

LEACHING OF A Cu-Co ORE FROM CONGO USING SULPHURIC ACID-HYDROGEN PEROXIDE LEACHANTS

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Abstract

A Cu-Co ore from Katinga Province, the Republic of Congo containing 1.5% Co and 1.6% Cu was tested to determine the leachability of Cu and Co using sulphuric acid and hydrogen peroxide mixtures at different conditions. Without hydrogen peroxide, the maximum extraction of copper and cobalt were found to be ~80% and ~15%, respectively when the acid concentration was varied between 0.36 – 1.1M. When hydrogen peroxide was added (0.008-0.042M), Cu recovery was enhanced to ~90%. Recoveries of ~90% of Co could be achieved at 20°C, using leachants consisting of 0.36M sulphuric acid and 0.025M hydrogen peroxide after 3 hours. The reaction time to reach 90% Co extraction was reduced to less than 2 hours at 30°C. Stabal modelling of the Eh-pH diagrams shows the importance of hydrogen peroxide as a reductant. The decrease of solution potential (300-350 mV) by adding hydrogen peroxide was confirmed by Eh measurements during the tests. The leaching follows the shrinking core model kinetics, where the rate constant is linearly dependent on hydrogen peroxide concentration in the range 0-0.025M and proportional to $(1/r^2)$ where r is the average radius of the mineral particles. The activation energy for the leaching process is 72.3 kJ/mol.

Keywords: Cu-Co ores; Leaching; Sulphuric acid; Hydrogen peroxide; Shrinking-core model; Stabal modeling

1. Introduction

Copper oxide ore deposits in the Central African copper-belt region such as Katanga province of the Republic of Congo contain high levels of well-oxidised copper (2-4% Cu) and cobalt (1-3% Co) [1,2]. The lack of response of Cu-Co oxide minerals during flotation [3] implies that heap or vat leaching should be considered for these ores. In industrial heap or vat operations, sulphuric acid is commonly used to leach copper from oxide minerals such as malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$), azurite ($2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) and chrysocolla ($\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$). Sulphuric acid was also used to easily leach copper from a roasted Cu-Pb matte [4]. Such a leaching scheme however needs to be modified to also extract cobalt as this metal exists mainly as Co(III). Common Co(III) minerals such as crystalline stainierite, $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or amorphous heterogenite (CoOOH or $\text{CoO} \cdot 2\text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) are found in most weathered copper oxide ores [5].

The leaching of Co(III) from spent LiCoO_2 cathode materials of lithium ion batteries (generally containing 5-15% Co) and its recovery have been dealt with in many studies lately [6-8]. Mineral acids such as HCl [9,10], HNO_3 [11] and H_2SO_4 [12,13] were used to dissolve Co(III) from spent batteries.

The use of hydrogen peroxide had been known to improve the Co dissolution rate and recovery [14]. Citric acid and hydrogen peroxide was also used to effectively leach Co from Li-ion cathode scraps [8].

Work on the leaching and recovery of Co from manganese nodules (generally containing >20% Mn and less than 1% each of Cu, Ni and Co) was earlier based on reductive leaching using H_2SO_4 and organic reductants such as phenols, amines, sucrose and glucose [15,16]. Inorganic reductants such as coal lignite, SO_2 gas, sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and hydrogen peroxide were found to be effective in dissolving Co(III) from manganese nodules [15], Co-Cu oxide ores [1,3,5] and zinc plant purification residues [17]. The reaction of synthetic Co_3O_4 (chemical reagent grade) with a NH_3 - SO_2 - H_2O mixture was also earlier studied [18,19].

