The University of Zambia

School of Mines

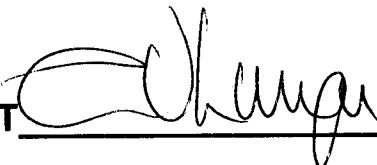## Department of Metallurgy and Mineral Processing

FINAL YEAR PROJECT-MM590

COMPARISON OF LIX 984NC VERSUS ACORGA M5774 FOR COPPER EXTRACTION PROCESS

BY

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Submitted in partial fulfilment of the requirement for the acquisition of the bachelors' degree in mineral sciences (B.Min.Sc) in metallurgy and mineral processing.
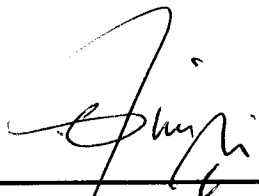
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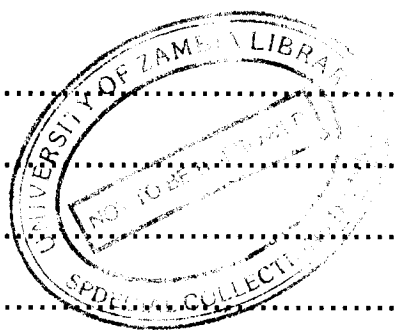HEAD OF DEPARTMENT _____

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Acknowledgement

I am greatly indebted to all whose contribution made possible for me to carry out the project work. Particular thanks go to Mr. Victor sichali metallurgist, at the solvent extraction plant of Mopani copper mine Nkana who was my project supervisor there.

Special mention should be made of my project of areas at the University of Zambia, school of mines, department of metallurgy and mineral processing, Dr. R.L Nyirenda for his helpful criticism, corrections and guidance.

I would also love to say many thanks to my family and friends for the love and Support shown to me through this whole period of my pursuit for a degree.

Abstract

This report looks at the selection of the best extractant amongst the available options on the market. It particularly focuses on the comparison of the two extractant, Lix 984N and Acorga M5774.

Mopani copper mines Nkana cobalt plant has a copper solvent extraction plant as one of the by processes to extract and produce copper in the quest to purify the pregnant solution into a cobalt concentrated solution. Therefore it is in the best interest of the company to minimise operation cost. Test works were carried out to come up with a very economical but effective extractant that will extract copper from the pregnant leach solution.

Test works were done on a bench scale by comparing the two extractants at the same conditions to see which one extract more and which one has better economics if all factors are considered. Acorga M5774 is cheaper than Lix 984N in terms of price per kilogram.

The test works have shown that Lix 984N easily extracts the copper from the pregnant leach solution but it is not easily striped by the spent electrolyte than Acorga M5774. Even though this is the case, Lix 984N has shown that on the overall, it is better than Acorga M5774 because it loses less copper to the tails and the economics are good.

LIST OF ACRONYMS

SX	Solvent Extraction
PBC	Pinned Bed Clarifier
CLS	Calcine Leach Solution
EW	Electrowinning
CLR	Calcine leach Raffinate
CoS	Cobalt Solution
DC	Direct Current
AAS	Atomic Absorption Spectroscopy
PLS	Pregnant Leach Solution

1. Introduction

1.1 Background

Mopani Copper Mines (MCM) Nkana Cobalt plant is situated in Kitwe Nkana west approximately 2km away from the town centre on the Copperbelt province of the Republic of Zambia.

The Nkana cobalt plant was commissioned in 1982. It is one of the only two existing cobalt electro winning refineries in Zambia. The plant is divided into two circuits, the Copper circuit and the Cobalt circuit. The Copper and Cobalt sulphides are treated via a fluidized bed roaster. This roaster converts the acid insoluble sulphides to acid soluble sulphates at an average conversion of 90% for both Copper and Cobalt mineral values.

The Copper is removed from the calcine leach solution by solvent extraction process in the Solvent Extraction (SX) plant with the extractant known as LIX 984NC. The solvent extraction plant was commissioned in January 2007. The raffinate undergoes further purification to remove impurities such as Zinc, Iron, Cadmium, Nickel and Organics before producing the Cobalt advance electrolyte for Cobalt electrowinning. The plate like Cobalt cathodes are then crushed to chip form, burnished, degassed and exported in 68 liter drums weighing 250 kg or 200 kg net.

The loaded organic is stripped with the spent electrolyte from the copper tank house. The spent electrolyte is highly concentrated with sulphuric acid.

The SX plant faces the common problems of crud formation, low stripping efficiencies and extraction efficiencies and thus the Company has been thinking and trying to improve the situation in the plant. Hence, a reagent that can replace LIX 984NC with improved performance, quality and cost is required. It is thus in the company's interest to test other products on the market and ascertain the possibility of having LIX 984NC replaced by any of these products that will prove to be beneficial to the company.

1.2 Objective

With the coming up of cheaper products like acorga M5774 and acorga opt5510 on the market, the company has decided to test possibility of these products replacing the current extractant. Hence, the aim of this project was to compare acorga M5774 and LIX 984NC for copper extraction process and determine the possibility Acorga M5774 replacing LIX 984NC without causing a great change in the production quality of the process. Acorga M5774 is cheaper than LIX 984NC hence, it would give better economics than LIX 984NC.

1.3 Present Plant Operations

1.3.1 Roasting

Sulphating roasting of Cobalt sulphides concentrates in slurry form at solid specific gravity of 1.8 to 2.0 is done in a fluidized bed reactor (Roaster) employing air at 550 tons per day. The bed temperature of the roaster is maintained between 695°C to 705°C to achieve good Copper/Cobalt.

Currently the bulk of concentrates treated is from the Mopani Nkana sulphide concentrator. Previously Nchanga cobalt concentrates and Chibuluma concentrates were treated through the plant. Pyrite is sometimes used to sustain the sulphur heat balance for roasting when the sulphur grade in the feed is low. The typical roaster feed grades are;

> Copper 8-10%
> Cobalt 1.4-1.8 %
> Sulphur 18-25%

Roaster concentrate through put of about 465 tonnes per day is currently being achieved with oxygen enrichment at 30% due to recent operational renovations, which have pushed this up from the previous capacity of 420 tons per day. The two realizable products of roasting are roaster-off-gas at about 3 to 4.5% sulphur dioxide and complex sulphate (Calcine). The roaster off gas is cooled in the cooling and cleaning section prior to acid production. Calcine is leached with sulphuric acid for the eventual electrowinning of both copper and cobalt respectively.

1.3.2 Leaching, Thickening and Filtration

Roaster calcine is quenched from about 700∘C to 80∘C and subsequently leached with copper spent solution containing 15 to 25gpl sulphuric acid in the calcine leach cascades. The pH of the leach cascades is maintained at levels below 1.5 by addition of fresh sulphuric acid if required. Leach slurry is pumped from the leach tanks at a volumetric flow rate of $\sim$ 110m^3/h to the calcine leach thickener. The feed is introduced into the thickener at a slurry solid concentration of $\sim$ 15% solids w/w and increased by the thickening process to > 35% solids w/w.

