

MICROWAVE-ASSISTED SO₂ FLUSHED ACID LEACHING OF MIXED COBALT-COPPER OXIDISED ORES

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Abstract

The existence of an impressive reserve of oxidized cobalt-copper bearing ores in the African copper belt area lead the GECAMINES (DRC) to develop specific and adapted mineral processing routes (Mulaba-Bafubiandi, 2001). During the conventional diluted sulphuric acid leaching of oxidized cobalt-copper bearing ores commonly referred to as “heterogenite”, more than 10% cobalt dissolution yield increase was observed in a plant situation (Mwema et al., 2002) when SO_{2(g)} was flushed into the acidified cobalt leaching solution. The present paper attempts to elucidate mechanisms involved which lead to the increase of total cobalt as SO₂ is flushed during the leaching of oxidized cobalt bearing minerals. The kinetics of cobalt dissolution as SO₂ is flushed into the acidic solution as well as a full characterization, using UV-Visible spectroscopy, of Co²⁺ and Co³⁺ species present in the collected leachate are presented while possible effects of the presence of Cu and Fe on the leachability of cobalt bearing minerals present in the oxidised ore will be discussed. In the view of speeding up the leaching process, the mixed cobalt-copper oxidised ores were microwaves pre-processed. Preliminary results were also discussed.

Introduction

Cobalt metal is commonly produced as a by-product of copper extraction in the Katanga Province of the Democratic Republic of Congo (DRC) whereas in SA it is produced as minor traces of the base-metal sulphides in platinum group metals (PGMs). However, it has been reported that challenges such as the poor leaching yield of cobalt are encountered during the extraction of cobalt from cobalt bearing ores (Mulaba et al., 2001). This is especially observed when the cobalt ores bear cobalt in the third oxidation state (Co³⁺). Literature survey indicates various reagents that have been applied in a plant situation to overcome this problem (Mwema et al., 2002), and in one report it was observed that direct reductive acid leaching of ores bearing cobalt as Co³⁺ particularly with the use of a suitable reducing agents such as Cu-powder, sodium metabisulphite (Na₂S₂O₅) and ferrous ions Fe²⁺ resulted in an improved solution-based cobalt recovery.

It was also indicated that the usage of the above mentioned reducing agents induced an unbearable increase in the operating costs (Mwema et al., 2002), where consumption of these reagents averaged 0.8 (metric) ton of $\text{Na}_2\text{S}_2\text{O}_5$ and 1.2 ton of copper powder per ton of dissolved cobalt, representing approximately 47% of the total operating cost per ton of cobalt metal produced. Alternatively, it is also reported that the use of sulphur dioxide (SO_2) in the cobalt and manganese leaching plant as a reducing agent has achieved interesting results (Jan et al, 1983). To the best of our knowledge, the use of SO_2 as a reducing agent during leaching of cobalt oxidized ores has not been thoroughly investigated.

This paper, therefore, reports on the use of SO_2 as a reducing agent in improving the leachability of Co^{2+} minerals from cobalt bearing ores. UV/Visible spectroscopy was used to affirm the levels of Co^{2+} in the leach liquor with and without the influence of SO_2 as a reducing agent. The reaction kinetics of this leaching process have also been investigated in this study. In the irradiation of the ore particles by microwave energy, heating by means of energy transfer occurs in minerals having specific dielectric properties (Bradshaw, 1999). This preferential absorption of microwave energy leads to selective heating of various components within the ore material (Kingman et al., 2000). Depending upon the nature of the ore material, the heat generated may lead to the greater proportion of free mineral grain within the ore material and the potential is thus the improvement in subsequent mineral leaching. This paper therefore also reports on preliminary results from four ore samples, all pre-concentrated samples of handpicked cobalt-copper mixed oxide ores from the Gecamines (DRC).

Experimental

Materials

The hand-picked pre-concentrated cobalt ores used in this research study were obtained DRC and were processed as received. The cobalt content in these ores ranges between 0.5% to 34% with the major constituents amongst other things being copper and iron. The results from X-ray diffraction (XRD) technique showed that the cobalt, copper, nickel and iron were in the form of Heterogenite (CoOOH), malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$), Nimitite-1M11b $\{(\text{Ni},\text{Mg},\text{Al})_6(\text{Si},\text{Al})_6\text{O}_{10}(\text{OH})_8\}$ with only minor quantities of gangue minerals were noted amongst which limonite ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) respectively. All chemicals used in this research study were of reagent grade and were obtained at high purity from suppliers. Unless otherwise stated, all experiments were carried out at room temperature.

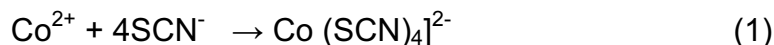
Leaching of cobalt ores

The main apparatus for the experiment consisted of a glass beaker (500 cm^3), magnetic stirrer, and a pH/Eh meter. Buffer solutions of pH4 and pH7 were used to calibrate the pH probe. The ore sample (20g) with the particle size distribution of less than $75 \mu\text{m}$ was poured into a glass beaker (500 cm^3) - charged with H_2SO_4 (400 cm^3 , 0.5 M). SO_2 gas

was flushed, when necessary, through a glass beaker (500 cm³) - charged with de-ionized water (400 cm³) at a flow rate of 50cm³/min. The residence time for all experiments was 2 hours. The magnetic stirrer was set at 300 rpm, and the flow rate of SO₂ gas was monitored with the help of calibrated bubble flow meters. Samples were collected at 30min time intervals and analyzed for cobalt using flame-AAS. Cobalt speciation by UV-Visible spectroscopy was only carried out on the final leach liquor.

UV/Visible spectroscopic analysis of the leach liquors

Analysis of solution samples for cobalt species before and after leaching of cobalt ores performed using a Varian UV-Visible Carry 50 Spectrophotometer at normal room temperature. All samples were measured after every leach experiment with a 10mm quartz cuvette cell used as the sample holder. Ammonium thiocyanate (NH₄SCN) was used as a chromogenic (colour forming) reagent to convert cobalt species to the complex forms which can readily absorb the visible light as shown the following reactions:



Microwave treatment prior to the leaching

Multimode microwave cavity with 900 watts (W) output power was used for heating the cobalt-bearing ores at 2.45GHz radiation frequency. A portable Infrared Thermometer Ministry 100 with an input range of -32 to 500 °C was used to measure the temperature of the irradiated sample. A 100ml beaker was used to contain of the ore material (20g) to be irradiated. The exposure time of the ore to microwaves was 30 minutes and leaching experiments were performed on the irradiated ore material. The leaching experimental conditions remained the same as indicated previously.