Safarzadeh et al [17] proposed the well-known shrinking core model to describe the leaching of Co(III) from a zinc residue. The reaction kinetics was controlled by the diffusion of the reactants through a product layer. Ferron [5] found that 95% of Cu from his samples was dissolved in mild sulphuric acid (pH 1.9) at 33°C within 45 minutes. Cobalt dissolution on the other hand was limited to less than 10% under these conditions. Only when >50 kg SO_2 /tonne ore

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was added that cobalt can be fully recovered (>98%) within 2 hours. A combination of both Fe(II) and SO₂ was found to increase the reaction rate, as Fe(III) formed from the leaching was then converted to Fe(II) by SO₂, thus maintaining the reductive environment for Co(III) leaching.

This study was therefore conducted to determine the response of the Cu-Co ores during leaching using sulphuric acid/hydrogen peroxide leachants and to identify the key parameters and reaction mechanism controlling the reaction rate.

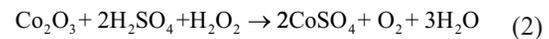
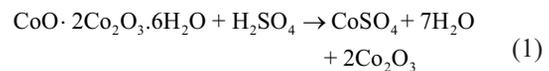
2. Materials and experimental methods

The Cu-Co ore was collected from an exploration site in Katanga province of the Republic of Congo. Samples were subjected to testing as received or after wet sieving and dried at 80°C in an oven. All chemical reagents were of analytical grade and deionized water was used in the study. The leachability of metal values was determined from experiments which were performed using a 1-litre three-necked Pyrex reactor fitted with a mechanical stirrer and a reflux condenser. The reactor was immersed in a thermostatic water bath, of which temperature was controlled to within +/- 1°C. To determine the effect of particle size on the leaching characteristics, the bulk materials required at different narrow size fractions were wet screened using sieves. The head grade for the each size fraction (Table 1) was determined from chemical analysis after full digestion of a representative sample in aqua regia. An experiment was started by adding 50 g of ore of a known size and hydrogen peroxide. During the experiment, 2mL samples were taken at different time intervals, filtered using a 0.5 micron filter and subjected to chemical analysis using ICP-MS (Agilent Technology, model 7700). Particle size distribution measurements (using Micromeritics Instrument) in duplicate were used to determine the average radius of the each sample.

3. Thermodynamic consideration

As shown later, Co (II, III) oxide minerals such as CoO·2Co₂O₃·6H₂O or Co₃O₄, in the raw ore require a reductant and an acid to be fully dissolved. The dissolution also needs to be controlled at a pH<1 as at a higher pH, the leaching would produce solid CoO·Fe₂O₃, thus passivating the reaction. A similar behavior is predicted for the Cu system, where CuO·FeO could be formed. The leaching characteristics and conditions (Eh and pH) could be predicted by the following Eh-pH diagram (Fig. 1) produced from Huang's Stabcal modelling software [20].

The reaction of hydrogen peroxide with Co(III) oxides is expected to follow the following reactions:



Figs. 2 show that by adding hydrogen peroxide (0.018-0.054 M at 20°C and 0.054M at 25°C), the solution Eh (measured against a saturated calomel electrode, SCE = 0.242 V vs standard hydrogen electrode) was reduced by 300-350 mV throughout the leach. Without hydrogen peroxide, the solution potential could reach >900 mV vs SCE by the end of the leach. The solution potential was reduced to 580-600 mV vs SCE throughout the leaching using hydrogen peroxide. Other copper oxide minerals such as CuO or malachite Cu(OH)₂·CuCO₃ should dissolve directly in sulphuric acid.

4. Results and Discussion

4.1 Characterisation of the ore samples

X-Ray Fluorescence (XRF) analysis shows the assaying consistency of most metals of interest (Co,