The thickened slurry is discharged as underflow and pumped to filtration for further solution removal prior to being disposed off as the tails. The filtrate is recycled to the leach thickener. The overflow pregnant solution from the thickener is pumped to the heat exchanger, where it flows in counter current to the raffinate bleed solution and it is reduced from 75°C to ~55°C, while the raffinate is heated from $\sim$ 30°C to $\sim$ 50°C. The pregnant solution is then further cooled in cooling towers to < 35°C, a temperature that is suitable for solvent extraction process.

The cooled pregnant solution gravitates to the clarifier thickener where suspended solids content is reduced to~ 250ppm in the overflow. The overflow is pumped to the surge tank then to the pinned bed clarifier (PBC) for further reduction of the suspended solids content in the pregnant solution to ~75ppm. The overflow from the PBC gravitates to the clarified pregnant solution surge tank from where it is pumped to the solvent extraction plant mixer/settler E_1. The PBC underflow is recycled to the calcine leach pregnant leach solution thickener.

The heated raffinate bleed solution is gravity fed from the heat exchanger into the iron (Fe) removal circuit. The raffinate bleed solution is contacted with lime and sulphur dioxide (SO_2) to form a Fe rich precipitate with minimal Fe left in the solution. The Fe precipitate is then separated from the Fe precipitation thickener. The underflow from this thickener is pumped to the filtration section to remove the entrained solution which is recycled to the Fe precipitation circuit. The overflow Cobalt solution is pumped to the Fe precipitation clarifier to reduce the suspended solids to $\sim$ 75ppm. The overflow Cobalt solution gravitates into the Cobalt solution surge tank from where it is pumped to the SX plant E_4 mixer/settler. The U/F is recycled to the Fe removal circuit.

The pregnant solution is the primary high grade feed to the SX with Cu grade of ~19gpl and ~9gpl Co while Cobalt solution is the secondary low feed to the SX with ~1.0gpl Cu and ~9gpl Co.

1.3.3 Heat Exchanger

The pregnant solution exits the leaching process at a high temperature of ~80°c, which is not suitable for the subsequent solvent extraction, hence necessitating cooling. The first stage of cooling occurs in the plate and frame heat exchanger, where the solution temperature drops to ~60°c. The temperature drop is due to the counter current flow of the pregnant solution and the raffinate bleed solution. Heat is transferred from the pregnant solution to the raffinate bleed and thus the raffinate bleed is heated up in the process.

1.3.4 Cooling Tower

The second stage of cooling occurs in the cooling towers. In the cooling towers, the leach solution is further cooled from ~60° to~ 35°c. The cooling towers are also heat exchange equipments; in this case heat is transferred from the leach solution to another external fluid (air/water).

The heat exchange equipments are forced draft cooling towers which operate two at a time with one standby unity.