Results and analyses

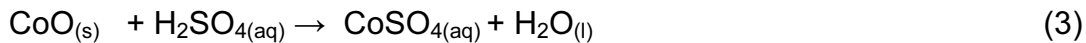
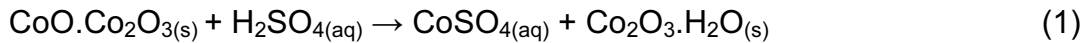
Leaching kinetics

Analysis of the high cobalt bearing ore

A series of experiments was carried out to investigate the behavior of cobalt when sulphur dioxide was used as a reducing agent. The general shape of the rate curves in Figures 3.1-3.4 suggested that the rate of ore leaching under any given medium initially accelerated and then gradually became progressively slower until the reaction reached completion. It can be seen from the plots that after 120 minutes, the extent of cobalt dissolution from the high cobalt bearing ore is relatively low reaching a minimum of 10% with the ore being leached in aqueous "H₂SO₄-only" medium. However, the rate of cobalt

dissolution improves substantially reaching a maximum of 90% in leaching experiments where sulphur dioxide is present such as $\text{SO}_2 + \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 + \text{SO}_2$.

It was further noted that leaching the high cobalt bearing ore under the same experimental conditions in saturated sulphurous acid (H_2SO_3 -Only) produced similar yields of cobalt leaching as compared to the yields obtained in $\text{SO}_2 + \text{H}_2\text{O}$ experiments. As a result, the substantial improvement in the cobalt dissolution efficiency was attributed primarily to the reduction potential of Co^{3+} to Co^{2+} by sulphurous acid which in turn readily dissolves in aqueous sulphuric acid. In all cases, the rate of cobalt dissolution levels out beyond 30minutes of the total leaching time. The percent dissolutions of cobalt as plotted per time in Figure 1 were derived from AAS measurements of the sample leach liquors. The percent cobalt content in the sample leach liquors were then converted to percent cobalt dissolution with respect to the cobalt content in the high cobalt bearing ore. Reaction 1 illustrates partial dissolution of CoO from Co_3O_4 with $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ remaining unreacted in H_2SO_4 . In reaction 2, SO_2 is flushed in H_2O to form H_2SO_3 which reduces $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ to the direct acid leachable CoO which is illustrated in reaction 3.



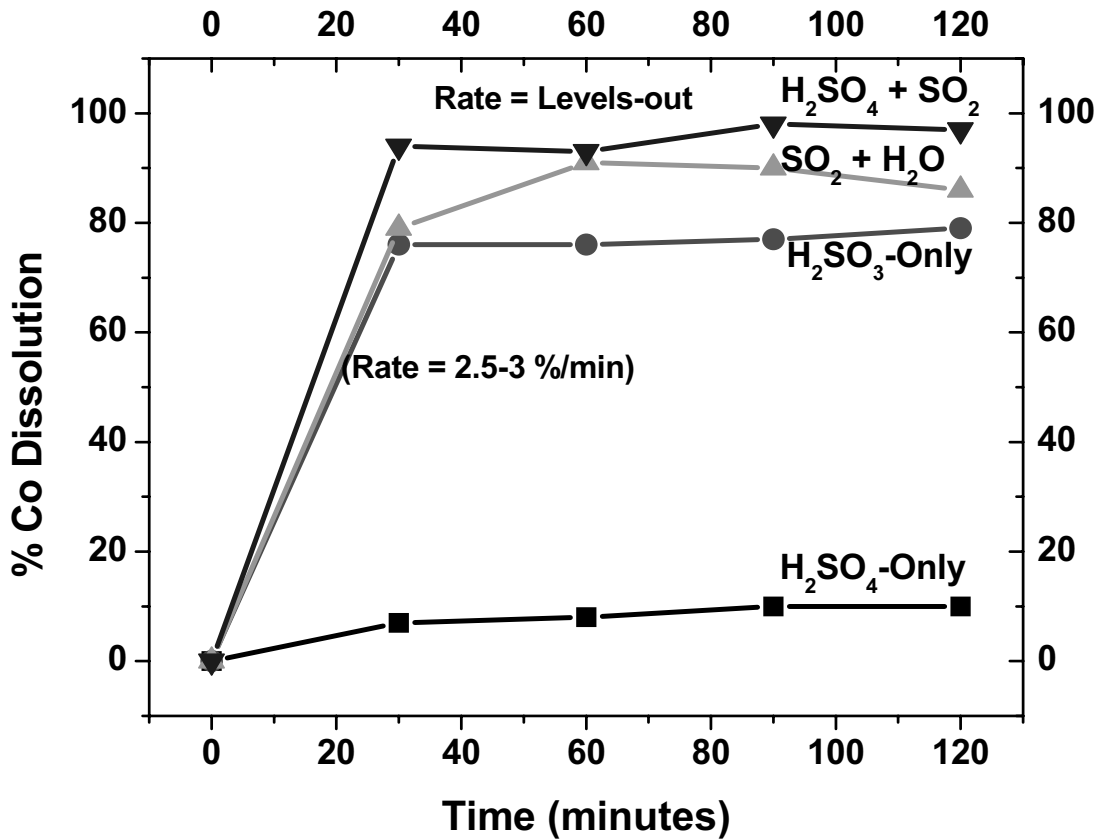


Figure 1: Leaching kinetics of cobalt in the high cobalt bearing ore.

Analysis of the high copper bearing ore with traces amounts of cobalt

In comparison, it was observed in Figure 2 that cobalt dissolution from the high copper bearing ore, which contains cobalt in small amounts (ca.0.5%), gives similar leaching trends as observed in Figure 1 during the leaching process of the high cobalt bearing ore which contains about 35% cobalt. The kinetic curves in Figure 2 show an elevated initial rate from 0-30 minutes of the leaching time, and then an approximately linear relationship from 30-120 minutes of the residence time. The causes of the kinetic curves flattening beyond the 30 minutes mark in Figure 2 are likely due to the rate of reactions taking place and extended reaction times. It was also observed in Figure 2 that the extraction of cobalt from the high copper bearing ore reached its endpoint at the 30 minutes mark under all the given experimental leaching media.