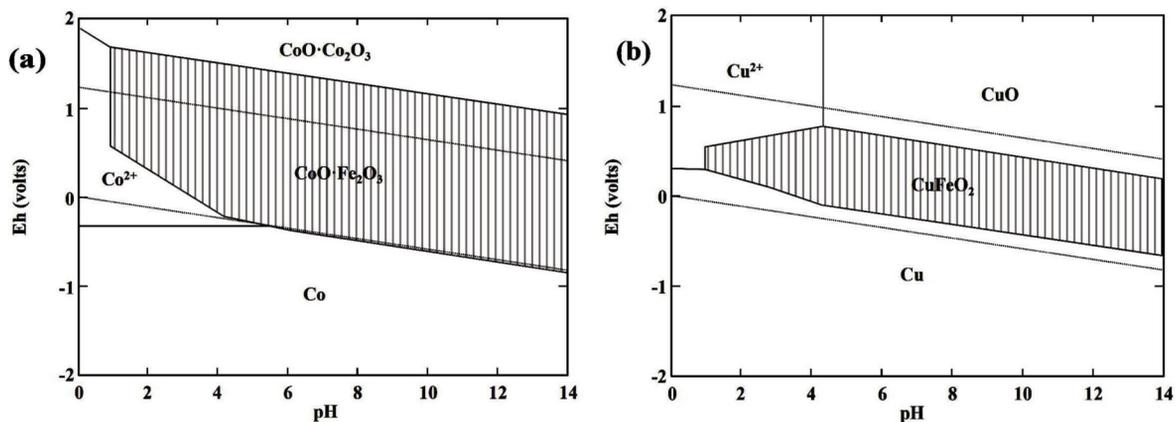


Figure 1. Eh-pH diagrams (25 °C) calculated for the (a) Co system and (b) Cu system, in the presence of Fe and other elements found in the ores

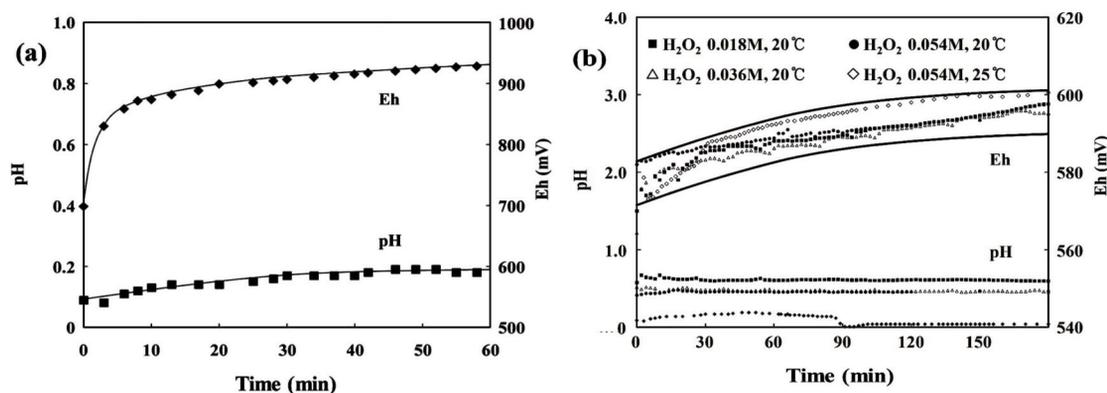


Figure 2. Variation of solution Eh and pH during the leaching, (a) 0.732M sulphuric acid at 20°C and (b) 0.732M sulphuric acid and (0.018-0.054M) hydrogen peroxide at 20 and 25°C.

Cu, Ni and Fe) in the ore 's different size fractions (Table 1). Due to the low levels of Cu and Co in the original samples (<1.6%) it is necessary to collect hand-picked samples rich in green malachite ($Cu_2CO_3(OH)_2$) and rich in grey heterogenite ($CoOOH$ or $CoO \cdot 2Co_2O_3 \cdot 6H_2O$) for X-Ray diffraction analysis. It was first noticed that the XRD pattern for the heterogenite-rich sample also contains malachite peaks (Fig. 3).

