A Solvometallurgical Approach to Copper Recovery from Low-Grade Sulphide Ore

Willie Nheta, Lusa Lwa Vidie Kishiko

***Abstract*—**The hydrometallurgical extraction of valuable metals, particularly copper, has long relied on aqueous leaching processes using inorganic acids. While this traditional method is economically viable, it faces significant challenges that limit efficiency, sustainability, and selectivity. This study explores the application of solvometallurgy as an alternative method for copper extraction from chalcopyrite ore, with the aim of avoiding silica gel formation and improving selectivity. Specifically, oxidative and complexing solvoleaching was performed using LIX 984N (a chelating extractant solvent) in combination with ethylene glycol, hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2), diluted in kerosene as a replacement for water. The results clearly indicated that the successive addition of ethylene glycol, HCl, and H_2O_2 significantly enhanced copper recovery, with temperature providing an additional positive effect. The optimum conditions were identified as 2.5 M H_2O_2 at 45°C with 50% ethylene glycol/LIX 984N-C and 2.5 M HCl, under which 88.11% of Cu was recovered within 150 minutes. Importantly, the process demonstrated selectivity towards iron, with only 1% Fe entrainment, highlighting the effectiveness of the method in minimising impurities. However, selectivity towards cobalt was less favourable, with 12.04% Co entrainment observed in the pregnant leach solution (PLS). Overall, this study demonstrates that solvometallurgy offers a promising alternative to traditional hydrometallurgical methods for copper recovery from chalcopyrite.

***Keywords*—**solvometallurgy, nonaqueous solvent extraction, base metals, copper, chalcopyrite.

I. Introduction

Solvent extraction (SX) is one of the essential techniques of separation and purification processes used in hydrometallurgy. In addition, processes such as ion exchangers and activated carbon are utilised to extract precious and base metals, rare earth elements [1]. The separation and purification procedures through the SX rely on the differential distribution of metal ions between two immiscible phases: the solvent phase containing the metals to be separated (usually an aqueous or polar phase) and the extractant phase diluted in a diluent (typically an organic or apolar phase) [2]. However, this process is associated with several disadvantages, such as high cost of organic solvents, solvent losses and degradation, complex designs and control, etc. Out of all these constraints forcing the stabilisation of both the organic phase and the aqueous phase to optimise the transfer of metal ions to the extraction phase and challenges encountered in hydrometallurgy, researchers appeal to using the non-aqueous solvent technique as a palliative to the aqueous phase.

Recently, researchers have devised a new method for separating mixed metals by replacing or adding polar organic solvents to the aqueous phase [3]. The extraction behaviour changes when polar organic solvents are added to an aqueous solution. Due to polar organic solvents, the aqueous-organic combination can no longer be referred to as an aqueous phase but rather a non-aqueous one. [4] designated two phases: the "more polar phase" and the "less polar phase." Incorporating polar organic solvents affects extraction efficiency by reducing water activity, altering (decreasing) dielectric constants that influence complex stability, modifying the mutual solubility of the two phases, and affecting interfacial tensions.

Non-aqueous solvent extraction (NASX) involves using a polar organic solvent to substitute water, which is considered the most polar phase in solvent extraction. The non-aqueous solvent extraction method uses two immiscible organic phases and is an experimental approach introducing solvometallurgy technology. The principle is similar to hydrometallurgy, but in the current case, it involves organic solvents instead of water to extract metals. Extraction of metals from non-aqueous solvent systems consists of the use of a small amount of water (generally <50 vol%) [5], [6]. In certain circumstances, a minimal quantity of water in a NASX system is permissible and potentially beneficial. This may reduce the viscosity of the more polar phase, decrease their miscibility, enhance the solubility of salts in the solution, and improve selectivity for the separation of metal ion combinations by modifying metal ion solvation [7].

This study investigated the use of solvometallurgy in the recovery of copper from a chalcopyrite ore. The process involved directly implementing a non-aqueous solvent to extract copper from sulphide ore.

II. Materials and Methods

A. Sample preparation

The sample used in this project is a concentrate produced from a metallurgical plant in the Democratic Republic of Congo (DRC). The as-received sample was first milled and classified into different size fractions. Before conducting

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experiments, the representative sample was characterised for chemical composition, mineralogy, and distribution using the X-ray fluorescence (XRF), X-ray diffraction (XRD) and Scanning Electron microscopy (SEM-EDS). The chemical reagents utilised were of high grade and were supplied by South African companies based in Johannesburg. The ACE company supplied sulphuric acid, hydrochloric acid, and hydrogen peroxide. Glassworld delivered ethylene glycol, while kerosene was obtained from Sigma-Aldrich. The organic extractant LIX 984N-C was sourced from BASF.