It was found that the feed solution of SO₂ - H₂O admixture gave the highest cobalt leaching yield (80%) after 120 minutes of leaching time. This observation amplifies the significance of cobalt leaching under reductive conditions (H₂SO₃-only) in contrast to

cobalt leaching from the high copper bearing under oxidative conditions (H_2SO_4 -only). This further serves to explain the maximum extraction percents obtained for cobalt when the admixture of two acids ($H_2SO_4 + SO_2$) was used rather than aqueous H_2SO_4 or SO_2 alone.

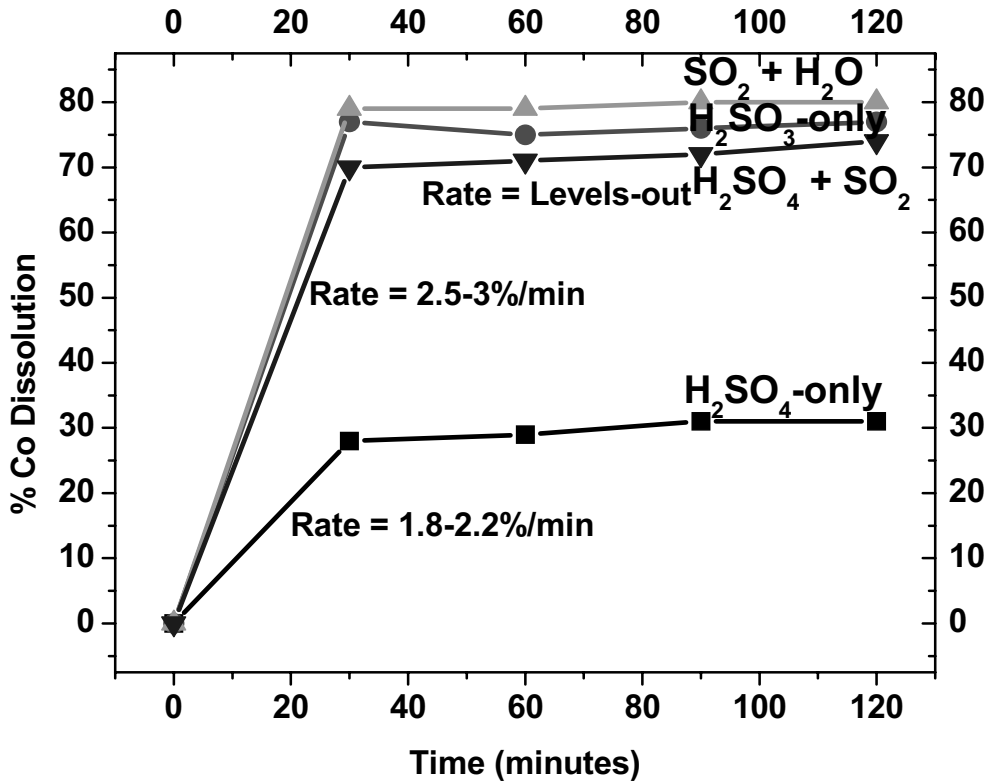


Figure 2: Leaching kinetics of cobalt in the high copper bearing ore.

Analysis of the low cobalt bearing ore (with mica).

The kinetic curves shown in Figure 3 for the leaching process of cobalt from the low cobalt bearing ore indicated that the maximum extraction of cobalt from this ore was achieved when the $H_2SO_4 + SO_2$ admixture was used as a leach medium. The gradually accelerating leaching rate for cobalt from the low cobalt bearing ore was observed from 0-60 minutes of the leaching time where $SO_2 + H_2O$ and H_2SO_4 were used as leaching media. In contrast, the cause of the $H_2SO_4 + SO_2$ kinetic curve reaching a plateau at 30 minutes and flattening thereafter was likely due the low pH (0.56) at the beginning of the experiment. In this case, it was thought that the lower the pH the higher the cobalt extraction efficiency.

Figure 3 was used to derive the rate of cobalt dissolution from the low cobalt bearing ore. The rate of cobalt dissolution was taken as the slope of each curve. The role of SO_2 as a

reducing agent during the leaching of cobalt has been illustrated significantly in the results presented in Figure 3. A big jump in the percent cobalt dissolution was observed when SO_2 was used with another reagent for the leaching process of the low cobalt bearing ore. This was evident when comparing percent cobalt dissolution from H_2SO_4 -only (ie.20%) to that of $\text{SO}_2 + \text{H}_2\text{O}$ (ie.96%) and $\text{H}_2\text{SO}_4 + \text{SO}_2$ (98%) admixtures after 120 minutes of leaching.