1.3.5 Copper Solvent Extraction

The calcine leach solution enters the SX plant at a temperature less than 30°c. CLS is pumped from the clarified CLS surge tank at ~125 M^3/h to the E_1 solvent extraction mixer/settler. The CLS contain about 19gpl Cu, ~9gpl Co as well as various other metals.

```
                        ┌──────────┐
                        │ Leaching │
                        └──────────┘
                              │
   Raffinate                  ▼                      ┌────────────┐
                        ┌────────────┐               │ Fe removal │
   Tail disposal ◄──────│ Thickening │               └────────────┘
                        └────────────┘
                              │
   Raffinate bleed            ▼
                        ┌────────────┐
   Raffinate bleed ────►│    Heat    │
                        │ exchangers │
                        └────────────┘

                                        Pregnant solution

        ┌──────┐     ┌──────┐        ┌──────┐
        │  E₃  │◄────│  E₂  │◄───────│  E₁  │
        └──────┘     └──────┘        └──────┘
   ┌──────────┐
   │    Zn    │
   │ removal  │
   └──────────┘
                  ┌──────┐     ┌──────┐
                  │  E₅  │◄────│  E₄  │◄────
                  └──────┘     └──────┘

   Stripped organic                          loaded organic
              ┌──────┐        ┌──────┐
              │  S₂  │───────►│  S₁  │
              └──────┘        └──────┘

   Spent electrolyte              strong electrolyte

                   (  Electrowinning  )

                   99.99% Cu cathode
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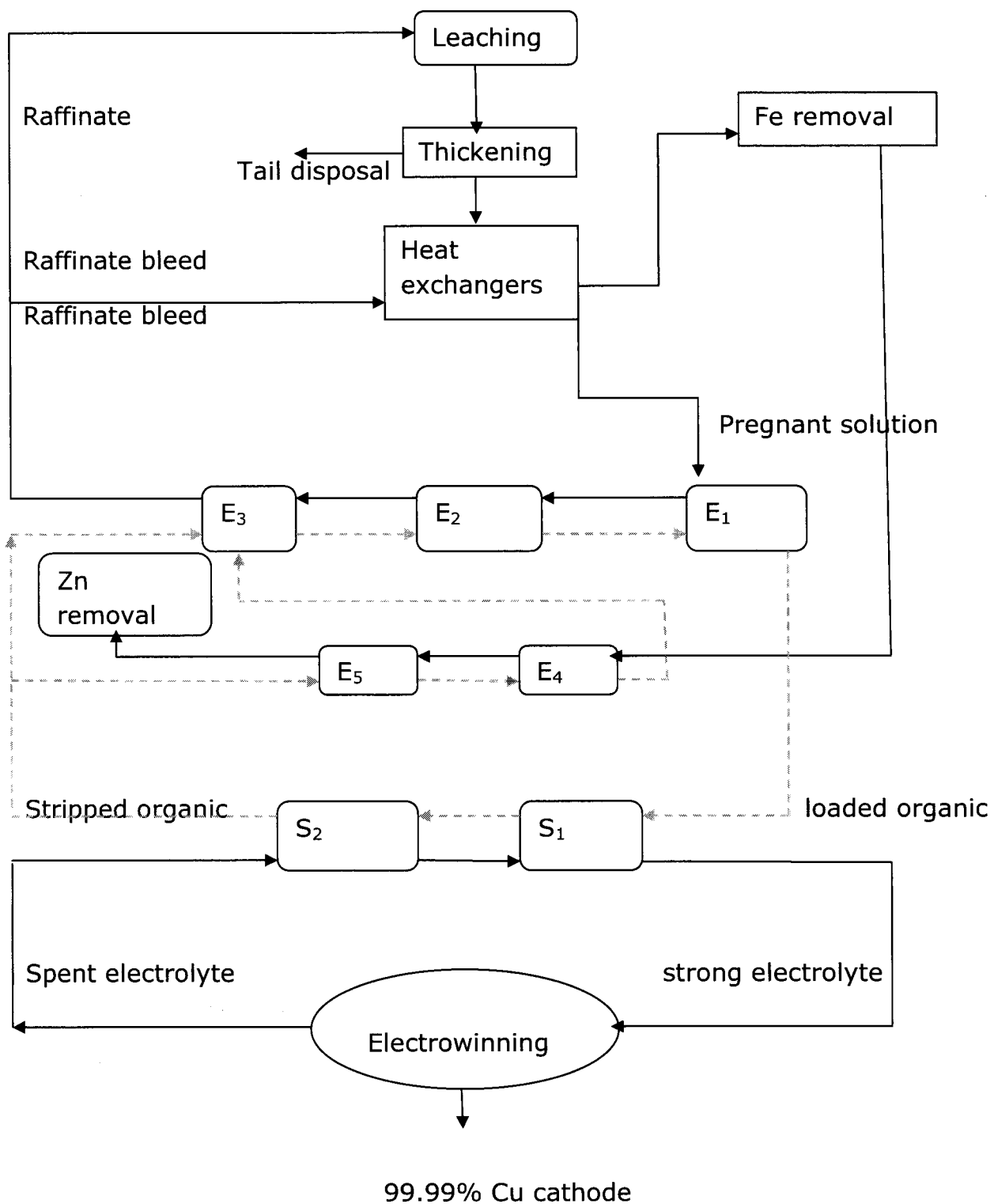
Figure 1.1.Leach solution preparation and Copper SX process

The SX is included in the process so that the copper rich pregnant solution is upgraded to a higher content suitable for electrowinning (EW) of copper. Essentially only copper is transferred via the SX process over to the higher grade electrolyte solution, referred to as advance electrolyte.

The leach solution contacts the recycled organic in the extraction stages E_1 and E_2 where Cu is extracted from the leach solution into the organic. The Cu level in the calcine raffinate (CLR) is ~0.5gpl and gravitates to the CLR pond.

The CLR is pumped to the CLR surge tank were a portion of it is recycled to the leach section for re-use in the calcine leach process and thus produce more pregnant leach solution and the other portion, referred to as the raffinate bleed, goes to Fe removal section prior to Cu extraction in the SX. The raffinate bleed is precipitated with lime to remove Fe from the solution. The slurry goes to the clarification thickener to for removal of the Fe precipitates. The thickener overflow cobalt solution (CoS) is pumped to SX process E_4.

CoS is pumped from the Fe precipitation thickener to at ~$50M^3$/h to the E_4 SX mixer-settler where it contacts recycled organic from E_5 settler. The loaded organic gravitates to the next settler E_3, while the aqueous gravitates to E_5 mixer-settler. In E_5 the CoS contacts the stripped organic from the strip settler S_1, further Cu extraction takes place and the organic advances to the next extraction stage in E_4. The aqueous solution is the final raffinate from the process and gravitates to the final raffinate tank and pumped to the Cobalt plant.

The loaded organic from E_1 is pumped to the strip process and contacts spent electrolyte containing ~35gpl Cu and ~180gpl sulphuric acid, from the electrowinning plant in the strip one (S_1) and strip two (S_2). The acid in the spent electrolyte strips the Cu from the loaded organic to produce a strong electrolyte containing ~50gpl Cu and ~157gpl acid.

Strong electrolyte leaves the strip stage and passes through a dual-media/multi media filter to remove entrained organic and suspended solids before the electrolyte enters the EW circuit.

Both the extraction and stripping stages are conducted in mixer settlers. The organic flows in a counter current direction to the pregnant leach solution, CoS and electrolyte solutions.

1.3.6 Solvent Extraction Chemistry

Extraction chemistry

Solvent extraction of copper can be represented by;

$$Cu^{2+}_{(aq)} + 2R\text{-}H_{(org)} = R\text{-}Cu\text{-}R_{(org)} + 2H^+_{(aq)}$$
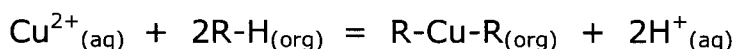
i.e. (preg. Soln) + Stripped Organic = Loaded organic + Raffinate

Where;

Cu^{2+} = is Cu in the calcine leach pregnant solution and Co solution
R-H = is the LIX984NC extractant i.e stripped organic
R-Cu-R = is LIx984NC copper complex i.e loaded organic
H^+ = is acid in raffinate.

Extraction of Copper occurs when leach solution containing copper is mixed with the stripped organic solution containing LIX984NC. The extractant releases its acid and absorbs copper so that the levels of copper in the aqueous solution decreases, the acid level increases and copper is transferred into the organic phase as a LIX984NC copper complex.

Stripping chemistry

The stripping process of the solvent extraction of copper can be represented by

$$R\text{-}H\text{-}R_{(org)} + 2H^+_{(aq)} = Cu^{2+}_{(aq)} + 2R\text{-}H$$
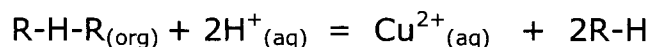
Stripping of copper occurs when a strong acid solution (180gpl acid) is mixed with the loaded organic containing LIX984NC copper complex. The levels of copper in the aqueous solution increase and the acid level decreases, as copper is transfers from the organic phase and is replaced by acid.

1.3.7 Electrowinning of copper

Strong electrolyte (45-50gpl Cu, 155-180gpl acid) flows from the strip settler in the SX plant into the strong electrolyte tank.
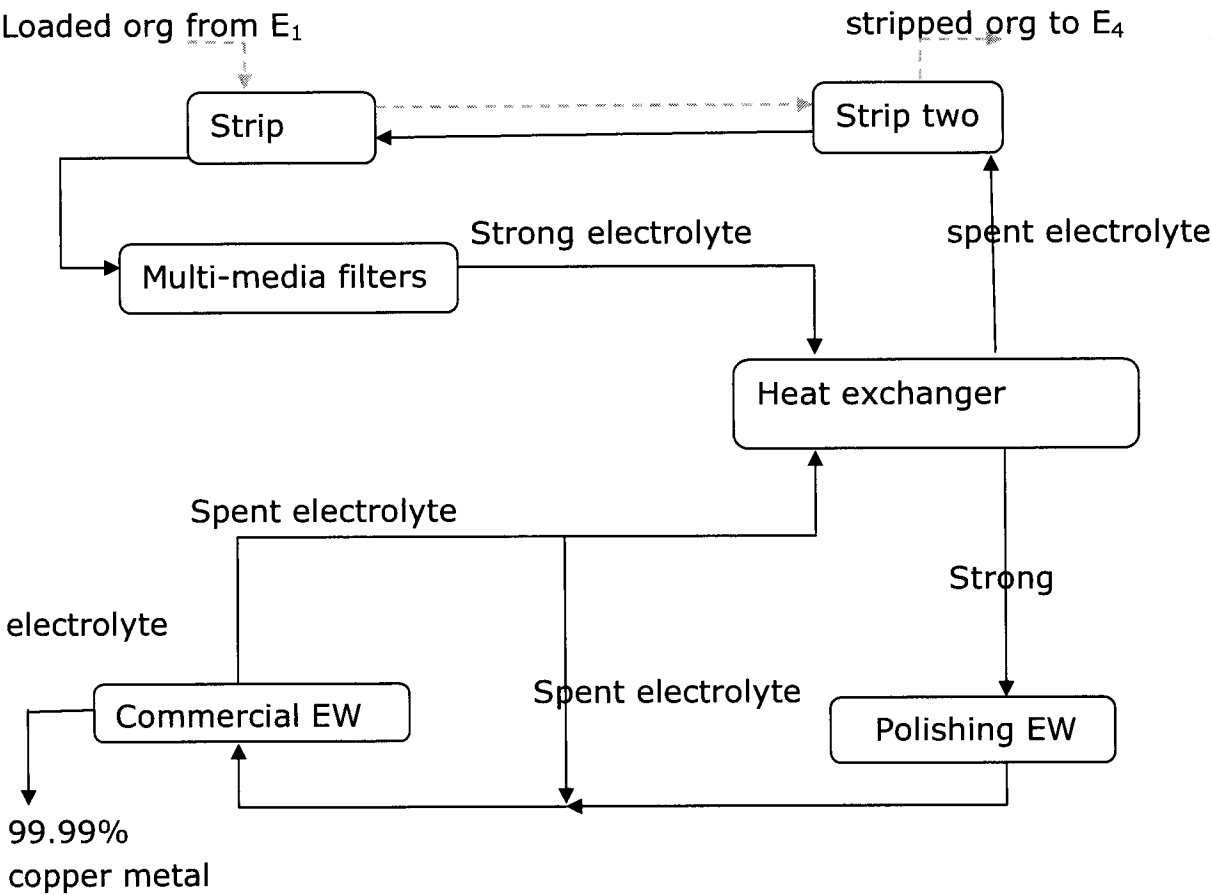
Loaded org from E_1 stripped org to E_4

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┌──────────┐ ┄┄┄┄┄┄┄┄┄┄┄┄┄┄┄┄┄┄ ┌──────────┐
│  Strip   │◄─────────────────── │ Strip two│
└──────────┘                     └──────────┘
```

