. Cu, Co, Ni, Fe recovery (A) in stage 1 leaching; (B) in stage 2 leaching, and (C) combined stage 1 and stage 2 leaching.

Table III. XRF results for the feed and residues of stage 1 and stage 2 during route 1 leaching process.

Components	Composition (%mass)						
	Cu	Ni	Co	Mg	Al	Si	Fe
Feed	12.19	1.40	4.5	6.75	3.18	19.67	5.67
Residue stage 1	1.05	1.20	4.69	8.64	3.21	22.78	7.33
Residue stage 2	0.33	0.34	0.26	7.15	2.75	45.13	5.44

Route 2: Leaching of Cu and Co with H_2SO_4–$(NH_4)_2S_2O_3$ mixture (stage 1) followed by leaching of the residue with H_2SO_4 (stage 2)

The dissolution of Cu–Co ore in H_2SO_4 (0.2–0.6 M) at room temperature, as in Route 1, is an acid-consuming process due the high amount of gangue minerals. It was motivating to investigate the reverse procedure in order to evaluate and compare the recovery of Route 2 to that of Route 1.

During stage 1 leaching, the optimum concentrations in the mixture were 0.5 M H_2SO_4 and 0.35 M $(NH_4)_2S_2O_3$ (Figure 2 A′) with recoveries of Cu (56.65 %), Co (25.33 %), Ni (28.96 %) and Fe (1.8 %). The result depicts that leaching by this mixture promoted the dissolution of Cu, Co and Ni against that of Fe. Thus, the use of H_2SO_4 in the presence of $(NH_4)_2S_2O_3$ favoured the reduction of Co^{3+} to Co^{2+} compared with that of the Route 1, stage 1 leaching process.

In stage 2 leaching, the residues from the mixture were subjected to 0.5 M H_2SO_4 leaching. Higher metal recoveries, as shown in Figure 2B′ after 60 min of Cu (42.3 %), Co (41.7 %) and Ni (18.9 %), were obtained with Fe (1 %). The higher recovery of Co was observed due to the fact that Co^{3+} has been reduced to Co^{2+} which is soluble in H_2SO_4. Cu and Ni were not inhibited by the probable dissolution of Si. Figure 2C′ showed an increase in cumulative dissolution of Cu, Co and Ni compared with that of Route 1. The optimum dissolution occurred at $(NH_4)_2S_2O_3$ (0.35 M) and H_2SO_4 (0.5 M) with excellent recoveries of Cu (96.1 %); Co (69.5 %); Ni (47.7 %) against Fe (3.3 %) after 2 hours.

The results in Table IV show that there is still some percentages of the base metal (Cu 0.31 %; Co 0.09 %; Ni 0.3 %) remaining in the residue which could be further liberated after the two-stage leaching.

Table IV. XRF results for the feed and residues of stage 1 and stage 2 after Route 2 leaching method.

Components	Composition (%mass)						
	Cu	Ni	Co	Mg	Al	Si	Fe
Feed	12.19	1.4	4.5	6.75	3.18	19.67	5.67
Residue stage 1	0.43	0.37	0.12	7.66	2.96	21.26	5.95
Residue stage 2	0.31	0.3	0.09	7.75	2.73	26.82	6.19

Time Effect for Route 1 and Route 2 leaching

As time plays an economic role in productivity, its effect was investigated in the range of 30 min to 240 min to evaluate the extent of recovery. Figure 3A″ showed that no changes were observed within the specified time ranges for the overall recovery of Cu, Co, and Ni in the Route 1 leaching process. To minimise the duration of the reaction, 60 min was chosen as optimum time and recoveries of Cu (77.2 %), Co (31.3 %), Ni (50.1 %) and Fe (5.6 %) were obtained. For Route 2 dissolution (Figure 3 B″), the recovery changed with time. The optimum time was chosen as 120 min given the excellent overall recoveries of Cu (99.9 %); Co (82.6 %); Ni (51.5 %) and Fe (4.6 %). These recoveries were excellent due to the lower Fe (< 5 %) content in the leach liquor. As a result, Route 2 leaching process is the best leaching procedure due to the high recoveries as well as lower Fe content.