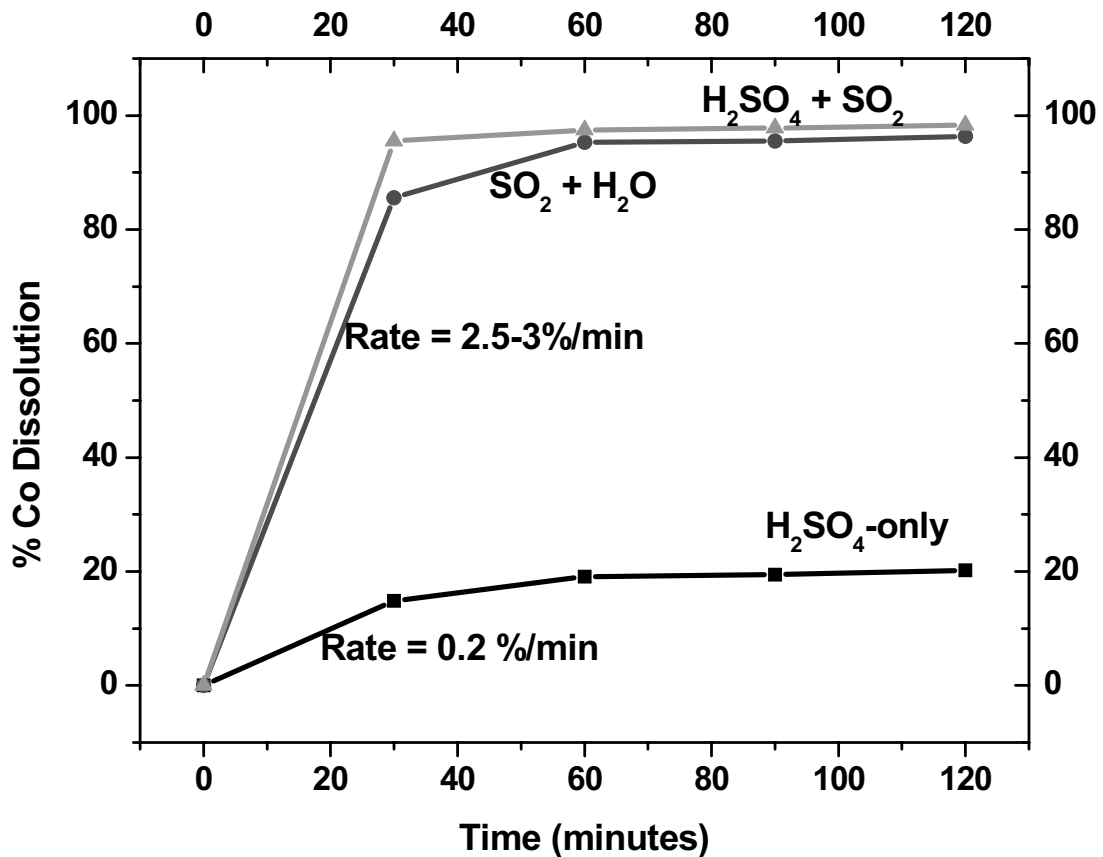


Figure 3: Leaching kinetics of cobalt in the low cobalt bearing ore (with mica).

Analysis of the low cobalt bearing ore (without mica).

The results obtained for leaching the low cobalt ore without mica are very close to those obtained for the low cobalt ore with mica. The rate of cobalt leaching in this case was close to that obtained in Figure 3, proving that the presence of mica did not affect the leaching efficiency of cobalt since the extractability remained as efficient.

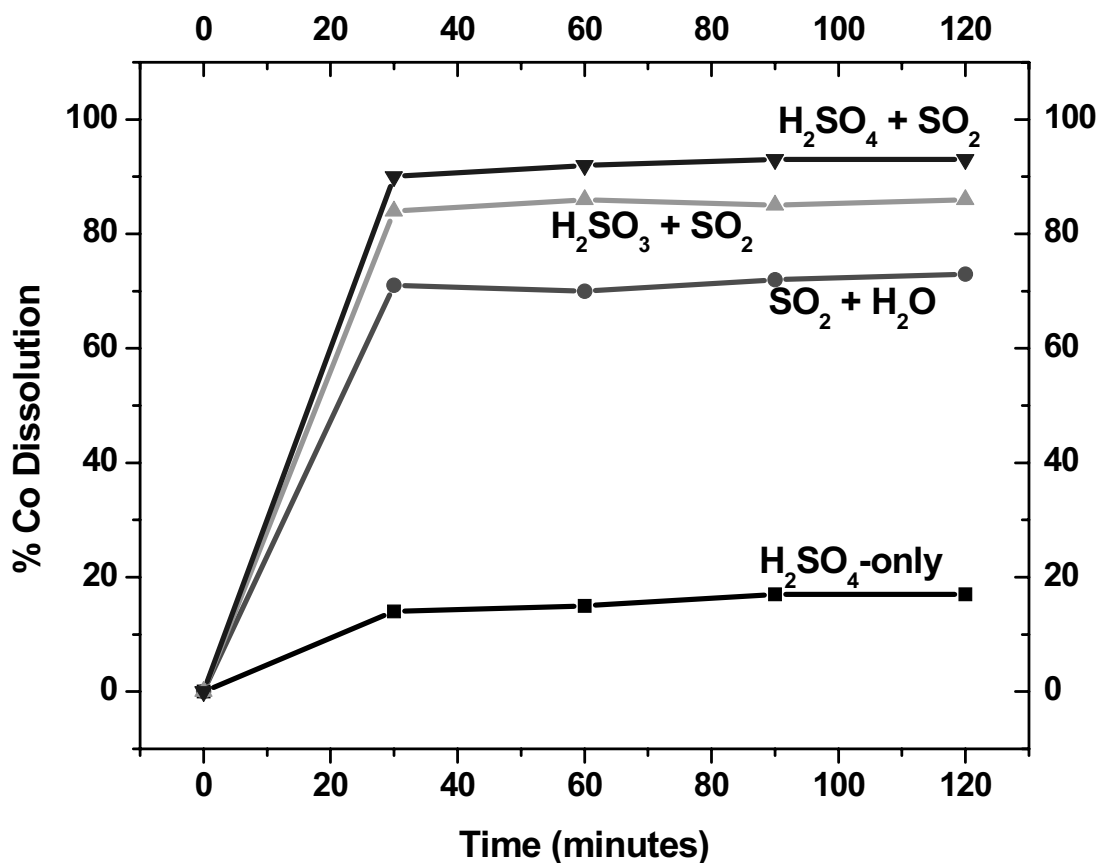


Figure 4: Leaching kinetics of cobalt in the low cobalt bearing ore (without mica).

UV/Visible spectroscopic analysis

UV/Vis spectra of Co²⁺ and Co³⁺ before SO₂ treatment.

Tetrahedral cobalt(II)thiocyanate complexes show an intensely blue color, and as such are readily distinguishable from octahedral cobalt(III) complexes. There was no ambiguity in the assignment of wavelengths of absorbance for the complexes because only two bands were expected, the lowest-energy band being at higher wavelengths in the visible region and the highest energy band of Co (SCN)₆³⁻(aq) at lower wavelengths. The reasons for the structure of both bands have been previously debated (Knowles et al, 1984). The reasons were attributed to spin-orbit coupling effects as well as transitions to doublet states. The sharpness of the bands were probably as a result of the ratio of the slope of the curve for the upper state to that of the ground state. It was also understood that during vibrations of the complex ion, the ligand field strength 10Dq varies about

some mean value. If the energy separation between two levels is not dependent on ligand-field strength, a sharp absorption band is expected.