For leaching and purification purposes, the following reagents were used.

Organic chemical agents

- More polar organic compound: Ethylene glycol (95%)
- Less polar organic compound: LIX 948 N-C
- Diluent kerosene

Mineral chemical reagents

- pH regulator: NaOH, H_2SO_4 (98%)
- Oxidising agent H_2O_2 (50%)
- Lixiviant : HCl (32%)

B. Experimental procedure

The solvoleaching of Cu from chalcopyrite using a solvent was applied under oxidising conditions. It was performed in a 200 mL beaker containing a solution made of the organic solvent and the oxidising agent (H_2O_2). The more polar phase, consisting of ethylene glycol and HCl at different concentrations, was mixed with the less polar phase, which consisted of the extractant and the diluent in various proportions under oxidising conditions. 5g of Cu-bearing sample was added to the mixture of the solvent. The pulp was stirred using the magnetic stirrer, and the temperature and the stirring rate were monitored according to the design.

The leaching parameters of chalcopyrite were optimised by varying the temperature, the leaching time, the concentration of the lixiviant HCl, the concentration of the oxidising agent H_2O_2 and the concentration of ethylene glycol according to the number of runs generated by the one-factor-at-a-time optimisation method. The proportion of the less polar phase varied from 50 to 90%.

Note that the leaching and the solvent extraction were done at the same time.

After leaching, Cu carried in the organic phase was stripped by putting the organic phase in contact with a solution of H_2SO_4 and then agitating for about 10 min at 25 °C to transfer Cu ions to the aqueous phase and generate a strip product of copper sulphate. After stripping, the aqueous phase was analysed using the Atomic Absorption Spectroscopy (AAS) to determine the amount of dissolved Cu. The dissolution and recovery efficiency of the Cu in the pregnant and pure solutions were evaluated using equations 1 and 2, respectively.

$$\textit{Dissolution efficiency}\,(\%) = \left(\frac{(C_1 \times V_1) + (C_2 \times V_2)}{(M_{Feed} \times g_{Feed})}\right) \times 100 \quad (1)$$

$$\textit{Recovery efficiency}\,(\%) = \left(\frac{(C_2 \times V_2)}{(C_1 \times V_1)}\right) \times 100 \quad (2)$$

Where:

C_1 and C_2: the concentration of Cu in the polar phase and the stripped solutions

V_1 and V_2: the volume of the polar phase and the non-polar phase

M_{feed} and g_{feed}: the mass of the feed and the grade of Cu in the feed.

It should be noted that Co and Fe's dissolutions were also investigated during the Cu recovery to account for the process's selectivity.

C. Optimisation of dissolution of Cu in organic solution

The dissolution of Cu was optimised using the one-factor-at-a-time optimisation method or the traditional method. This method determines the optimisation by dissolving Cu from the chalcopyrite by varying one parameter while keeping others constant. Therefore, Table I summarises the different operating conditions for the recovery of Cu from the chalcopyrite ore.

TABLE I
PARAMETERS INVESTIGATED DURING THE SOLVO DISSOLUTION OF COPPER FROM CHALCOPYRITE ORE

Parameters	Levels				
Ethylene (%)	10	20	30	40	50
HCl(M)	0.5	1	1.5	2	2.5
H_2O_2(M)	0.5	1	1.5	2	2.5
Temperature(°C)	25	30	35	40	45
Time(min)	30	60	90	120	150

III. RESULTS AND DISCUSSION

A. Chemical composition of the as-received sample

The chemical composition analysis was performed on the as-received ore sample, and the results are presented in Table II. The sample contains a considerable amount of SiO_2, associated with no non-negligible amount of MgO, Al_2O_3, CaO, and K_2O forming the gangue fraction. Furthermore, results show valuable elements, such as Cu, the primary metal of interest, and Co, as an element of high economic interest. Fe and S are found at around 5.38 and 4.55 %, respectively.

