Int'l Journal of Research in Chemical, Metallurgical and Civil Engg. (IJRCMCE) Vol. 1, Issue 1(2014) ISSN 2349-1442 EISSN 2349-1450

Polarization and Potentiometric Studies of Cobalt and Copper Oxidised Ores in Ammonium Chloride Medium

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Abstract— This research study was conducted to evaluate the dissolution and electrochemical behaviour of low grade Cu-Co oxide ore (0.4% Cu; 3% Co) in ammonium chloride media (NH_4Cl) by means of polarization and potentiometric measurements. Polarization measurements were carried out to evaluate the electrochemical behaviour as well as the leaching and re-passivation behaviour of the ores at pH of 9.5, 9.6, 9.7 and 9.8 in NH_4Cl solution. In all the pH tested, the potential changed from negative to electropositive values suggesting formation of passive film on the surface of the ore which lowered the dissolution rates. Stable behaviours as were as high dissolution rate were observed at pH of 9.5. Potentiometric measurements were carried out at constant current and varying potential to study the reactivity of Cu-Co oxide ores in 0.25M, 0.5M and 1M of NH_4Cl solution. In this test the dissolution rates increased with increasing concentration and the pH decreased with increasing concentration and time suggesting production of acid as oxidation reaction takes place, the ranges of pH are depicted in the Pourbaix diagrams. Stable behaviours were observed in 1M of solution. All observations made in these measurements are confirmed by AAS, XRF, SEM and XRD analysis.

Keywords— Ammonium chloride, ore, polarization, potentiometric.

I. INTRODUCTION

COPPER (Cu) and cobalt (Co) are important materials with a wide range of applications. Copper is a very good conductor of electricity as such it is widely used for electrical equipments such as electrical wiring and industrial heat exchangers. Cobalt on the other hand is used in alloys and super-alloys such as rechargeable batteries and catalysts.

In the Democratic Republic of Congo (DRC), Co is mined from strata bound deposits and recovered as a by-product of Cu and Ni productions. Cobalt is less abundant in comparison to copper and nickel and occurs in sulphide and oxide deposits. The oxide deposit can be divided into two main groups; one with high content of nickel (laterites) and the other where copper is predominant. In the copper dominant ore, heterogenite (Co-OOH) is the main Co mineral found in the trivalent state [1].

The surficial Co-oxide deposits in the DRC represent a large resource of Cu and to date a number of deposits are under development. Efforts have been made by researchers to extract cobalt as the main ore with copper being the by-product. This is a result of Co being an important constituent for most alloys with high demand for specialized applications such as rechargeable batteries, catalysts, and super-alloys [1]. Cobalt, nickel and copper can be produced by following either the hydrometallurgical or pyrometallurgical routes. Studies have been done on selecting the most efficient technique to use and hydrometallurgical route has been found to be more efficient than pyrometallurgical processes. This is because ores which contain too much gangue can result in high metal extractions. The main operating cost in hydrometallurgical processes is only the purchase of chemical reagents which can often regenerated causing little or no atmospheric pollution [2]. Hydrometallurgical plants allow for effective treatment of lower grade and more complex ores in comparison to pyrometallurgical plant requirements. In pyrometallurgical plant high temperatures will be required to extract valuable metals from ore which has large amount of gangue which then will require large smelters in order to extract the ore leading to high capital cost in terms of energy consumptions as well as materials needed to construct the smelter. For many years low grade oxidised Cu-Co ores were not utilized for the extraction of Co and Cu due to non-availability of cost and technologically effective mineral processing and metal extraction technologies. With increasing demand of copper (Cu), nickel (Ni) and cobalt (Co) metals for different applications coupled to a fast depletion of natural land based resources, worldwide efforts are being made to look for alternative ways for the recovery of these metals [3].