The association of Cu in Co minerals was also confirmed by Electron Probe Micro-Analyser

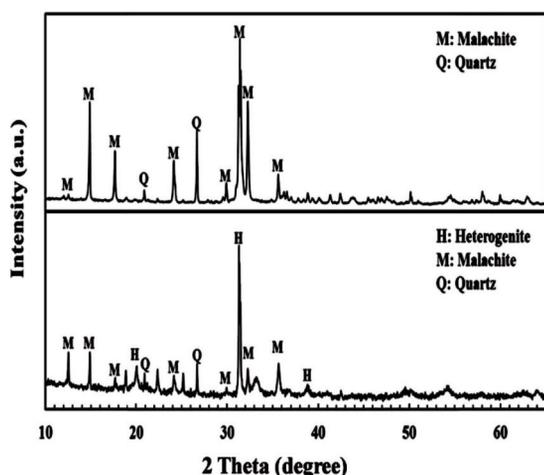


Figure 3. X-ray diffraction peaks of hand-picked grains of minerals (green malachite and gray heterogenite)

(EPMA). Fig. 4 shows the scattered grains of Cu oxide minerals in the original (Grains b), but some Cu might be associated with Co mineral grains (Grain a). This is confirmed by compositional analysis of a few hand-picked samples. EPMA scans of selected materials (rich in malachite and heterogenite) across 10 points of the samples also showed the composition of these mixed Cu-Co grains (Table 2).

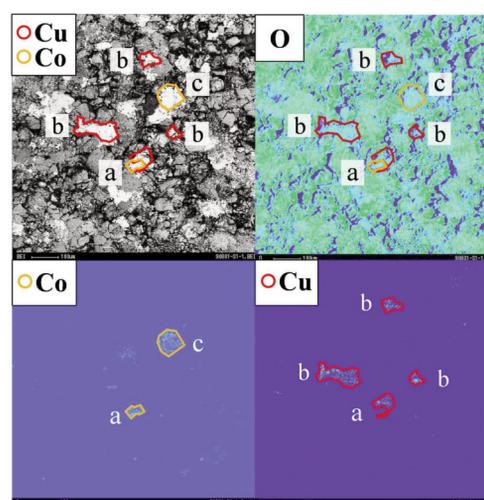


Figure 4. EPMA photograph of the original ore and scans for Cu, Co and O show the presence of Cu in mixed Co-Cu grains (a) and pure Cu grains (b); Co in pure Co grains (c). Oxygen is the main matrix for this oxidic ore.

Table 1. XRF Analysis (%) of samples of different size fractions.

Elements	Na	Mg	Al	K	Mn	Fe	Co	Ni	Cu	Zn
>150 microns	0.19	0.61	0.75	0.15	0.4	3.88	1.61	0.12	1.85	0.02
150-125	0.16	0.72	0.72	0.18	0.45	2.88	1.9	0.12	1.72	0.02
125-106	0.28	1	0.85	0.15	0.4	2.48	1.46	0.09	1.47	0.02
106-90	0.19	0.88	0.99	0.13	0.47	2.54	1.38	0.1	1.55	0.02
90-75	0.24	0.51	0.58	0.07	0.44	2.49	1.22	0.09	1.49	0.02
75-52	0.71	0.75	0.84	0.14	0.52	2.61	1.25	0.1	1.56	0.03

Table 2. EPMA-scanned composition analysis (average of 10 samples) showing composition (%) of Co in malachite-rich and Cu in Co-rich materials. EPMA cannot differentiate between Co(II) and Co(III) and therefore its composition is reported as CoO.

Oxide	Heterogenite-rich	Malachite-rich
CuO	10.97	67.53
CoO	61.3	0.83
Al ₂ O ₃	0.09	0.22
SiO ₂	1.26	0.06
FeO	7.03	0.83
MnO	0.71	0.01
Total	81.47	69.51

4.2 Leaching

The leaching of the ores was conducted at different solution compositions (of sulphuric acid and hydrogen peroxide), temperatures and particle size