TABLE II
CHEMICAL COMPOSITION OF THE AS-RECEIVED SAMPLE

Components (Wt %)								
MgO	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**	**K_2O**	**CaO**	**V_2O_5**
9.37	8.75	55.86	0.34	4.55	0.07	1.39	4.01	0.04
Cr_2O_3	**MnO**	**Fe_2O_3**	**Co_2O_3**	**NiO**	**CuO**	**ZnO**	**As_2O_3**	**ZrO_2**
0.05	0.26	5.38	1.16	0.03	8.29	0.02	0.01	0.02

B. Mineralogical characterisation of the as-received sample

The mineralogical analysis results (Fig. 1) show that Cu occurs in the sample in a sulphide form associated with Fe and S as chalcopyrite and simply as covellite. Co was also found

in the form of a Carrolite. One fraction of Fe was found in the sample as Pyrite, while the other was Hematite. Further analysis revealed that the as-received sample was characterised by a silicate gangue, which occurred in a multiform association of several minerals such as Quartz, Muscovite, Kaolinite, Almandine, Epidote, Biotite, Orthoclase, and Sanidine.

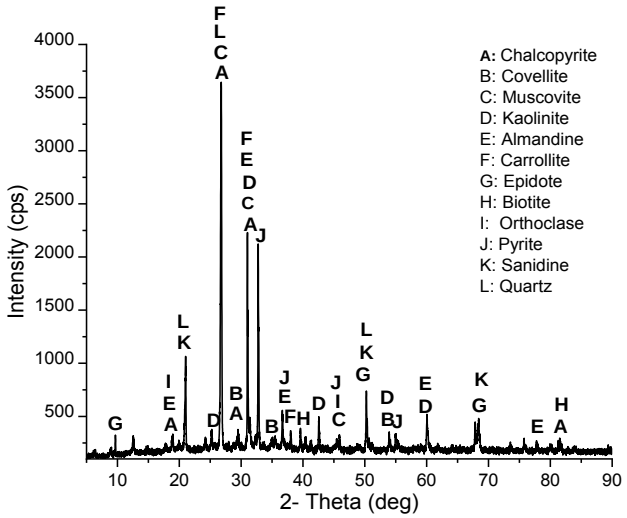

Fig. 1 Mineralogical analysis of the as-received sample

C. Petrographic analysis of the as-received sample

The SEM-EDS analysis performed on the as-received sample revealed the results shown in Fig. 2. The sample micrographs (A) and (B) revealed that the as-received sample is characterised by two significant morphologies: brighter phases represent valuable fractions, and the grey represents the gangue dominated by silicate materials.

Micrograph (A) shows a simultaneous interlocking of valuable phases bearing minerals and those of the gangues, which will require fine milling to liberate values. In contrast, the micrograph (B) reveals a distinct distribution of the valuable fraction, requiring less energy for liberation. Further analysis was also performed on selected sports depending on the difference in contrast.

The results revealed that the bright fractions are probably made of chalcopyrite, chalcocite, carrollite, and pyrite due to their higher molecular weight. In contrast, the greys and dull fractions are probably characterised by Quartz, Kaolinite, Biotite, Almandine, Epidote, Smectite, and Muscovite, characterised by lighter minerals.

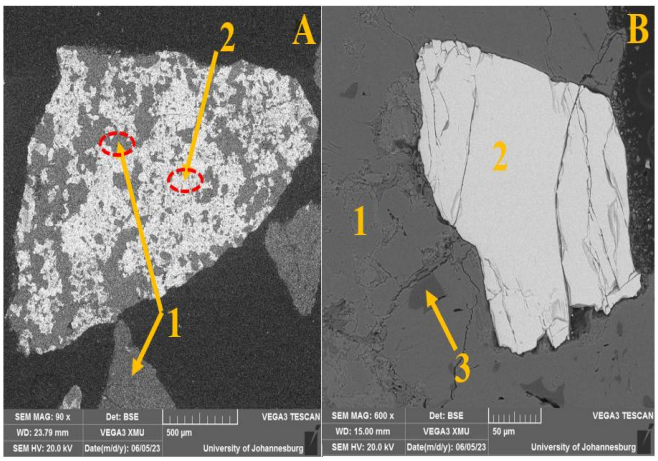

Fig. 2 Micrograph representation of the as-received sample

TABLE III
EDS ANALYSIS OF THE AS-RECEIVED SAMPLE ON SELECTED SPOTS

	spot	Mineral
A	1	Quartz, orthoclase, chalcopyrite
	2	Kaolinite, Quartz, chalcopyrite
B	1	Biotite, Quartz, Almandine
	2	Chalcopyrite, chalcocite, carrollite, pyrite
	3	Epidote, smectite, muscovite

D. Solvoleaching Experiments

Effect of the ethylene glycol concentration on Cu recovery and Co and Fe.