Strong electrolyte   spent electrolyte

Multi-media filters

Heat exchanger

Spent electrolyte

Strong

electrolyte

Commercial EW   Spent electrolyte   Polishing EW

99.99%
copper metal

Figure 1.2.Electrowinning process flow

From the strong electrolyte tank the electrolyte is pumped through (3) multimedia filters to remove any entrained organic and also to remove any fine solids that exist in the electrolyte and is then passed through the electrolyte heat exchanger and into the 20 polishing EW cells. As the strong electrolyte passes through the heat exchanger, it picks up waste heat from the spent electrolyte which is being pumped to S_2.

A portion of the strong electrolyte is passed through the electric heat exchanger, where it is heated. Heating this stream of electrolyte enables the temperature of the electrolyte to be maintained at~ 45°c. the strong electrolyte overflow the polishing cells into the circulating electrolyte tank.

8

Electrolyte is pumped from the circulating electrolyte tank into the 106 commercial EW cells.

Electrolyte, depleted of copper, overflows each conventional cell and returns to the spent electrolyte tank. Approximately 80% of the spent electrolyte flows out of the spent electrolyte tank back into the circulating electrolyte tank as a cycle. The remainder of the electrolyte is pumped, via the heat exchanger, to S_2 where it is used to strip copper from the loaded organic.

Copper is stripped from the cells on a six or seven day cycle, depending on growth rate of the cathode. One third of the cathodes from a cell are removed and placed in the wash water. The cathodes pass through a wash chamber where they are washed with hot water to remove any electrolyte. New starter sheets are replaced in the cell to initiate another growth rate.

Chemistry

Each EW cell contains 66 starter sheet cathodes and 67 lead alloy anodes. Copper is deposited on the starter sheet electrolytically. The lead anode transfers electrons across the cathode in an even dispersion pattern. The reaction taking place at the cathode surface is represented as

$$Cu^{2+} + 2e^- = Cu$$
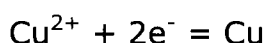
The other reaction taking place at the anode is

$$2H_2O = O_2 + 4H^+ + 4e^-$$
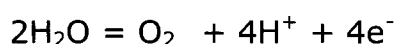
As copper metal is plated, acid is produced. The acid is then used to strip copper out of the loaded organic in the SX strip stage leading to a continuous recirculation circuit. When a direct current (DC) up to 25, 000 A is applied to the cell, copper metal is deposited on the starter sheet cathodes and oxygen is evolved at the lead anode.

1.3.8 Cobalt Circuit

The decopperised solution from the Cu SX plant is fed to the cobalt purification and concentration circuit. Impurity control at purification circuit is achieved by precipitation using limerock and quick lime as precipitants under controlled pH conditions.

The first stage is mainly for iron and residual copper removal, termed the ferric precipitation circuit. The overflow from the ferric thickener, which is maintained at a terminal pH of 3.0-4.0, is fed to the second precipitation circuit, called the clean up stage, for zinc removal. A bleed (~25-30%) of this liquor is fed to the zinc SX plant, and the raffinate returned to the ferric cascades.

The underflow is filtered and washed prior to discard. Overflow from the clean up circuit (pH up to 6.7) is fed to the hydroxide circuit for total cobalt precipitation (at pH of 8.7-8.9), whilst the underflow is recycled back to the ferric stage.

The underflow, which is filtered, is repulped with cobalt spent electrolyte and pumped to the resolution cascade for redissolving the precipitated cobalt. Sulphuric acid is added as necessary to control the pH between 6.2 and 6.5. This pH range is necessary to maintain zinc in the overflow below 1.0ppm, which is important for the production of quality cobalt metal.

The resolution thickener overflow is passed through carbon columns to remove soluble sulphides and entrained organics which arise merely from lime and flocculants used in the circuit. A bleed from carbon columns discharge is routed to the nickel plant for nickel removal before joining the carbon column discharge (cobalt advance electrolyte). Rejection of Ni is by ion exchange process.