Many studies have been conducted on dissolution of Co-Cu oxide ores but only few dealt with the electrochemical behaviour of these ores. Electrochemical techniques are mainly used in studying behaviour of metals with respect to corrosion. A study conducted by [4] on the corrosion behaviour of stainless steel, shows that the corrosion behaviour of stainless steel can be described by polarization curves in order to represent active passive behaviour and a

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http://dx.doi.org/10.15242/ IJRCMCE.E1113572

pseudo-passive behaviour . In passive behaviour, observations were made which point that stainless steels corrode in the active region, which exists at potentials below the passivation potential (Epp). In the active-passive region current increases with potential until the passivation potential, Epp is reached. Critical current density is obtained at maximum current, after this point current tends to drop to a very low value called passive current density; at this value passivation begins which is accompanied by the formation of the protective film of Cr_2O_3 layer. During passivation the metal still corrodes but at a very low rate. Any further increase in potential will lead to transpassive region, in this region the corrosion rate of the metal increases again. In the pseudo-passive system, the current does not decrease with increasing potential, rather the potential increases at constant or small increase in current.

Another study was conducted by Olubambi [5] on the Influence of microwave pretreatment on bioleaching behaviour of low-grade complex sulphide ores, the bioleaching behaviours of the ore were studied using potentiometric test by varying potential with time at constant current by observing the reactivity, passivation and pH changes with time. A decrease in solution pH was noted and associated with possible increase in microbial activities in the ores which led to increased cracks in the ore. A positive shift of potentials was noted and attributed to passivation which is the formation of passive film on the ore surface thus reducing the ore reactivity. Currently, sulfuric acid leaching has been considered as the leachant to recover copper and cobalt from a copper–cobalt ore of the Democratic Republic of Congo (DRC) [6]. However, many mine sites in DRC are remote and the supply of chemicals is a challenge. It is important that new techniques be found to solve the above stated problems. Therefore, this study will evaluate the behaviour of Cu-Co ore in NH_4Cl medium using electrochemical techniques such as potentiometric and Potentiodynamic polarisation.

II. METHODOLOGY

A. Materials

Ammonium Chloride (NH_4Cl) was the chemical reagent used in the leaching of Co and Cu from oxidized Cu-Co ore. The ores were pulverized for size analysis using the sieve in the laboratory. The sieving was performed to homogenized the ore particles and obtain -75µm. The powdered ore were subjected to elemental analysis in order to obtain composition of the bulk ore using X-ray fluorescence (XRF). The identification of mineral distribution within the sizes and quantitative analysis of the mineralogical composition was carried out by X-ray diffractometer (XRD). Morphological studies were performed using SEM and EDX analysis.

B. Working electrode preparation for electrochemical studies

The working electrodes were prepared from the bulk ore compressed under pressure. 2g of the ore were compressed under pressure using Buehler Simplimet II compressor in order to form pellets, sucrose was used to allow the binding of the ore and also the pressure produced pellets as shown in Fig. 1. The pellets were then mounted, with one surface exposed, in a cold setting resin and the other surface sealed with copper wire using aluminium (foil) conductive tape, to enable electrical contact of the ore with the copper wire. After drying of the pellets in resin for about three hours they were removed with 220 grade silicon carbide paper to remove any resin which might have covered the surface to be exposed in solution.

Fig. 1 Compresses Cu- Co ores into pellets demonstration and exposed pellets into settling resin in the making of working electrode

C. Electrochemical cell

Electrochemical studies were conducted using a conventional 500 ml Pyrex conical glass suitable for a three-electrode system. The cell consisted of a silver/silver chloride, 3 M NaCl as reference electrode, platinum wire as counter electrode, and the working electrode made from the ore.