A direct dissolution of Cu using different volume ratios of ethylene glycol/Lix 984N-C while leaching for 1 hour at room temperature was investigated. The outcomes of the current investigation are presented in Fig. 3. The results reveal that ethylene glycol impacts the dissolution of Cu, Co, and Fe. However, since the selected Lix 984N-C used in the current investigation was prompt for collecting Cu, results show a high recovery of Cu estimated at 17.26% at a ratio of 30%. After analysing the raffinate collected after stripping, it was noticed that traces of Co and Fe were present in the Cu solution, which were evaluated to be 1.81 and 0.51%, respectively. As a green solvent, the outcomes are supported by the observation of [8], who demonstrated that ethylene glycol can enhance the dissolution of metals such as Cu, Co, and Fe due to the presence of the hydrogen bond donor capable of forming stable metal complexes in the leachate. This complexation reduces the activity of any eventual aqueous phase that is ready to occur as much as possible.

By reducing the copper and iron activities in the solution by creating Cu (II)-EG and Fe (II, III)-EG complexes, the investigation's findings demonstrate that EG prevents H_2O_2 degradation.

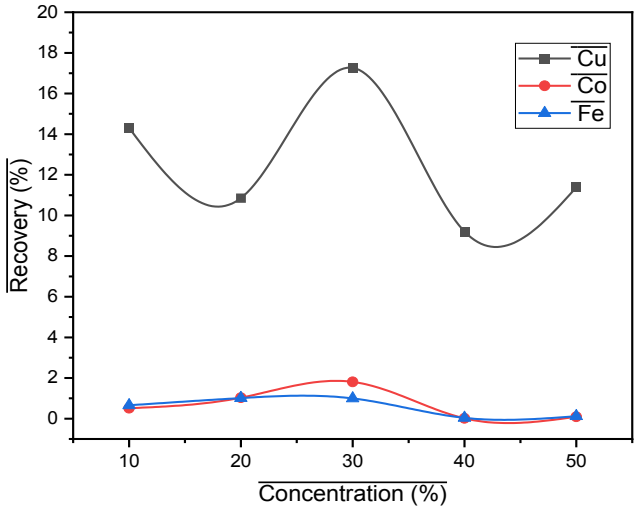

Fig. 3 Effect of the ethylene glycol concentration on Cu recovery and Co and Fe entrainment for 1 hour leaching at 25℃

Effect of HCl addition on Cu dissolution in the presence of ethylene glycol

Different concentrations of HCl (0.5, 1, 1.5, 2, 2.5 M) were added at fixed volume ratios of ethylene glycol/Lix 984N-C + kerosene of 30% ethylene glycol, and the experiments were performed at room temperature for one hour. Results displayed in Fig.4 show that the recovery of Cu increased proportionally with the concentration of HCl. In contrast, a slight increase of Co and Fe was also observed when adding 2M of HCl. Further increased HCl concentration promoted a drastic rise in Fe. The optimal conditions were selected when leaching with 2M to address the selectivity of the process. Results revealed that about 36.87% of Cu was recovered. It was also noticed that 5% of Co and 0.2% of Fe were reported to the strip solution.

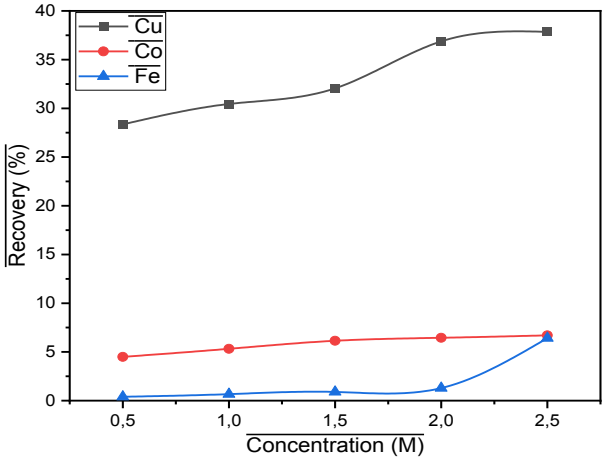

Fig. 4 Effect of HCl concentration in 30% of ethylene glycol concentration on Cu recovery and Co and Fe entrainment at room temperature after 1 hour

The leaching efficiency may be increased due to the formation of complexes of chloride ions in the solution, promoting the formation of metal ions [9]. [10] revealed that using chloride solutions in chalcopyrite leaching is beneficial due to the aggressive nature of the chloride ion and to the stabilisation of cuprous ions as chloro-complex ions.