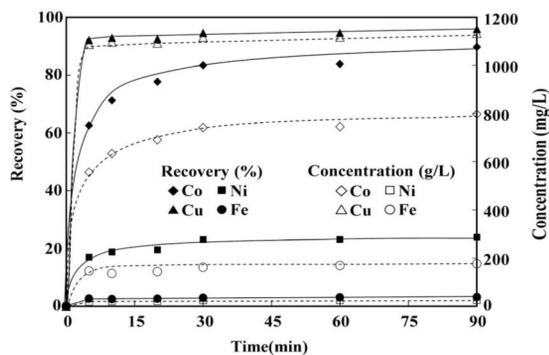


Figure 5. Concentration (g/L) and recovery (%) profiles for the leaching of Cu, Co, Ni and Fe at 20°C (Test conditions: 53-75 microns, 0.732M sulphuric acid and 0.036M hydrogen peroxide).

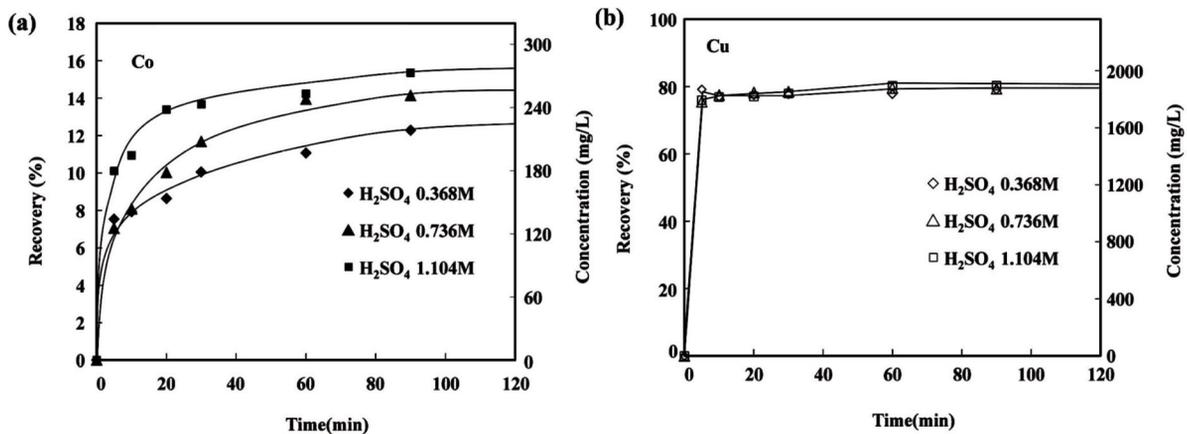


Figure 6. Effect of sulfuric acid concentration (0.368M to 1.104M) on the leaching of (a) Co and (b) Cu (Test conditions: 20°C, particle size 75-90 microns).

fractions. Fig. 5 shows typical leaching characteristics (53-75 microns, 0.732 M sulphuric acid and 0.025 M hydrogen peroxide) of different metal values existing in the ore. Only copper and cobalt could be extracted to yield solutions having >800 mg/L at test conditions. Copper could be extracted to achieve >90% recovery after 15 minutes whereas 90% cobalt could be recovered in 90 minutes under these conditions. Other metals of interest such as Ni and Fe were extracted to yield <200 mg/L each and will therefore be ignored in the following optimization study.

Co could not be leached past 15% recovery, using sulphuric acid alone (Fig. 6a) indicating the predominance of Co(III) minerals in the raw ore. Approximately 80% of the available Cu could be extracted within 20 minutes at ambient temperature using sulphuric acid at different concentrations from 0.036 to 1.10 M (Fig. 6b).