D. Electrochemical technique

All electrochemical measurements were carried out at room temperature (25 ± 1^0C) using the General Purpose Electrochemical Software (GPES) version 4.9 in an Auto-lab potentiostat (PGSTAT30 computer controlled). Electrochemical measurements conducted on the electrodes include the potentiometry (open circuit potential) and potentiodynamic polarization techniques. Polarization aims at determining the active and passive characteristics of a given metal solution. The potentials were set to vary between -0.6V to 1.2V at a scan rate of 1.6 mV. Potentiometric test was carried out with the aim of studying the passivation behaviour of the oxide ores at constant current with only variation in potential. This test was carried out in different NH_4Cl solution concentrations (0.25M, 0.5M and 1M). The results were interpreted by observing the changes in potential with time as well as variation in pH with time; the changes in pH with time are represented by Pourbaix diagrams, generated using MEDUSA software. Atomic absorption spectroscopy (AAS) techniques were used to determine the dissolution of the ore in ammonium chloride solution.

III. RESULTS AND DISCUSSIONS

A. Particle size of the ore

The ore particle size of -75µm was achieved during crushing. This particle size was necessary for the mineralogical studies such as XRF and the leaching of the ore.

B. Quantitative and phase analysis of Co-Cu oxidized ores

The XRF results shown in Table I reveal that most of the minerals are in their oxide state. The amount of cobalt as Co_2O_3 was 3.32% since this percentage was low; it could be an indication that it was a low cobalt ore. The amount of CuO was 0.403% which was less than that of the cobalt present in the same sample, also an indication of low copper ore. The dominant mineral was SiO_2 being 64.9%. The mineral contains also in substantial amount were MgO, Al_2O_3, NiO and MnO in order of decreasing mass percents.

TABLE I
QUANTITATIVE ANALYSIS OF CO-CU OXIDISED ORES USING XRF.

Components	Composition (mass %)
F	0.28
Al_2O_3	8.82
SiO_2	64.9
P_2O_5	0.26
SO_3	2.22
Cl	0.045
K_2O	0.66
CaO	1.48
Cr_2O_3	0.041
MnO	1.26
F_2O_3	3.35
Co_2O_3	3.32
NiO	1.61
CuO	0.403
ZnO	0.009
Ga_2O_3	0.004
Rb_2O	0.0023
Nb_2O_5	0.004
MoO_3	0.0075
PbO	0.146
U_3O_8	0.0722

X-ray diffraction (XRD) patterns obtained from the samples are presented in Fig. 2. The major phases observed on the sample were Coesite (SiO_2), clinochlore, chromian (Mg_5, $Al_{0.75}$, $Cr_{0\cdot25}Al$) and copper cobalt oxide ($Cu_{.27}$ $Co_{2.73}$ O_4). A higher intensity of Coesite which was mainly Silicon oxide was observed, this agrees with the XRF results obtained whereby SiO_2 had the highest composition. A shorter intensity peak of $Cu_{.27}$ $Co_{2.73}$ O_4 was observed, this was as a result of the low content of Co and Cu ores in the sample. Some of the other phases in the ore could not be identified by the X-ray diffractometer, as they did not give any diffraction peak.

C. Morphological studies of Co-Cu ores

The samples were scanned at different magnifications and the SEM micrographs are presented in Fig.3. The micrographs were taken for the full scale of the ore surface. The SEM image shows a wider range of the grayish morphology (representing SiO_2) with bigger microstructures in comparison to the white and black morphologies (clinochlore and Copper Cobalt oxide respectively) with smaller microstructures.

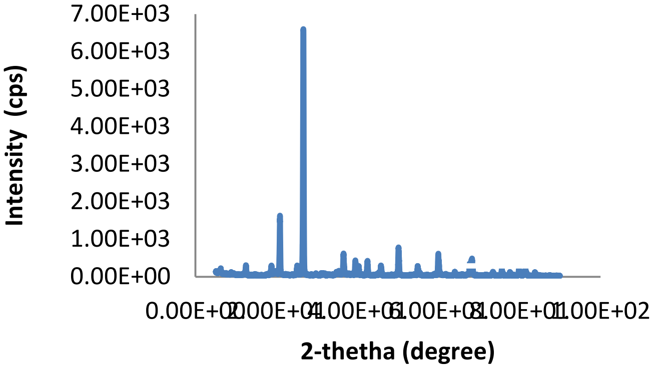

Fig. 2 Phase identification of Cu-Co oxidized ores by the method of XRD Phase identification of XRD