The electro plated cathodes are striped and crushed into cobalt flakes using a roll crusher and drummed for export.
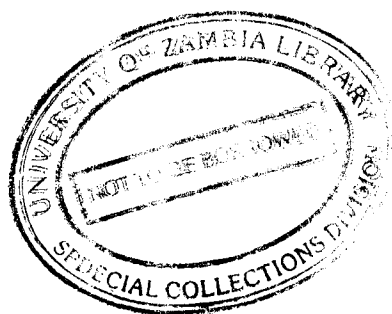
2. LITERATURE REVIEW

2.1 Solvent Extraction

Leaching processes are rarely if ever completely selective, consequently the resulting pregnant leach solution contain impurities and often require purification prior to recovery of the sought metal. Enrichment of the dilute solution may prove particularly beneficial in the subsequent metal recovery process in that much smaller volumes have to be handled, lower capital costs may result as well as more effective metal recovery. [1]

Solvent extraction (SX) is a hydrometallurgical process for the separation, purification and concentration of metal ions in solution. Most used application of solvent extraction is the recovery of Copper from oxide Ores. In its simplest form the process consist of the following steps;

> Leaching of metal from ore at controlled pH
> Solvent Extraction (SX) with suitable extractant
> Stripping (Back extraction) with acid solution (e.g. 180 g/l H_2SO_4 and 30 g/l Cu)
> Electrowinning (EW)

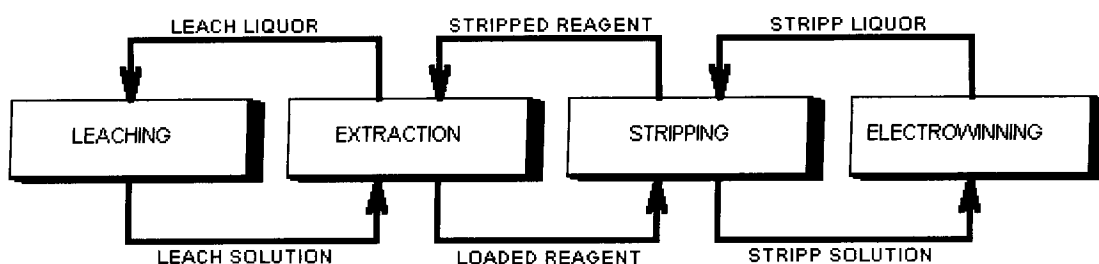| LEACH LIQUOR	STRIPPED REAGENT	STRIPP LIQUOR	
LEACHING	EXTRACTION	STRIPPING	ELECTROWINNING
LEACH SOLUTION	LOADED REAGENT	STRIPP SOLUTION	

Figure 2.1 typical solvent extraction process

The typical equipment used in industrial Solvent extraction process is mixer/settler unit. The mixer/settlers can be attached in series or in parallel

in order to achieve desired results. Usually there is more than one mixer/settler unit or stage in the process.

There are several ways by which a metal-containing species may transfer from aqueous phase to an organic phase they have been classified in different arbitrary ways.

Aqueous feed, which contain the metal ion, is contacted with the organic solution. This organic feed is a mixture of extractant and the diluents. The diluent is typically hydrocarbon mixture, such as kerosene. Mopani Copper Mines uses shellsol as the diluents. The extractant is an amphiphilic molecule and consists of both lipophilic and hydrophilic parts. The hydrophilic part of the extractant reacts on the phase interphase. As a result of the extraction reaction, the charge of the metal ion is neutralized and the formed metal-extractant complex can transfer into the organic phase.

Copper in particular is extracted by the formation of uncharged co-ordination compounds. Co-ordination compounds are formed between complexing agents which have excess electron pairs and metal ions with electron deficiencies.[2] The transition elements, which have unfilled lower electron orbitals, are particularly susceptible to complex formation. The most important group of co-ordination compounds from the Solvent Extraction view point is the chelates.

2.1.1 Chelating

Chelating agents are reagents having at least two ligand atoms in the molecule and thus give rise to ring formation. They are generally insoluble in the aqueous phase but readily soluble in non-polar solvents. The compound formed by a chelating agent and a metal is called a "chelate". The word chelation comes from the root word "chele" which is Greek for the claw of a lobstar or crab. So, "chelation" refers to a grabbing action as when a lobstar grabs something with its claw. Chelation is a process where substance binds to another substance with the involvement of the action of atoms.[3]

The extraction of divalent metal with chelating extractants is an equilibrium reaction and can be shown to be as;

$$M^{2+} + 2RH = MR_2 + 2H^{2+} \qquad\qquad (1)$$
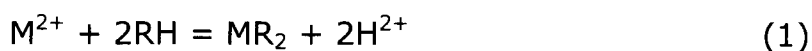
Where RH denotes the extractant molecule.

The reverse is called Stripping. The complex containing MR_2 has no charge as the complex contain two extraction molecules which cancel the charge of the metal ion.

There different types of extractants, Hydroximes which are chelating extractants are widely used in copper extraction. This report looks at the two chelating extractants LIX 984NC and Acorga M5774. The advantages of aldoximes are;

> They have rapid copper transfer kinetics and very good copper over iron selectivity.
> Are very strong copper extractants, so strong that they are always used in conjunction with an equilibrium modifier or with a ketoxime in order to increase the strip efficiency.
> Equilibrium modifiers often increase crud formation and entrainment probably via hydrogen bonding to solids in the pregnant leach solution. They can increase or decrease oxime stability depending on the modifier.

1.2 Properties of LIX 984NC and Acorga M5774

2.2.1 LIX 984NC

It's a 1:1 volume blend of LIX 860N-I and LIX 84-I, a mixture of 5 nonylsalicylaldoxime and 2 hydroxyl-5-nonylacetophenone oxime in a high flash point hydrocarbon diluent which forms water insoluble metallic cation in a manner similar to equation (1)

$$M^{n+} + nRH = MR_n + nH^+$$
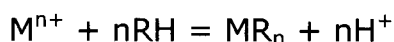
According to Cognis Cooperation Mining Chemicals, because this extractant contains no added modifier, it may show advantages when used for copper extraction from solution containing soluble silica or finely divided solids.

The cost of LIX 984NC is US \$11.14/kg as of up to February 2008.

Typical properties

Physical properties

Extractant appearance;	fluid amber liquid
Specific gravity (25°C);	0.89-0.91
Flash point;	>71°C
Copper complex solubility;	>30 g/l Cu at 25°C

Performance specification

Maximum copper loading;	>5.1 g/l Cu
Extraction isotherm point;	>4.40 g/l Cu
Extraction kinetics;	>95% (30 seconds)
Extraction Cu/Fe selectivity;	>2000
Extraction phase separation;	<70 seconds
Strip isotherm point;	<1.8 g/l Cu
Net copper transfer;	>2.7 g/l Cu
Strip kinetics;	>95% (30 seconds)
Strip phase separation;	<80 seconds

These performance parameters are determined using the standard Cognis quality control test.[4]

2.2.2 ACORGA M5774

Acorga M5774 is a product of Cytec Industries Inc and costs US $8.10/kg as of upto February 2008.

A. **Physical properties**

Appearance;　　clear amber-coloured liquid free from impurities

Specific gravity (25°C);　　0.96-0.98

Viscosity, cP at 25°C;　　<200

Flash point °C;　　>100 (pmcc)

Performance specification

Copper uptake;　　0.56-0.59 g/l Cu per V/O

Cu extraction isotherm point 25°C; org > 4.5 g/l
aqueous < 1.6g/l

Extraction kinetics 25°C;　　>90% 15 seconds
> 95% 30 seconds

Strip kinetics 25°C;　　>95% 15 seconds

Cu strip isotherm point 25°C;　　organic < 2.1 g/l
aqueous < 32.0 g/l

Extraction Cu/Fe selectivity;　　> 3000

Phase disengagement;　　extraction <60 second
stripping < 60 seconds

In order to thoroughly investigate the performance of these two reagents, there are important parameters that should be studied and understood.[5]

2.3 Important parameters in solvent extraction

It is not intended that the theory of solvent extraction be exhaustively examined in this text. Rather, it is intended to provide sufficient background for the interpretation and what is to follow in the report.