UV/Vis spectra of Co^{2+} and Co^{3+} before SO_2 treatment.

In order to elucidate the role of SO_2 during the leaching process SO_2 was flushed into the mixture of Co^{3+} and Co^{2+} whose UV-Spectrum is shown in Figure 5. The UV spectroscopic measurements therefore serve to explain why there was an enhanced leaching of Co from its ores in the presence of SO_2 compared to the yield obtained when there was no SO_2 included. Thus, unequivocally, the role of SO_2 as a reducing agent during the leaching experiment was clearly defined in Figures 5 and 6.

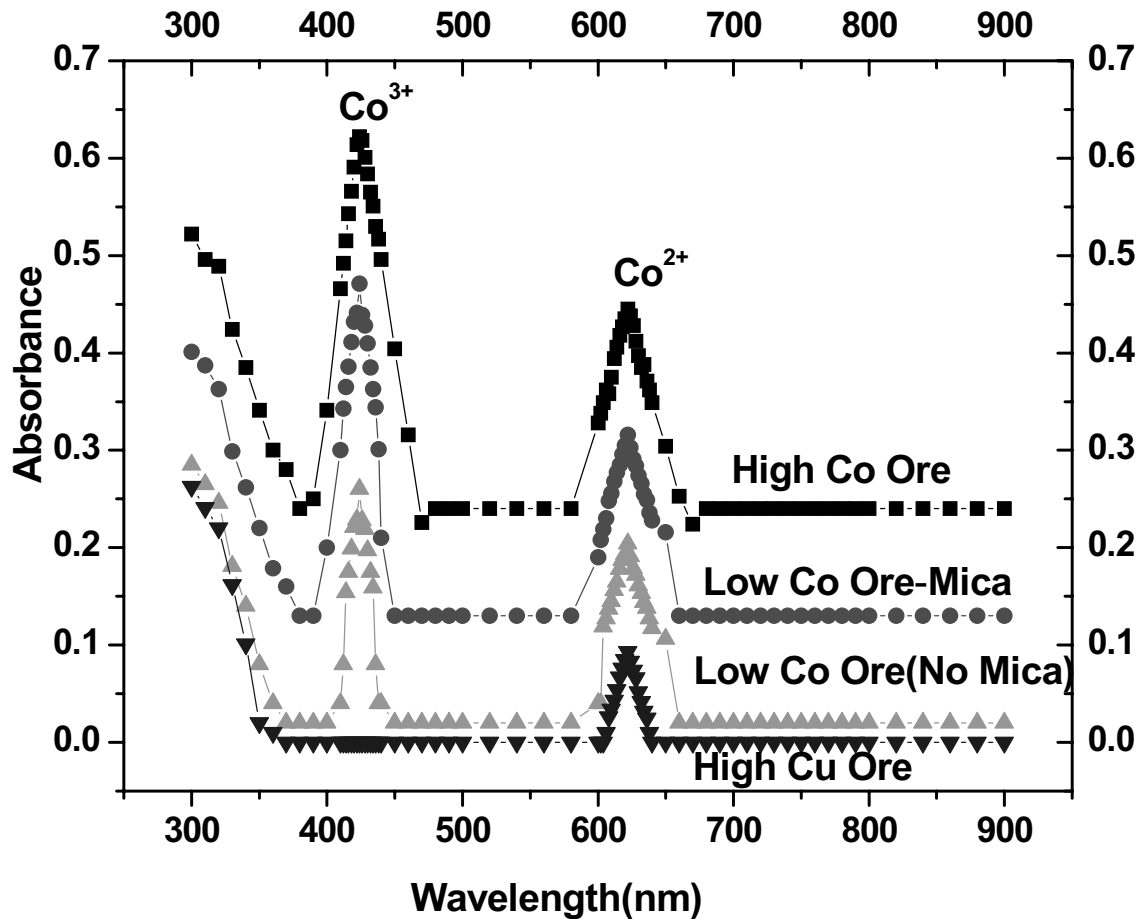


Figure 5: Co^{3+} and Co^{2+} spectrum before SO_2 treatment.