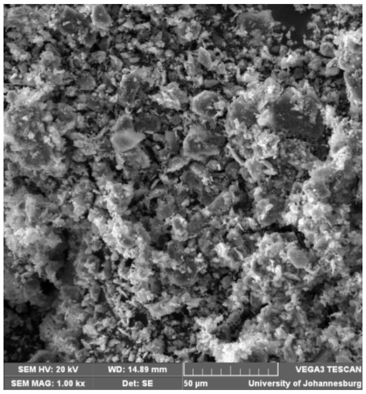

Fig. 3 SEM micrograph of Cu-Co particles

Fig. 4 shows the SEM micrograph of the Co-Cu ore after compressing it into the working electrode. Similar morphologies were observed with the working electrode compared to the particles before compaction. However, there was reduction in the microstructural sizes of the different morphologies after compressing into working electrode.

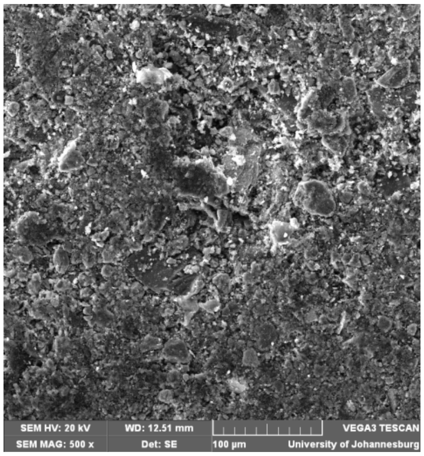

Fig. 4 SEM micrograph of Co-Cu working electrode

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D. Polarization Test

Potentiodynamic polarization measurements were carried out to evaluate the electrochemical behavior as well as to determine the leaching and repassivation behavior of the ore in NH_4Cl solutions. The electrochemical data obtained from the potentiodynamic polarization scans in 0.25M NH_4Cl with pH in this range 9.5 - 9.8 for oxidized Cu-Co ores are summarized in Table II, while Fig. 5 gives the graphical representation of their responses to polarization. It was noticeable that pH of 9.8 and 9.6 produced a higher potential at a lower current density. This behavior could result in low leaching of the ore at this pH.

In all the three pH tested it was observed that the potentials changed with current density from negative to more electropositive values. This positive shift of potentials could be due to passivation that might decrease the dissolutions of the ores. Also the increase in potential observed can result from the formation of passive films on the surfaces of the minerals and as well as decrease in the ore reactivity [5].

The condition at pH of 9.7 was characterized by the active dissolution of the ores whereby the current density increased drastically with respect to the applied potential. At lower potentials, where dissolution current density was lower, the ore surfaces were passivating. According to Lu et al [7], during initial leaching stages, the oxidation of the ore at lower potential is slowed by the formation of sulphide on the surface of a low-grade metal, where oxidation of this mineral is developed per partial reaction. However, upon increasing the potential, dissolution rates could possibly be controlled by the rate of passive layer decomposition. Nava et al [8] observed that the passive product could decompose to form porous layers of non-stoichiometric polysulfide thereby allowing diffusional transport of charged species and the dissolution of the mineral.

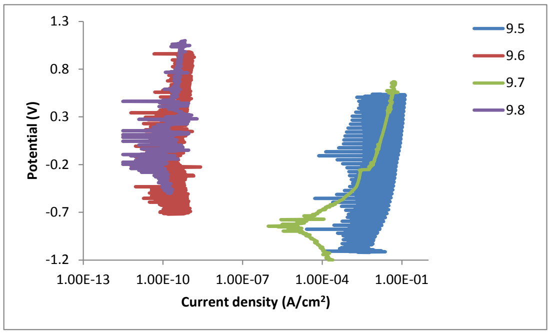

Fig. 5 Potentiodynamic polarization of oxidized Cu-Co ores at 0.25M and varying pH