2.3.1 Extraction coefficient

The analytically determined distribution ratio of a metal between an aqueous phase and an organic phase is known as the extraction coefficient, designated E. it is a measure of how well a solvent will extract a metal, that is, a measure of the overall driving force of a solvent extraction system, and is thus concentration dependant.

$$E = \frac{concentraion\ of\ metal\ in\ organic\ phase}{concentration\ of\ metal\ in\ aqueous\ phase} \tag{2}$$

Metal concentrations are determined analytically as total concentrations of metal, in whatever form, in each phase. This very simple relationship is basic to solvent extraction studies, and provides much of the data on which solvent extraction processes are based. Calculation of E, based only on the initial metal concentration in the aqueous phase and its concentration in the raffinate, assumes that the mass balance of the metal ion is obtained. There conditions where such will not be the case, and these must be taken into consideration in the use of this approach to the determination of E. these conditions are:

> That no volume change occurs on shaking the two phase
> That a third phase is not formed and
> That no crud formation occurs

As defined E is a number, has no units and is not a constant. The value of E depends on many factors, such as the phase ratio, extractant concentration, temperature, pH, metal complexation in the aqueous and organic phases, and the metal concentration in the aqueous phase.

By itself the value of the extraction coefficient has no meaning, simply because it is dependent on the variables noted above. Thus, to say an extractant is good because the extraction coefficient is high, without stating the conditions under which the result was obtained, is of little value to

anyone. It cannot be emphasized too strongly that the values of E are unique to a particular system, and comparisons of different systems should be done only when the experimental conditions are identical for each.

In spite of these restrictions, the extraction coefficient E is the most used parameter in solvent extraction studies.

2.3.2 Extractant concentration

For a given metal ion concentration in the aqueous phase the extraction coefficient will increase with an increase in the extractant concentration, other factors being constant. Thus for a fixed metal ion concentration, pH, and phase ratio, the amount of metal extracted will increase with an increase in extractant concentration. As the extractant concentration is increased, the distribution curve for a metal as a function of pH will shift to towards the lower pH values as predicted by the equation (16) below. Equation (16) is derived from the following equations;

The simplest equation that can be written to illustrate the extraction of metal ion, M^{2+}, by an extractant, RH, is

$$M^{n+} + nRH = MR_n + nH^+ \qquad (1)$$

From the above equation an equilibrium constant (K_E) can be established. As defined, E is independent of the phase ratio of the aqueous and organic phases. However, it should be evident that the phase ratio will influence the amount of metal extracted since, for example, at a given concentration of extractant (RH), the amount of extractant available for extraction purpose is given by its concentration multiplied by the phase volume;

$$total\ amount\ of\ RH = [RH] \times V \qquad (3)$$

Where V is the volume of the organic phase.

Now the equilibrium constant (K_E) for the system described by equation (1) is given by;

$$K_E = \frac{MR_n}{M^n} \frac{[[H]^+]^n}{[RH]} \qquad (4)$$

This is the mathematical expression for the law of mass action. This law, due to Guldberg and Waage states that the velocity of a chemical reaction is

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proportional to the active masses of the reacting substances. For this discussion, active mass will be taken as concentration.

If the law is applied to a simple reversible reaction at constant temperature, such as;

$$A + B \rightarrow C + D \tag{5}$$

Then the rate or velocity at which A and B react is proportional to their concentrations;

$$V_f = K_f(A)(B) \tag{6}$$

Where V_f is the velocity of the forward reaction which produces the reaction products C and D, and K_f is the proportionality constant. In the same way the reverse reaction can be written in which the products of equation (3) react to form the initial reactants A and B as;

$$V_r = K_r(C)(D) \tag{7}$$

Now at equilibrium, $V_f = V_r$ since the equilibrium here is dynamic, thus

$$K_f(A)(B) = K_r(C)(D) \tag{8}$$

Or

$$\frac{(C)(D)}{(A)(B)} = \frac{K_f}{K_r} = k_E \tag{9}$$

Where K_E is defined as the equilibrium constant for the reaction at constant temperature.

Notice the similarities between equation (4) and (9). Obviously the equation says nothing about the kinetics of the process, that is, the rate at which equilibrium is attained. It does, however, show that if one of the reactants or products concentrations is changed, the equilibrium will adjust itself in such a way that it maintains the constant K_E. For example, if the concentration of the metal ion in the aqueous phase is increased, then the amount of metal being extracted will increase to compensate and maintain K_E constant. This assumes, of course that there is sufficient free extractant available in the solvent to extract more metal. If this were not so, K_E would not be maintained constant. This effect is prevalent in solvent extraction processes

in which the solvent is loaded near its maximum; an increase in metal concentration in the feed cannot be extracted and hence reports to the raffinate.

From equation (2) and (4) it can be shown that;

$$K_E = E \frac{\left[(H)^+\right]^n}{(RH)^n}$$

(10)

Thus

$$E = K_E \frac{(RH)^n}{[(H)^+)^n}$$

(11)

Also from equation (11), E is independent of the total metal concentration, and thus the extraction should be independent of the total amount present. Consequently, this equation should hold for both high and low (trace) concentrations.

Equation (11) can further be simplified by including the condition that the concentration of the extractant be sufficiently high that extraction of a metal does not change its concentration by any significant amount. Thus (RH) can be regarded as a constant, and equation (11) can reduce to

$$E = \frac{K^*}{(H^+)^n}$$

(12)

Where $K^* = K_E(RH)^n$.

Under these conditions E is a function of H^+. Thus is a useful equation to employ in some investigation because of its (relative) simplicity.

Of course, the reactions involved in solvent extraction of metals are not usually as simple as indicated above, and especially not when dealing with actual plant solutions such a leach liquor. Let us consider some of these reaction and their effects on metal extraction. Also, by making certain assumptions regarding a system we can eventually arrive back at equation (1)

Let us now consider further, the relationship which exists between the various parameters involved in the solvent extraction of metals. Taking logarithms of equation (11) we obtain;

$$\log E = \log K_E + n\log (RH) - n\log(H^+) \qquad (13)$$

Thus, by plotting log E versus pH at constant (RH), we should get a curve, whose slope is equal to n. Further, if we write this equation as;

$$\log E = \log K_E + n\log (RH) + npH \qquad (14)$$

Then plot of *log E* versus (*log (RH)* + *pH*) will give a straight line of slope n and an intercept equal to log K_E . Such plots are useful in getting around the problem of having to reproduce extractant concentrations and identical pH values in experimental studies. By suitable manipulation, we see that we can obtain an expression involving $-\log(H^+)$, which is, pH. So multiplying by n^{-1} we have;

$$^1/_n \log E = {}^1/_n \log K_E + \log(RH) - \log[(H]^+) \qquad (15)$$

Or

$$-\log[H^+] = pH = {}^1/_n \log E - {}^1/_n \log K_E - \log[RH] \qquad (16)$$

Where;

> E is the extraction coefficient
> K_E is the extraction equilibrium constant
> [RH] is the extractant concentration
> n is the number of extractant molecules

Thus for a fixed metal ion concentration, pH and phase ratio, the amount of metal extracted will increase in the extractant concentration. The resulting effect being one of shifting the distribution curve.