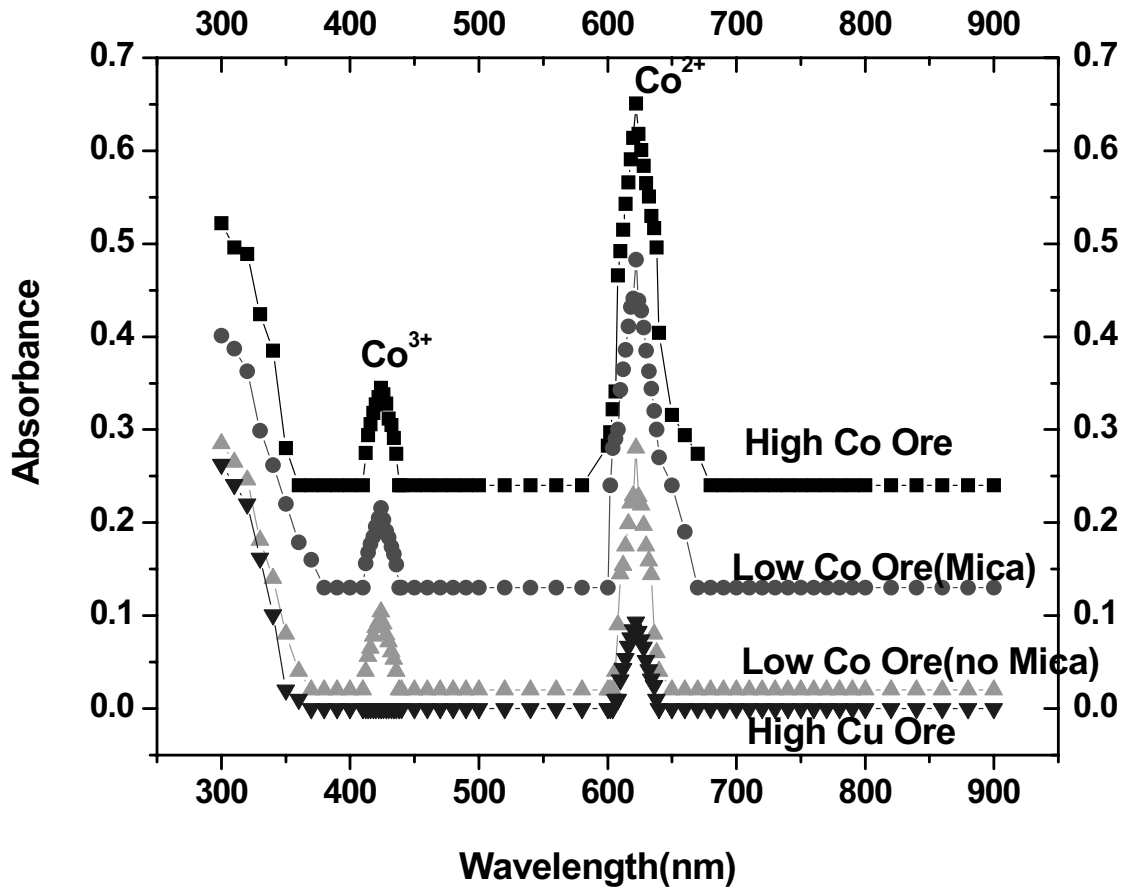


Figure 6: Co³⁺ and Co²⁺ spectrum after SO₂ treatment.

It was observed that in all leach experiments without flushing of sulphur dioxide in the system, the ratio of Co³⁺ to Co²⁺ was high(Figure 5). In all cases where sulphur dioxide is flushed through the leaching system, a substantial reduction of the Co³⁺ content in solution with an increase in the Co²⁺ content was observed (Figure 6). This therefore, predicts a reduction effect of Co³⁺ to Co²⁺ during dissolution as SO₂ was flushed in the leaching system.





The reactions 1 and 2 show an equilibrium system involving $\text{Co}(\text{SCN})_4]^{2-}(\text{aq})$ and $\text{Co}(\text{SCN})_6]^{3-}(\text{aq})$. The hydrated hexaaqua cobalt(II) ion reacts with thiocyanate ions forming a tetrahedral $[\text{Co}(\text{SCN})_4]^{2-}$ at a ligand coordination number of 4 which goes into equilibrium with the octahedral $\text{Co}(\text{SCN})_6]^{3-}$ at the ligand coordination number of 6. This complexation was carried out in a mixed solvent system made-up of 50% water and 50% acetone to facilitate ligand-exchange on the cobalt ions.

Microwave treatment prior to leaching

Leaching of cobalt ores before and after microwave treatment

It was generally observed that microwave pre-treatment of mixed cobalt-copper oxide ores led to the improvement in the leaching efficiency of cobalt as can be seen from Figures 7-10. It was also observed that the energy distribution in the microwave cavity was not uniform hence hot and cold spots of the irradiated material due perhaps to under/over-exposure of the ore material. The response of cobalt leaching after microwave treatment demonstrated by Figures 7-10 is not compatible to the response obtained when sulphur dioxide was used to improve the leaching yield of cobalt from mixed cobalt-copper oxide ores discussed previously.

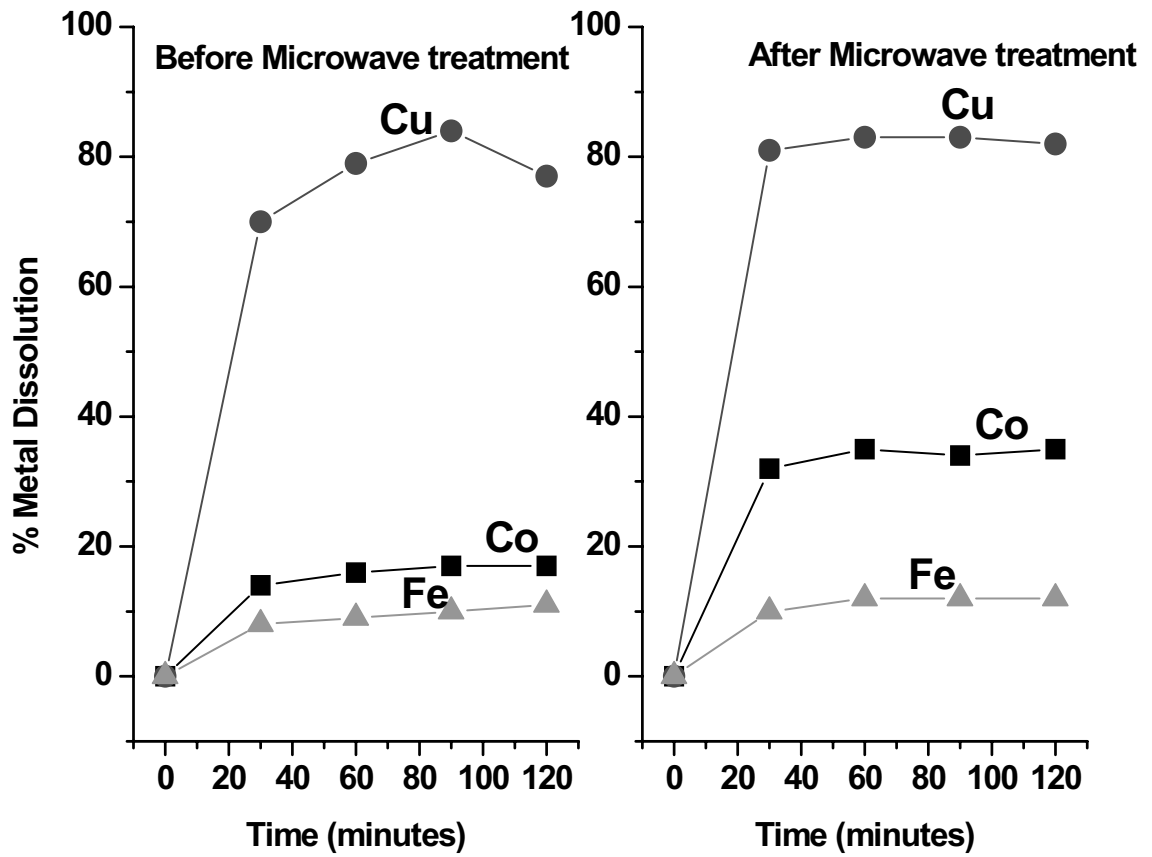


Figure 7: Kinetic curves for leaching high cobalt bearing ore before and after microwave pre-treatment.