TABLE II
POTENTIODYNAMIC POLARIZATION DATA

pH	OCP (V)
9.5	-0.661
9.6	-0.264
9.7	-0.589
9.8	-0.182

1) AAS analysis after polarization study

The results for the elemental concentration of Co and Cu present in the NH_4Cl solution after polarization studies as determined by flame AAS are shown in Table III. The AAS analysis results revealed that concentration of Cu present in the NH_4Cl solution at a pH of 9.5 was 0.7451 ppm which increased to 1.1742 ppm at a pH of 9.6; the trend was not stable though as the concentration decreased again at a pH of 9.7 then increased to 2.3024 ppm at a pH of 9.8. The concentration fluctuates in a sinusoidal manner. For Co, the concentrations also followed the same trend as in Cu analysis, whereby there was fluctuation from 5.1574 ppm to 0.3705 ppm and then to 0.2745 ppm at pH of 9.5, 9.6 and 9.7 respectively and then increased 0.5138 ppm at a pH of 9.8. Meanwhile, the concentration of Cu and Co as determined from the aqua regia was 163.87 ppm and 1511; respectively. The results from aqua regia as well as AAS were used to determine the percentage leached as shown in Table IV. As observed from the AAs results, higher elemental concentration and recovery of Co was obtained at pH 9.5, whereas for Cu it was at a pH of 9.8, this confirms the polarization behavior (sinusoidal) of the oxidized ore at this pH as shown in Fig. 5. This could mean that noise was created in the electrolyte as the oxidized ores were leached into the solution.

TABLE III
QUANTITATIVE ANALYSIS OF CO-CU OXIDIZED ORES BY FLAME AAS

pH	Concentration (ppm)	
	Cu	Co
9.5	0.745	5.157
9.6	1.174	0.371
9.7	0.589	0.275
9.8	2.302	0.514

TABLE IV
PERCENTAGE LEACHED OF CO-CU AT VARIED PH FROM POLARIZATION AAS DATA

pH	% leached	
	Cu	Co
9.5	0.457	0.341
9.6	0.717	0.025
9.7	0.359	0.018
9.8	1.405	0.0340

E. Potentiometric study

A study on the reactivity of Cu-Co oxidized ore in ammonium chloride media was carried out using open circuit potential (OCP) measurements. The variations in the OCP values as well as pH of the oxidized ores were studied at zero applied current immediately after the immersion of the oxidized ores in the form of pellet in 0.25M, 0.5M and 1M of ammonium chloride media for 30 minute in each solution. The change in solution pH with time was observed to be shifting from neutral to acidic media even though the experiments were performed in basic media. This phenomena indicate the production of more acid in the leaching of Cu-Co oxidized ores, the decrease in solution pH would also be as a result of the possible increase in microbial activities in the ores due to the increased electrochemical sites within the ore resulting from increased cracks [5].

The variation in open-circuit potential as a function of time for the oxidized ores tested in 0.25 M, 0.5M and 1 M NH_4Cl solutions are presented in Fig. 6. The potential was observed to generally shift from positive toward negative values in 0.5M solutions, in a fluctuating manner, this suggested that there was leaching at the initial stage followed by breakdown and repassivation of the film on the surface of the ores after dissolution. The potential in 0.25M depicted a nearly constant trend and then a sudden increase in potential toward the last minutes. However, in 1 M ammonium chloride, a small and progressive increase in potential with time was observed. The potential in 1M solution has a defined trend with fewer fluctuations, more stability was observed.