Generally plots of extractant concentration against extraction coefficients show a linear relationship provided that the concentration of the metal is not too high. The slope of the line is equal to the number of extractant molecules n, associated with the metal atom in the extracted species. This number may or may not be an integer, the latter case may arise, for example when the extractant solvates the extracted species or when two different metal complexes are extracted.

The slope of the extractant concentration against the extraction coefficient gives the value n, as shown by the following derivations,

$$M^{n+} + nRH = MR_n + nH^+ \qquad (17)$$
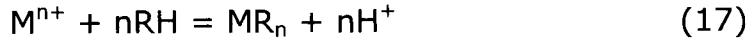
$$K_E = \frac{[MR_n][H^+]^n}{[M^{n+}][RH]^n} \qquad (18)$$
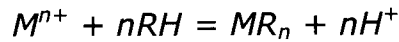
$$K_E = \frac{E}{[RH]^n}$$

$$E = K_E[RH]^n$$

Taking logs,

$$\log E = n \log[RH] + consntant. \qquad (19)$$

This is the equation of a straight line on a log-log plot.

2.3.3 Effect of pH

All extractants of the chelating type used in solvent extraction process liberate hydrogen ions on the extraction of a metal;

$$M^{n+} + nRH = MR_n + nH^+$$

And the greater the amount of metal extracted (that is, the higher the solvent loading) the more hydrogen ion is produced. This result in a decrease in pH of the system and consequently a decrease in the amount of the metal extracted (reverse reaction). The higher the equilibrium pH of a metal or system, the lower will be the extractant concentration needed to achieve a given percent metal extraction and vice versa. This is predicted by equation (16).

At constant extraction concentration, extraction coefficient will increase as the pH is raised, unless of course other factors such as metal complexation or hydrolysis occur in the aqueous phase. The number of hydrogen ion and molecules of extractant involved in the formation of extractable species depends on the type of extractant used. All commercially available extractant are monobasic in nature and release one hydrogen ion for every molecule which combines with a metal. The number of molecules of

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extractant involved in the formation of an extractable species depends on the oxidation state or coordination number of the metal ion, and the number of places at which bonding can occur to the extractant.

The pH of the system affects both the metal ion and the extractant. Thus, if the pH is increased the metal will eventually hydrolyse and will not extract. Decreasing in pH, increase in the level hydrogen ion concentration may result in the formation of non-extractable metal species as a result of metal complexation with components of the aqueous phase. This occurs, for example, in systems which involve sulphuric acid due to equilibria between SO_4^{2-}, HSO_4^- and H_2SO_4 resulting in the formation of metal complexes with these anions. All extractants suffer protonation as the pH of the system decrease. If the extractant is unable to ionize as a result of the concentration of hydrogen ion, it will not be able to form a complex with the metal ion, and hence extraction will not occur.

It should be apparent that pH is of prime importance in solvent extraction systems and affects other variables significantly. Thus it is always important to determine the pH isotherm which shows the concentration of metal in organic extract as a function of the pH of the aqueous solution from which the pH has been extracted.[6]
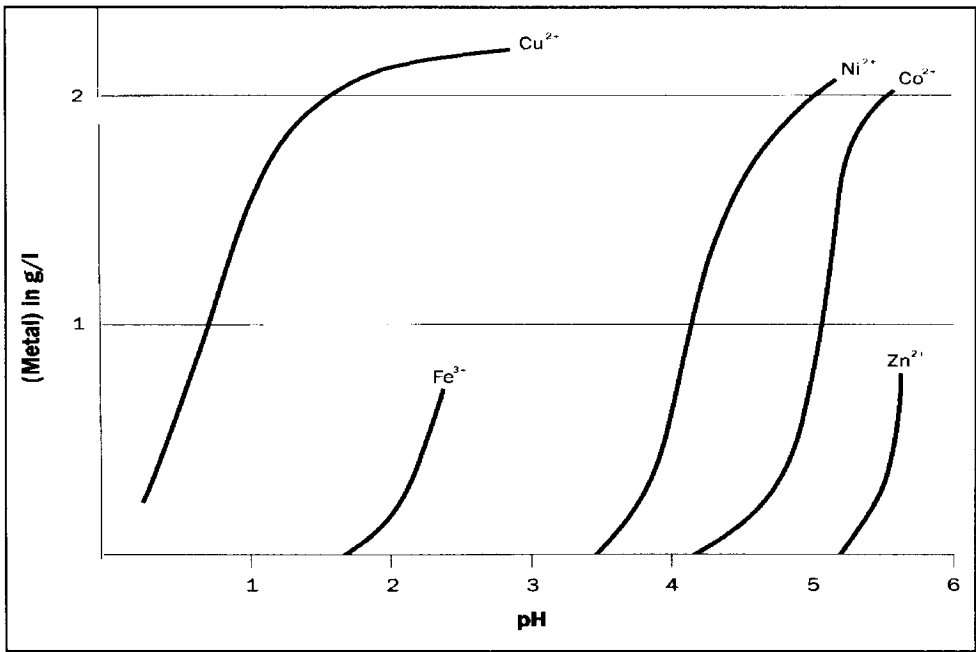
Figure 2.2.pH isotherms for one of the commercial LIX-reagents [7]

2.3.4 Effect of aqueous to organic ratio

During extraction, the organic to aqueous phase ratio (O/A) plays an important role in the determining the extent of soluble extraction into the organic phase.

An extraction distribution isotherm can be constructed using the data obtained from experiments in which different O/A ratios are used while or other solvent extraction parameters are kept constant. Solute analysis is made in the organic and aqueous phases at different O/A ratios. For the different organic to aqueous aliquots contacted at different O/A ratios, a plot of the solute concentration in the organic extract against the solute concentration in the corresponding raffinate is termed as an extraction distribution isotherm. The greater the displacement of an extraction isotherm from the horizontal axis, the greater is the ability of an extractant to concentrate solute into the organic phase. However, the most important use of an extraction distribution (as determined in the laboratory) is that it enables estimation of the number of stages that would be required in solvent extraction process to achieve a specified level of extraction under specified conditions.

The aqueous flow volume in the counter current operation can be designated as A, while the corresponding organic flow volume by O. The concentration of extractable species are X and Y in the aqueous phase and organic phase respectively.