4.3 Effect of hydrogen peroxide concentration

Using (75-90) micron material the effect of hydrogen peroxide concentration on the leaching Co and Cu was examined in the leaching tests conducted at 20°C and 0.357 M sulfuric acid. Without hydrogen peroxide, the dissolution of Co was very low, reaching ~9.2% after 2 hours. The recovery of Co increased significantly at the addition of 0.008-0.042 M hydrogen peroxide (Fig 7a). As shown before, the dissolution of copper by sulphuric acid alone achieved a steady state very quickly and reached ~80% after 20 minutes (Fig. 6b). This dissolution could be further increased to ~90% at the addition of 0.008-0.042 M hydrogen peroxide (Fig. 7b). The fast reaction of Cu minerals with the leachant compared to a slower increase of Co dissolution indicates different reaction mechanisms controlling the Cu and Co extraction process.

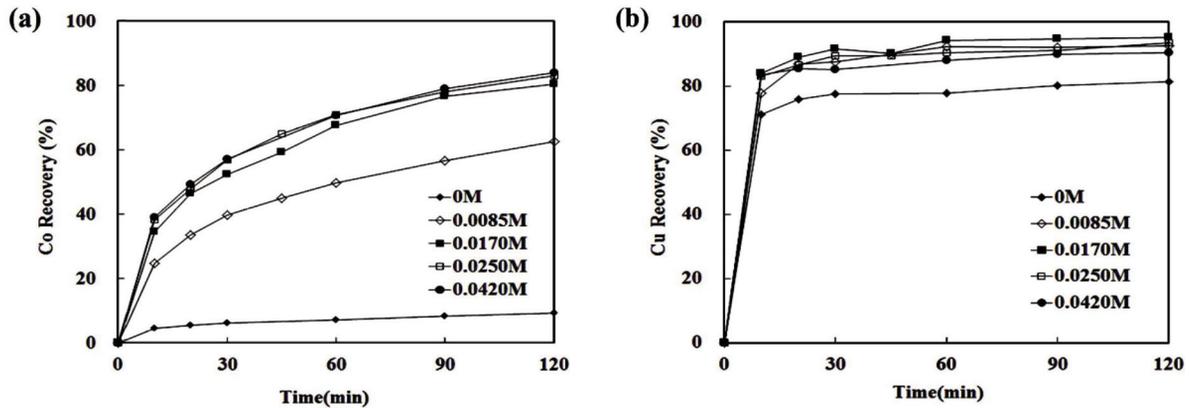


Figure 7. Effect of hydrogen peroxide concentration within the range 0.008-0.042M on the leaching of (a) Co and (b) Cu (Test conditions: 20°C, 0.36M sulphuric acid, particle size range: 75-90 microns)

4.4. Reaction kinetics – modelling of the Co dissolution process

The subsequent study focused on optimizing conditions to achieve ~90% Co recovery. A series of tests was therefore conducted covering also the effect of particle size and temperature. The Co recovery data were also fitted to the following equation based on the shrinking core model [21]:

$$1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}} = k \frac{1}{r^2} [H_2O_2]^x t \quad (3)$$

where t is the leaching time (min), α is the fraction reacted, r is the average radius of particles in the range tested, k is the intrinsic rate constant and x is the reaction order for H₂O₂. For this model, the rate determining step is the diffusion of the reactants through a product layer.

Recovery data from Fig. 7 fit well into Equation 3 yielding straight lines (of slopes A) having linear regression coefficient R² > 0.96 in all cases (Fig. 8).

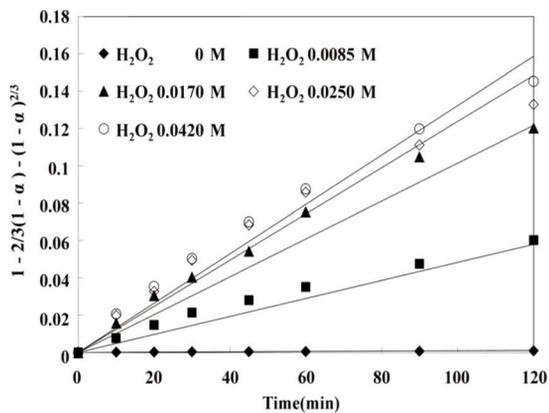


Figure 8. Plots of $1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}}$ expressions versus time yielding slopes A, for data at different hydrogen peroxide concentrations (0-0.042M) - Test conditions: 20°C, 0.36 M sulphuric acid, particle size: 75-90 microns.