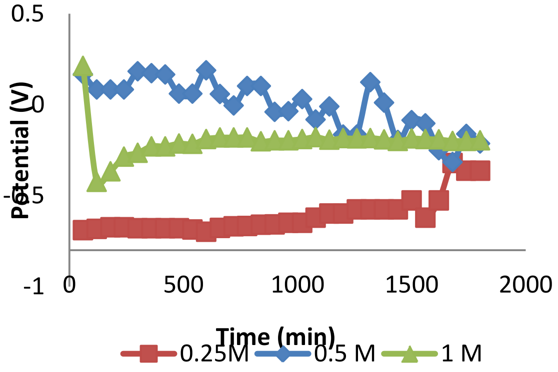

Fig. 6 Open circuit potential of Cu-Co oxidized ores in 0.25, 0.5 and 1 M Ammonium Chloride.

The relationship between potential and pH of the oxidized Cu-Co ores in 0.25M solution of NH_4Cl is depicted in Fig. 7 There was a nearly stable potential achieved at the pH of 6.4 to 6.83, but as the pH increased further instability was observed in the potential as it changes from smaller value to bigger one. The change in potential indicate passivation of the ore which implied that there was leaching at lower pH and then as the pH increased to basic zone passivation or break down of the ore occurred. The diagram indicates also that Co^{3+} is unstable above the dotted line and must oxidize to form Co^{2+} which is soluble. Both Co^{2+} and $CuCl_2^-$ ion and anions are stable at pH less than 3.

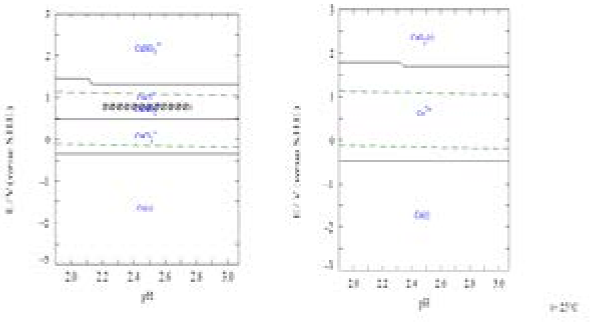

Fig. 7 Pourbaix diagram for the potential and pH variations obtained during leaching in 0.25M of ammonium chloride.

pH increased with time, the potentials dropped from positive values to negative values. The diagram indicates that Co^{3+} is unstable above the dotted line and must oxidize to form Co^{2+} which is soluble. Both Co^{2+} and $CuCl_2^-$ ion and anions are stable at a pH below 6.8.

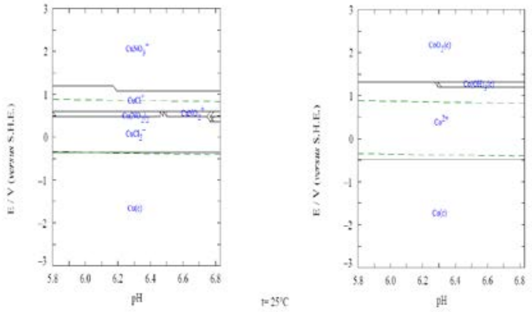

Fig. 8 Pourbaix diagram for Cu-Co oxidized and open circuit potential and pH variations obtained as a function of time during leaching in 0.5M of ammonium chloride.

The study of the potential and pH of the oxidized Cu-Co ores in 1M solution is shown in Fig. 9 The potential was high at a pH of 2 with increasing pH it was observed that the potential dropped to minimum value of -4 V and then increased with time; the increase in potential observed was attributed to the formation of passive films on the surfaces of the ore. The diagram also indicates that Co^{3+} is unstable above the dotted line and will oxidize to form Co^{2+} which is soluble. Both Co^{2+} and $CuCl_2^-$ ion and anions are stable at a pH below 7.1. This pH is higher than the pH required to reach stability in 0.5M and 0.25M, this is proof of the fact that the less concentrated the solution the more acidic it becomes.