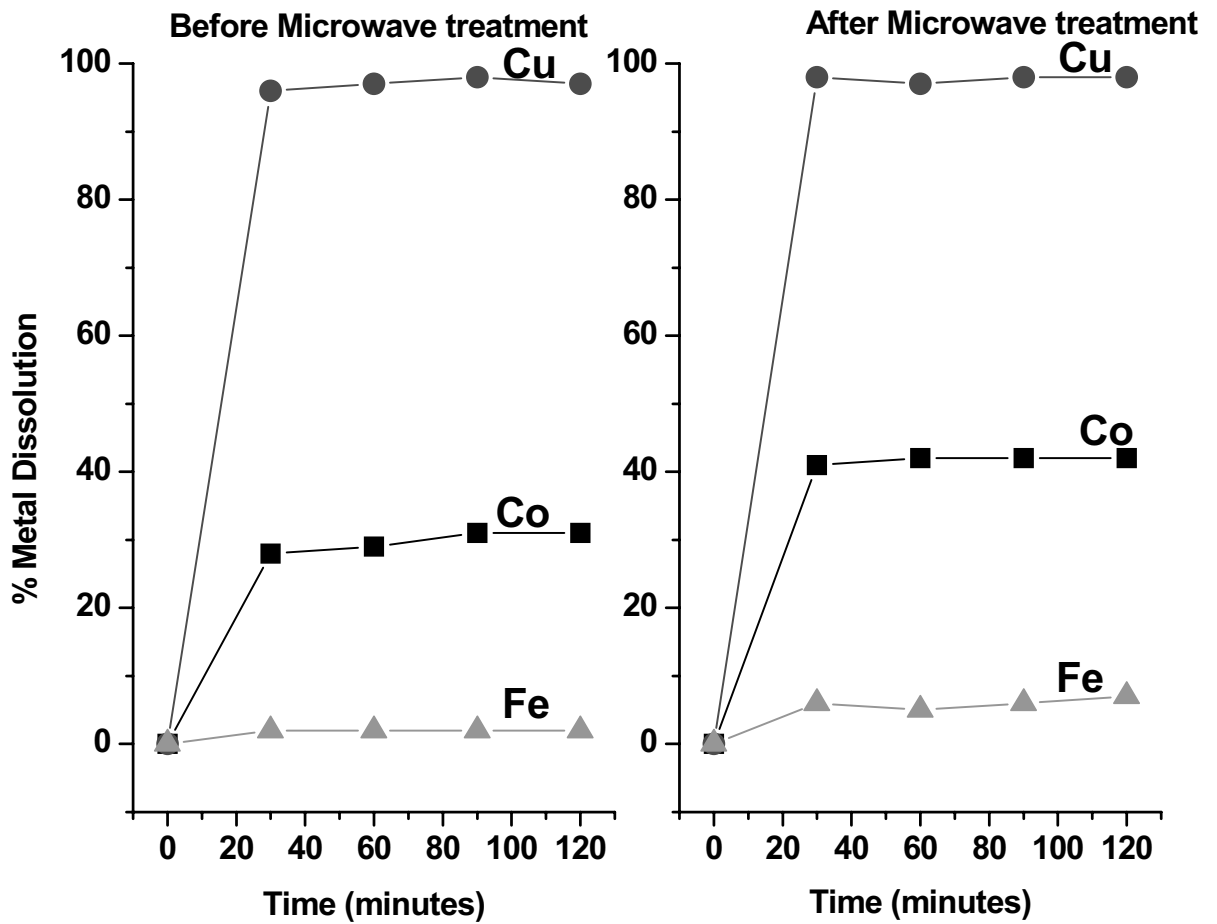


Figure 8: Kinetic curves for leaching high copper bearing ore before and after microwave pre-treatment.