Effect of H_2O_2 addition on Cu dissolution in the presence of a mixed solution of ethylene glycol and HCl

The impact of H_2O_2 addition at varied concentrations (0.5, 1, 1.5, 2, 2.5 M) was studied for one hour during the leaching process and the results are represented in Table IV and Fig.5. The results show that a high recovery of Cu (65.77%) was observed at an H_2O_2 concentration of 1.5M. Co and Fe were reported in small concentrations in the stripped solution, which was found to be 7.45 and 0.42%, respectively. However, the rise of Cu and Co recovery in these conditions is due to the presence of both the HCl and H_2O_2, which were prompt to form metal complexes characterised by stability constants of formation.

TABLE IV
THE STABILITY CONSTANTS OF METAL COMPLEXES IN HCL SOLUTION AT 25℃

Reaction	logK
$Zn^{2+} + Cl^- = ZnCl^+$	0.43
$Zn^{2+} + 2Cl^- = ZnCl_2^o$	0.61
$Zn^{2+} + 3Cl^- = ZnCl_3^-$	0.5
$Zn^{2+} + 4Cl^- = ZnCl_4^{2-}$	0.2
$Pd^{2+} + Cl^- = PdCl^+$	4.47
$Pd^{2+} + 2Cl^- = PdCl_2^o$	7.74
$Pd^{2+} + 3Cl^- = PdCl_3^-$	10.2
$Pd^{2+} + 4Cl^- = PdCl_4^{2-}$	11.5

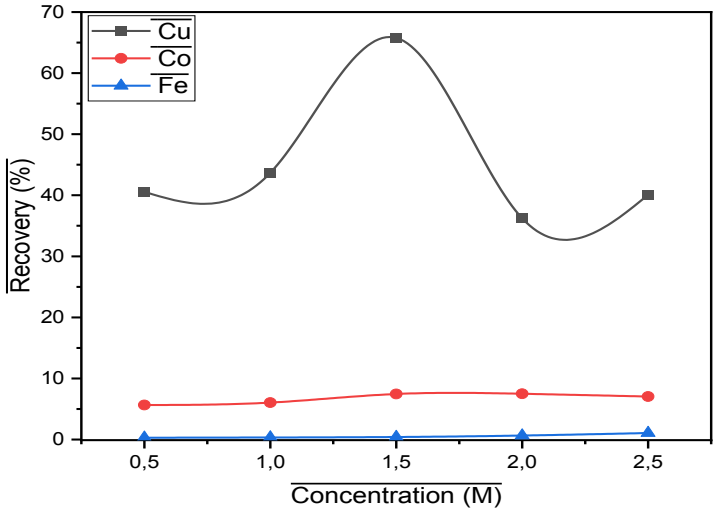

Fig. 5 Effect of H_2O_2 concentration addition on Cu recovery and Co and Fe entrainment in 2M HCl, 10% ethylene glycol at room temperature for 1 hour

Effect of temperature on Cu recovery while leaching in three different conditions

The effect of temperature on copper recovery was investigated and the results presented in Fig. 6 revealed that temperature has a positive effect on the dissolution of Cu in

all the leaching environments. However, it should be noted that the recovery of Cu increases as the temperature rises in the order "Ethylene glycol < Ethylene glycol + HCl < Ethylene glycol + HCl + H_2O_2"with recoveries of 37.84, 43.3 and 52.6 % at a temperature of 45℃, respectively. Furthermore, results demonstrated that a considerable amount of Co co-leached together with Cu in all the conditions despite using LIX 984N-C, which was recommended for the collection of Cu. A minimal amount of Fe was noticed in the final product, which was slightly pronounced when ethylene glycol was used alone.

The results showed that the best conditions were found when leaching with the combination of the "1M HCl, 1.5M H_2O_2, 30% ethylene glycol for one hour" at a temperature of 45℃.