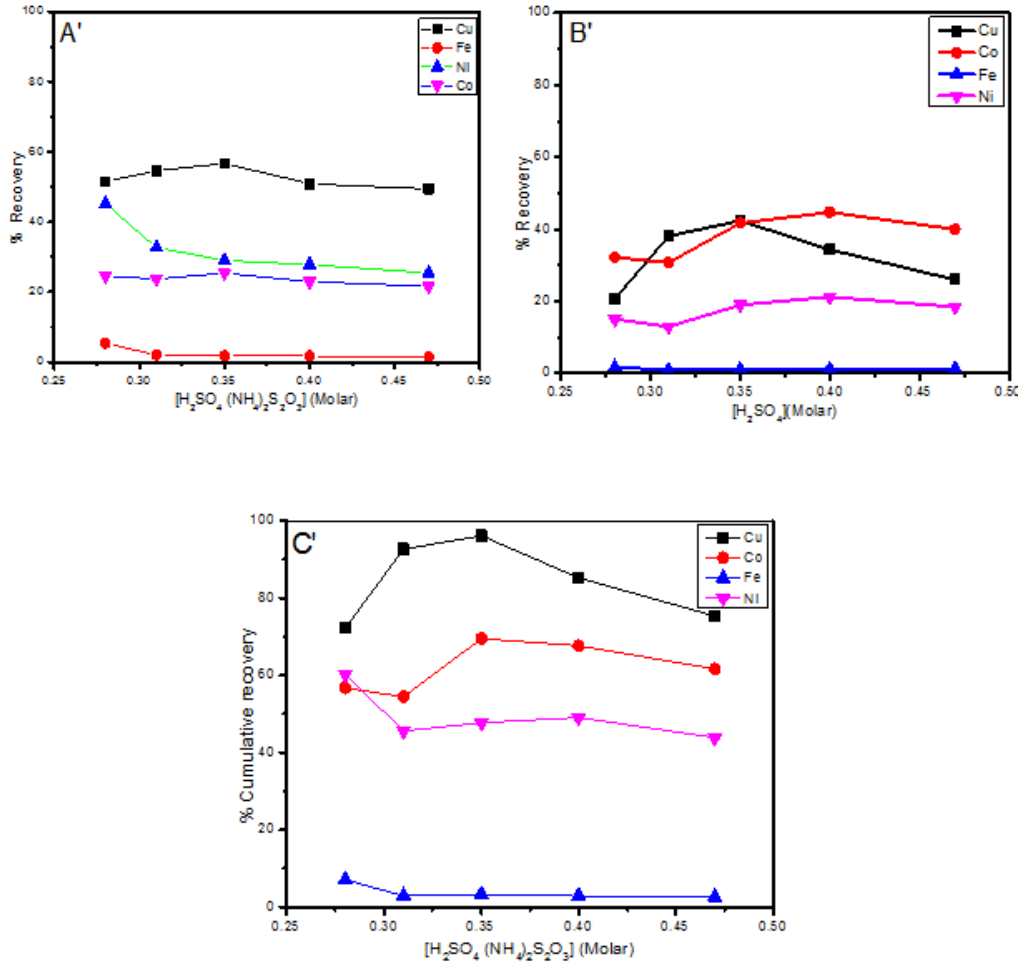

Figure 2. Cu, Co, Ni, Fe recovery (A') in stage 1 leaching (B') in stage 2 leaching and (C') combined stage 1 and stage 2 leaching.