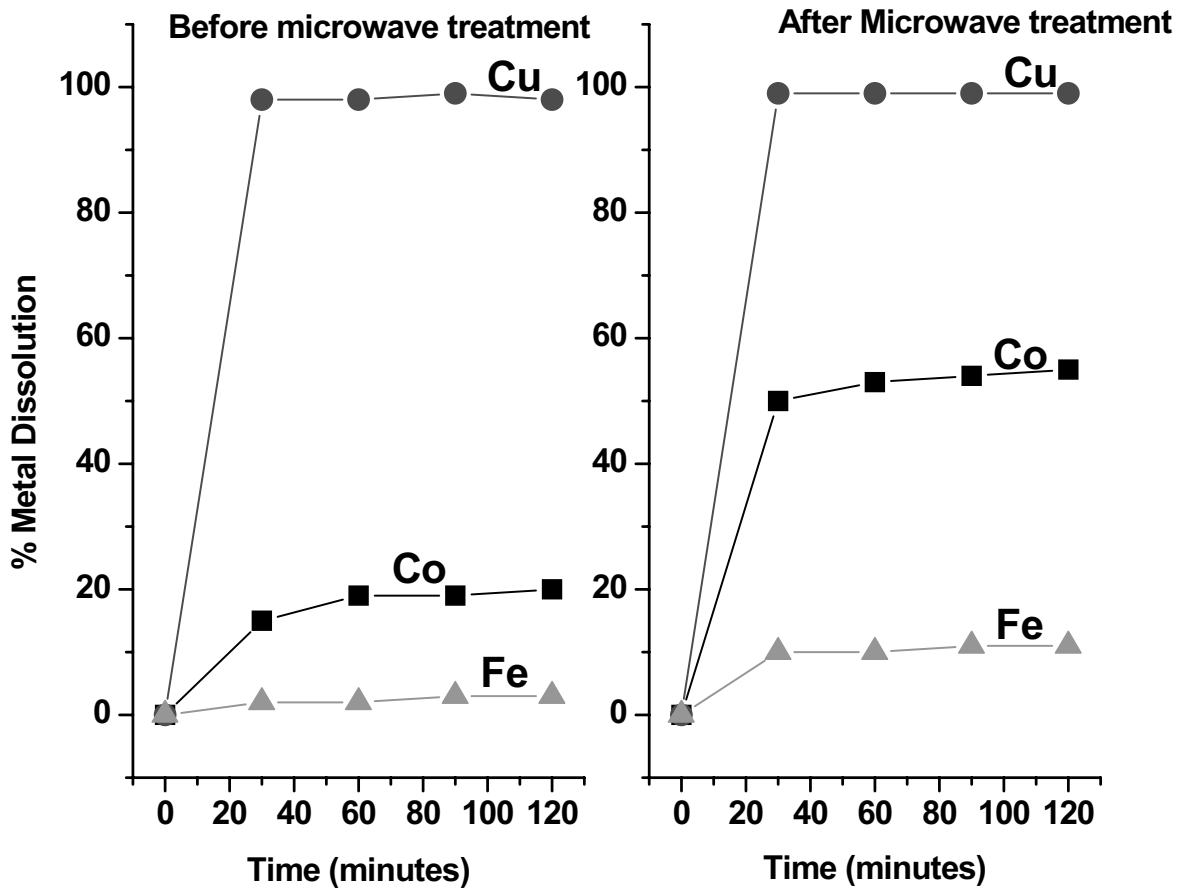


Figure 9: Kinetic curves for leaching low cobalt bearing ore (with mica) before and after microwave pre-treatment.

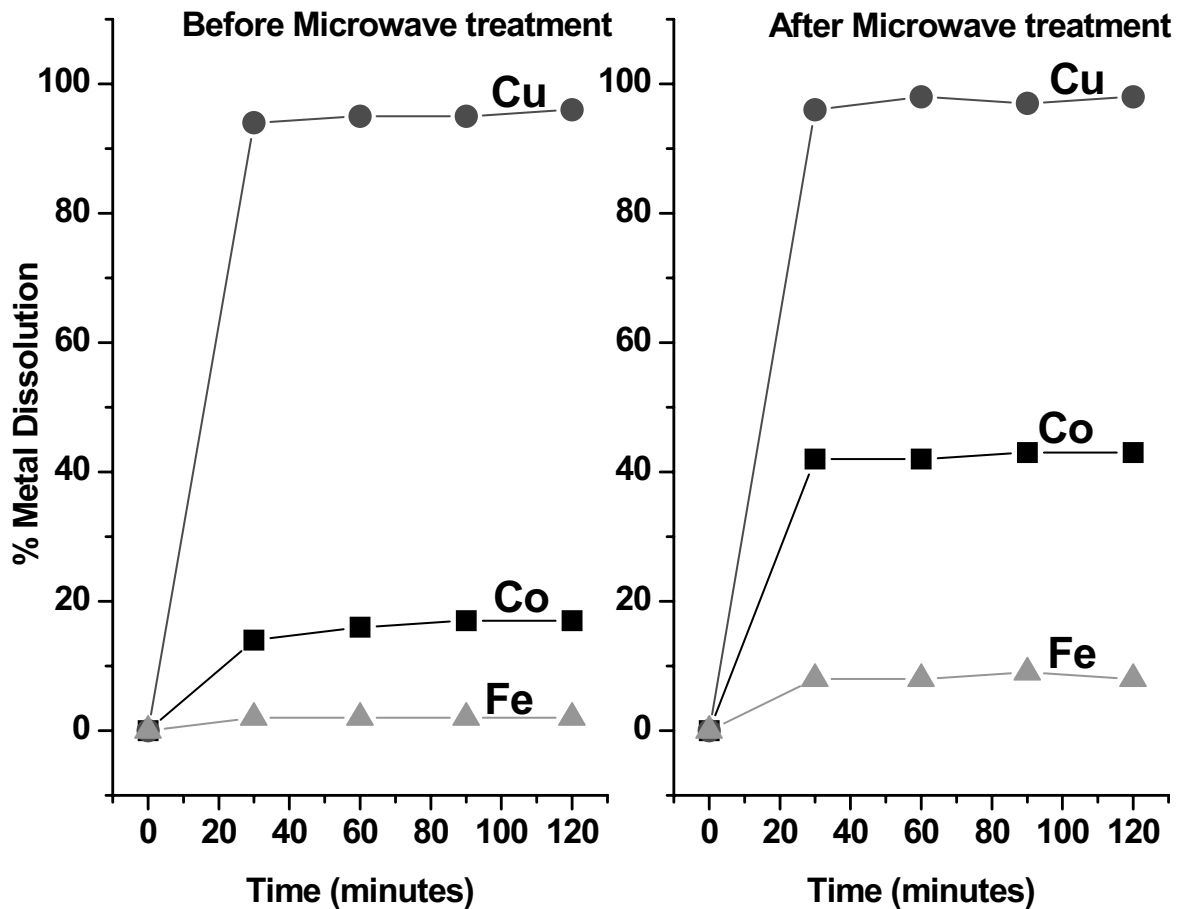


Figure 10: Kinetic curves for leaching high cobalt bearing ore (without mica) before and after microwave pre-treatment.

Conclusions and recommendations

A high yield of Co (85-95%) was obtained where the leaching process was performed in the presence of SO₂ for all four cobalt bearing ores. In fact, from the reaction kinetics it was evident that the rate of leaching was very high after 30 minutes given the yields of at least 80% that was obtained. Furthermore, the UV spectroscopic determination confirmed the role of SO₂ as a reducing agent during the leaching process. A comparison between the behavior upon microwave irradiation and the role of sulphur dioxide during leaching of mixed oxide ores leads to conclude that while the technique (i.e. microwave irradiation) is also appropriate to improve the leaching efficiency of cobalt from mixed cobalt-copper oxide ores, it does not seem to yield exceptional results compared to sulphur dioxide.

The hand-picked cobalt oxide samples are of such physical composition that knowledge gained from their examination is unlikely to be valid for cobalt sulphides ores. However, in view of the results obtained and the demonstrated response of the cobalt oxide mineral to microwave irradiation, ores of more realistic composition should be examined in the same manner to arrive at proper conclusions of this work.

Acknowledgements

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