The plot of slopes A of these lines for different hydrogen peroxide concentrations (0-0.042 M) versus hydrogen peroxide concentration yields a straight line from 0 up to 0.025 M H₂O₂ as shown in Fig. 9. The reaction rate becomes less dependent on hydrogen concentration above this range, indicating that the kinetic-controlling mechanism based on diffusion through a product layer governed by Equation 3 no longer holds past 0.025 M H₂O₂. The linear relationship between Slope A and hydrogen concentration also implies that the order for H₂O₂ in Equation 3 above (being x) is 1.

4.4.1 Effect of particle size

The effect of different particle sizes on the recovery of Co at 20°C, 0.36 M sulphuric acid and 0.025 M hydrogen peroxide was evaluated using 5 size fractions, namely 52-75, 75-90, 90-105, 105-125 and 125-150 microns. Recovery of ~90% or higher could be achieved in 3 hours for all sizes <125 microns. The recovery data also fits well to the

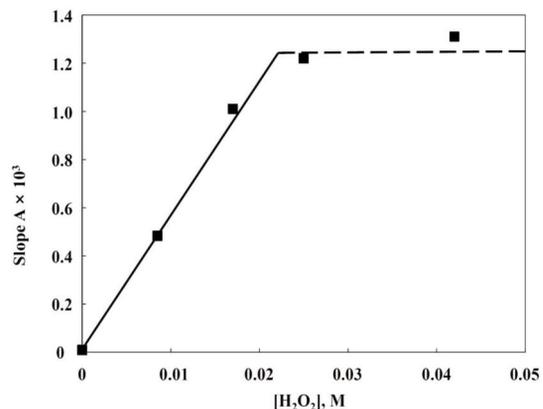


Figure 9. Variation of slopes A vs hydrogen peroxide concentration. (Test conditions: 20°C, particle size: 75-90 microns, 0.36M sulphuric acid).

shrinking core model kinetics (Fig. 10) of which all straight lines (of slopes B) representing Equation 3 were obtained with regression coefficient $R^2 > 0.96$. As shown in Fig. 11, the straight line plot of slopes B vs $1/r^2$, where r is the average radius measured for the samples tested also indicates that Equation 3 is a true representation for the kinetics controlling the leaching of Co from the ore.

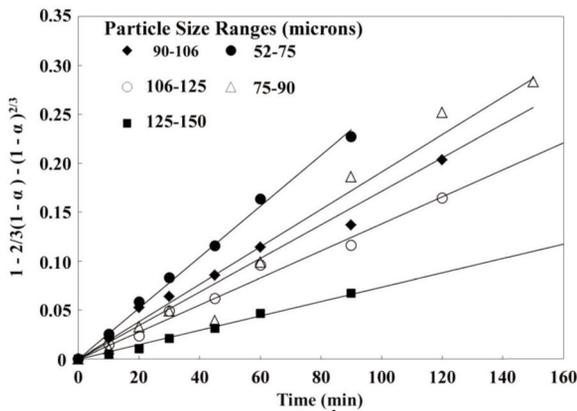


Figure 10. Plots of $1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}}$ expressions versus time yielding slopes B for data at different particle size ranges. (Test conditions: 20°C, 0.36 M sulphuric acid, 0.025M hydrogen peroxide).