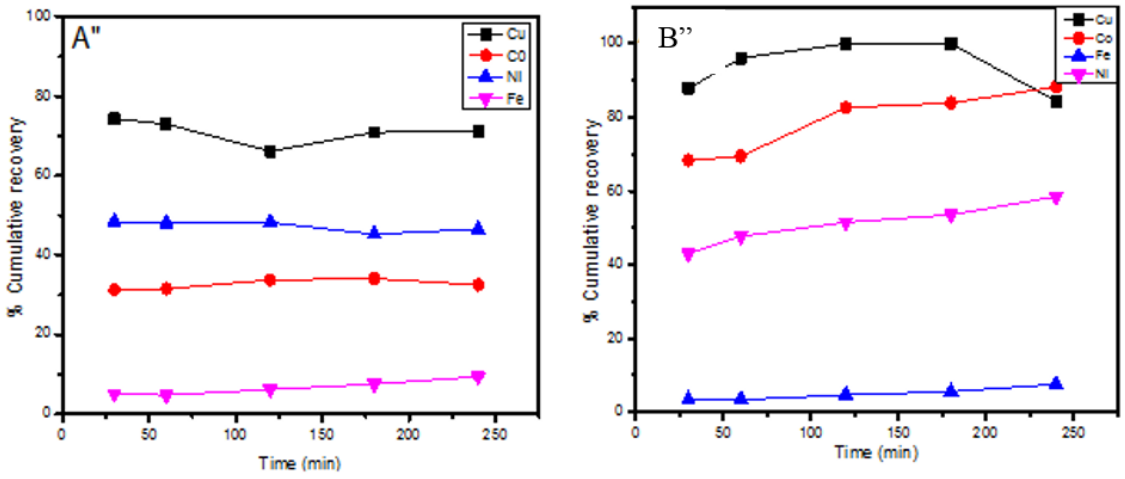

Figure 3. Comparative dissolutions of Cu, Co, Ni and Fe using different Routes A'': Route 1 and B": Route 2 with time.

CONCLUSION

The present study was conducted in order to develop an efficient route for leaching Cu and Co without co-leaching of Fe. Leaching Cu and Co from an oxide Cu–Co from DRC was achieved using H_2SO_4 in the presence of $(NH_4)_2S_2O_3$. With the two routes developed, Route 2 was concluded to be the most efficient due to the high cumulative recoveries of 99.9 % Cu, 82.6 % Co, 51.5 % Ni and 4.6 % Fe and a low content of Fe in the leach liquor.

Further studies are currently conducted on the electrochemical behaviour of the Cu–Co ores using Route 2. Kinetic, economic and environmental studies are also being examined to draw conclusive results before application on a pilot-plant level.

REFERENCES

Apua, C.M. and Mulaba-Bafubiandi., A.F. (2011). Dissolution of oxidised Co-Cu ores using hydrochloric acid in the presence of ferrous chloride. *Hydrometallurgy*, 108, 233–236.

Chen, A., Zhao, Z.W., Jia, X., Long, S., Huo, G. and Chen, X. (2009). Alkaline leaching of Zn and its contaminant metals from refractory hemimorphite zinc oxide ore. *Hydrometallurgy,* 97 (3–4), 228–232.

Crundwell, F.K., Moats, M.S., Ramachandran, V., Robinson, T.G. and Davenport, W.G. (2011). *Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals*. Elsevier.

Dewaele , S., Muchez, P.V.J., Fernadez-Alonzo, M. and Tack, L. (2006). Multiphase origin of the Cu–Co ore deposits in the western part of the Lufilian fold-and-thrust belt, Katanga (Democratic Republic of Congo). *Journal of African Earth Sciences.* Available online at www.sciencedirect.com.

Lydall, M. and Auchterlonie, A. (2011). The Democratic Republic of Congo and Zambia: a growing global 'hotspot' for copper-cobalt mineral investment and exploitation. *Sixth Southern Africa Base Metals Conference*. Southern African Institute of Mining and Metallurgy, Johannesburg. pp. 25–38.

Mulaba-Bafubiandi, AF., Ndalamo, J. and Mamba, B. (2007). Microwave-assisted SO_2 flushed acid leaching of mixed cobalt-copper oxidised ores. *Africa's Base Metals Resurgence.* Southern African Institute of Mining and Metallurgy, Johannesburg. pp. 9–26.

Mwema, M., Mpoyo, M. and Kafumbila, K. (2002). Use of sulphur dioxide as reducing agent in cobalt leaching at Shituru hydrometallurgical plant. *Journal of the Southern African Institute of Mining and Metallurgy*, 102, 1–4.

Seo, S., Choia, W., Kima, M. and Trana, T. (2012). Leaching of a Cu-Cu ore from Congo using sulphuric acid-hydrogen peroxide leachants. *Journal of Mining and Metallurgy, Section B: Metallurgy,* 49 (1), 1–7.

Stuurman, S., Ndlovu, S. and Sibanda, V. (2014). Comparing the extent of the dissolution of copper-cobalt ores from the DRC Region. Journal of the Southern African Institute of Mining and Metallurgy, 114 (3), 347–353.