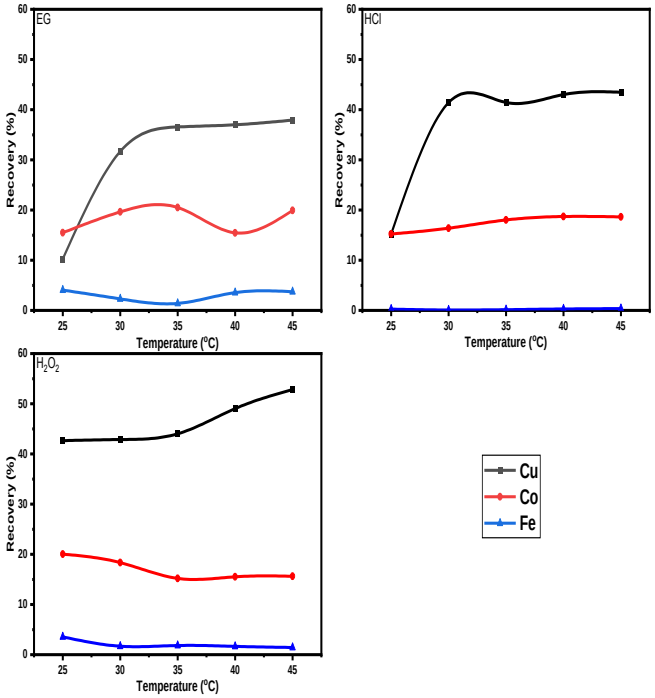

Fig. 6 Effect of temperature on Cu recovery and Co and Fe entrainment while leaching with 1M HCl, 1.5M H_2O_2, and 30% ethylene glycol for 1 hour

Effect of time on Cu dissolution

The effect of time was applied to the recovery of Cu and the dissolution of Co and Fe while leaching with 1M HCl, 1.5M H_2O_2, and 30% ethylene glycol at a temperature of 45℃. The results shown in Fig. 7 revealed that the increase in time promotes the dissolution of Cu and Co proportionally, while the Fe dissolution decreased. Cu increased proportionally with time to a recovery of 45.5% after 120 min. In comparison, Co was more stable at 90 min, where a drastic increase of 6.8 to 21.41% was observed after 120 min, which was the optimum time for Cu dissolution with a recovery. Fe dissolution shows good behaviour since it decreased gradually as the time increased from 5.7% after 30 min to 0.4 % after 120 min.

After investigating different parameters, results show that 88.11% of Cu was recovered after a leaching period of 150 min when leaching with 50% ethylene glycol/Lix 984N-C combined with 2.5 M HCl and H_2O_2 where 1% of Fe and 12.04% Co were entrained into the final solution.

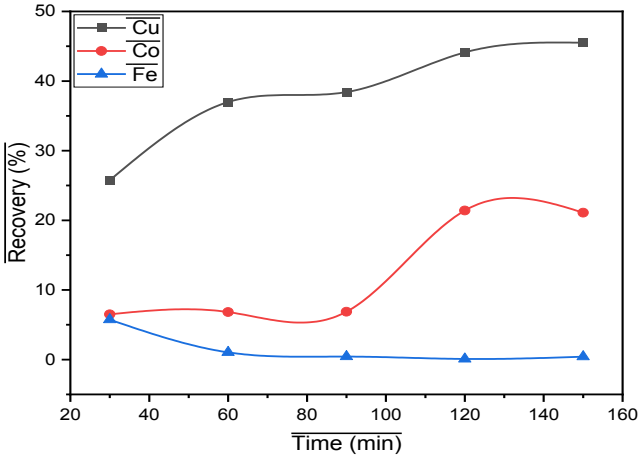

Fig.7 Effect of time on Cu recovery and Co and Fe entrainment while leaching with 1M HCl, 30% ethylene glycol, and 1.5 M H_2O_2 while leaching at 45℃.

IV. Conclusion

Solvoleaching was applied to a sulphide mineral using oxidative and complexing reagents such as ethylene glycol, HCl, and H_2O_2 in an organic phase of Lix 984N-C dissolved in kerosene as a diluent. The Lix 984N-C was selected as a Cu carrying organic phase to assess the selectivity by checking Co and Fe entrainment. Results demonstrated that it was possible to directly leach Cu efficiently from the chalcopyrite in a non-aqueous medium and the synergic effect of glycol, HCl, and H_2O_2 promoted this. However, temperature plays a significant role in the Cu recovery besides the synergic impact of complexing and oxidising reagents. The optimum conditions revealed that about 88.11% of Cu was recovered after a leaching period of 150 min when leaching with 50% ethylene glycol/Lix 984N-C combined with 2.5 M HCl and H_2O_2 where 1% of Fe and 12.04% Co were entrained in the PLS.

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