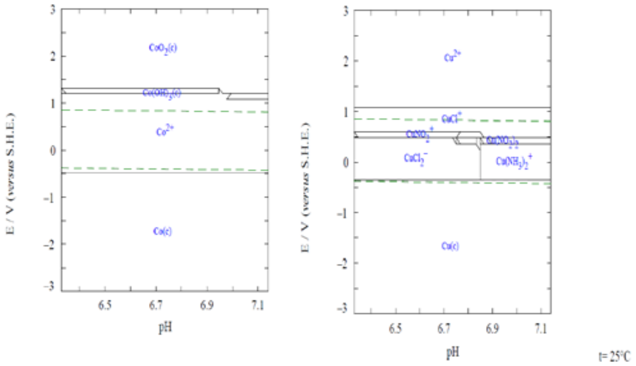

Fig. 9 Pourbaix diagram of the open circuit potential and pH variations obtained as a function of time during leaching in 1M of ammonium chloride.

1) AAS analysis after potentiometric study

The results for the elemental concentration of Copper and Cobalt present in the NH_4Cl solution after potentiometric studies as determined by flame AAS are shown in Table V. The AAS analysis results revealed that composition of Cu present in the NH_4Cl solution at 0.25M was 1.1160 ppm which increased to 1.5794 ppm in 0.5M solution and then to 2.6453 in 1M solution. The compositions increase with increasing concentration of NH_4Cl. For Co, there was similar trend as in Cu analysis, whereby the concentrations increased from 12.8383 ppm to 14.1179 ppm and then to 21.7505 ppm in 0.25M, 0.5m and 1M solution of NH_4Cl, respectively. Meanwhile, the concentration of Cu and Co as determined from the aqua regia was 163.87 ppm and 1511 ppm, from the aqua regia results and AAS at different concentrations, the percentage leached was obtained as shown in Table VI. As observed from the AAS results, higher elemental compositions were obtained in the 1M solution of NH_4Cl for both Co and Cu and thus higher percentage leached.

TABLE V
QUANTITATIVE ANALYSIS OF CO-CU OXIDIZED ORES BY FLAME AAS AFTER POTENTIOMETRIC STUDY

NH_4Cl (M)	**Concentration (ppm) %**	
	Cu	Co
0.25	1.116	12.83
0.5	1.579	14.12
1	2.645	21.75

TABLE VI
PERCENTAGE LEACHED OF THE EXPOSED SURFACE OF CO-CU AT VARIED CONCENTRATION OF NH4CL FROM POTENTIOMETRIC

NH_4Cl (M)	**% leached**	
	Cu	Co
0.25	0.681	0.849
0.5	0.963	0.934
1	1.614	1.439

IV. CONCLUSION

Electrochemical techniques have been used to study the behavior of copper and cobalt oxidized ores in NH_4Cl solution with the ultimate aim of obtaining optimum operating condition. Both Co and Cu possessed a strong pH dependence on leaching. The metals (Co and Cu) exhibited a significant increase in leachability at low pH. The pH ranges obtained were within the confines required for formation of stable copper and cobalt complexes. The effect of pH range on the leaching corresponds to available literature with regard to the stability of the metal complexes that were formed during the leaching process as indicated with the Pourbaix.

The percentage leached increases with increasing concentration of NH_4Cl and also that there was production of acid which led to the lowering of pH from the working region of basic to acidic media but increased with time. It is thus concluded from this trend of lowered and increasing pH that NH_4Cl is not favorable since the pH is lowered and afterward increased to the alkaline region. It was also shown that at the lower pH more of Co-Cu ores were leached than in the case where a higher pH was maintained in polarization test. In this case acidic media is preferred than basic.

Based on the results obtained from the present study, pH of 9.7 and 0.25M of ammonium chloride can be concluded as the optimum operating condition in polarization test since these conditions produced favorable results.

ACKNOWLEDGMENT

The authors wish to acknowledge the Mineral Processing and Technology Research Centre, University of Johannesburg, South Africa for the use of SEM, XRF and XRD machines, Department of Chemical Engineering Technology, University of Johannesburg, South Africa, where this study was conducted and Department of Applied Chemistry University of Johannesburg, South Africa for making their Potentiostat available for this study.

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