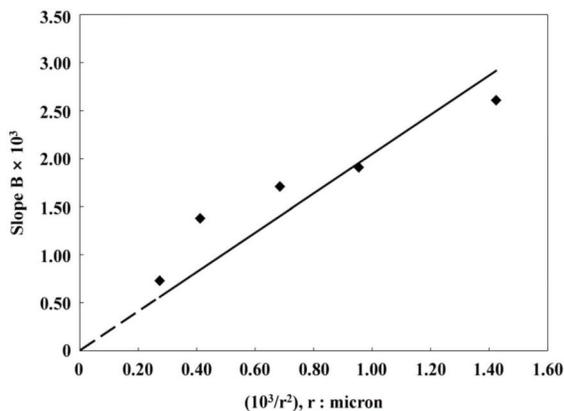


Figure 11. Plot of Slopes B vs $(1/r^2)$, r: average radius measured from particle size distribution curves

4.4.2 Effect of temperature

The effect of temperature on the kinetics of leaching Co was evaluated at 10, 20 and 30°C, using 0.36 M sulphuric acid and 0.025 M hydrogen peroxide mixtures for the two particle size ranges of 52-75 microns and 75-105 microns. The leaching was faster as temperature was increased as expected, with >90% Co recovered in less than 2 hours at 30°C. Data also fits well to the shrinking-core model (equation 3) yielding slopes C which can be plotted as the Arrhenius plot ($\ln[\text{slope C}]$ vs $1/T$) shown in Fig. 12.

From the Arrhenius slopes for the two size ranges tested (Slope = -Activation Energy/Gas constant) an average activation energy of 73.2 kJ/mol was derived for the leaching process.

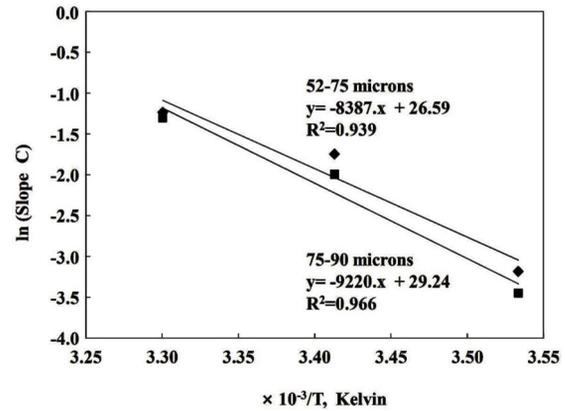


Figure 12. Arrhenius plots ($\ln[\text{Slopes C}]$ vs $1/T$) showing the effect of temperature on the reaction kinetics

The high activation energy indicates the resistance of the product layer on the diffusion of hydrogen peroxide to the reaction interface. Such a high activation energy (compared to liquid diffusion of 25 kJ/mol) is normal for this type of process, as also found with the leaching of Cu, Ni and Co Raney catalysts (having activation energy of 40-110 kJ/mol as reported by Smith et al [22]). One possible reaction scheme which explains the leaching process is illustrated as Equations 1 and 2, where the product layer of Co_2O_3 is formed after the CoO component of heterogenite ($\text{CoO} \cdot 2\text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) is first leached by acid.

5. Conclusion

A Cu-Co ore from Katinga Province, the Republic of Congo was tested to determine the leachability of Cu and Co at different conditions, namely (a) 5 particle size ranges from 52 to 150 microns, (b) temperature: 10, 20 and 30°C, (c) sulphuric acid: 0.046-1.10 M and (d) hydrogen peroxide: 0-0.42 M. Copper can be leached to achieve 80% recovery using sulphuric acid, which can be further improved to >90% by adding hydrogen peroxide (0.008-0.042M). Cobalt requires hydrogen peroxide addition of at least 0.025 M to be fully leached to ~90% at 20°C. The thermodynamics of the leaching (Eh and pH diagrams) determined using Stabcal software and monitored during the tests confirmed the role of hydrogen peroxide as a reductant. The leaching followed the shrinking core model kinetics, of which the controlling factor is the diffusion through the product layer, possibly the intermediate product Co_2O_3 . The rate constant is linearly dependent on

hydrogen peroxide concentration in the range 0-0.025 M and proportional to $(1/r^2)$ where r is the particle average radius.. The activation energy for the leaching is 72.3 kJ/mol.

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