A McCabe-Thiele diagram is useful for estimating the number of theoretical stages required to obtain specified results in a solvent extraction system.

The operating line is based on a mass balance. Hence, the concentration of the solute in the aqueous feed entering any stage, and the organic phase leaving any stage, are coordinators of the point on the operating line, since the operating line is a straight line, it is fixed by two points. Alternatively, it can be established by only one point and the ratio of the aqueous to organic feed that determines the slope of the line.
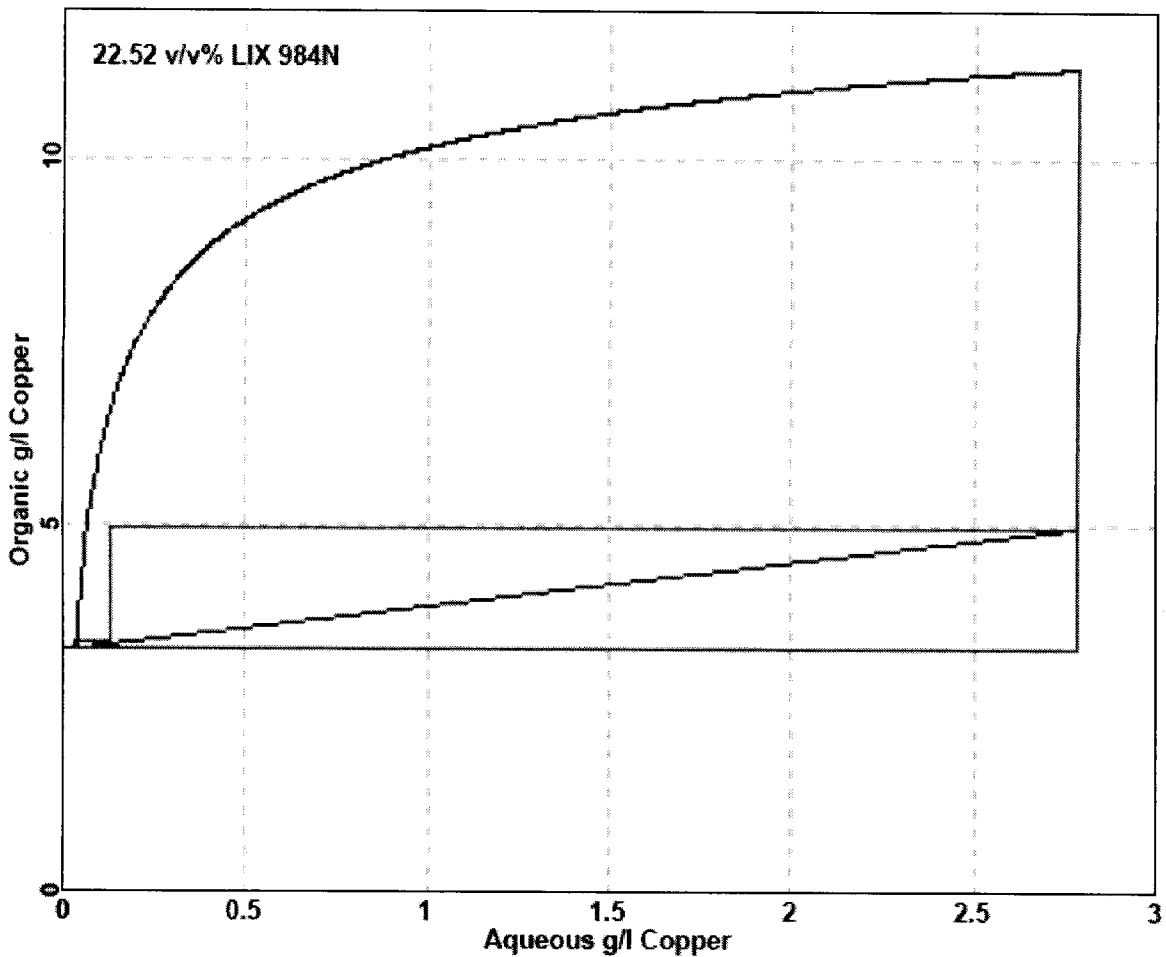
Figure 2.3 a typical McCabe-Thiele diagram

2.3.5 Effect of contact time in solvent extraction

Solvent extraction involves contacting the aqueous phase with the organic phase. It is therefore imperative that the effect of contact time i.e. the time the extractant is in contact with the aqueous phase, is investigated so that a comparison can easily be made between the two extractants in question. A good extractant should extract more in the shortest possible time.

The Mopani Copper Mine solvent extraction plant currently uses two minutes as the optimum contact time for both extraction and stripping.

3. TESTWORK PROCEDURE

3.1 Materials

The following samples and materials were used in the experiments in this project;
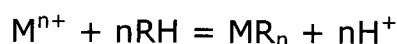
3.1.1 Extractants

Lix 984NC

It's a 1:1 volume blend of LIX 860N-I and LIX 84-I, a mixture of 5 nonylsalicylaldoxime and 2 hydroxyl-5-nonylacetophenone oxime in a high flash point hydrocarbon diluent which forms water insoluble metallic cation in a manner similar to equation (1)

$$M^{n+} + nRH = MR_n + nH^+$$

According to Cognis Cooperation Mining Chemicals, because this extractant contains no added modifier, it may show advantages when used for copper extraction from solution containing soluble silica or finely divided solids.

Acorga M5774

This is a Hydroximes extractant which is chelating extractant and also used in copper extraction. It is a product of Cytec Industries. The advantages of aldoximes are;

> ➤ They have rapid copper transfer kinetics and very good copper over iron selectivity.
> ➤ Are very strong copper extractants, so strong that they are always used in conjunction with an equilibrium modifier or with a ketoxime in order to increase the strip efficiency.
> ➤ Equilibrium modifiers often increase crud formation and entrainment probably via hydrogen bonding to solids in the pregnant leach solution. They can increase or decrease oxime stability depending on the modifier.

Diluent

In the experiments conducted the diluent used was shellsol. The term diluent refers to the organic liquid in which the extractants and modifiers are dissolved to form a solvent.

Pregnant solution

A bulk of the pregnant solution was collected in a bucket in order to have a pregnant solution of same concentration for comparison purposes. For the first two experiments the concentration of the pregnant solution used was different from that of the rest. This is due to the fact that the storage capacity of the bucket was quiet low to cater for the rest of the experiment. But still for comparison purposes the same concentration was used when investigating a particular parameter.

The pregnant leach solution was taken from the stream entering the first stage of extraction. The stream flows from the surge tank to the first mixer/settler unit. Shellsol was taken from the storage tank in the solvent extraction (SX) plant. LIX 984NC and Acorga M5774 were taken from the mine store house. The two extractant were tapped off from the sealed 1000liter containers.

3.1.2 Strippers

Concentrated sulphuric acid

Synthetic concentrated sulphuric acid was used for stripping purposes. The lab had in stock H_2SO_4 of about 98% and was diluted to required concentrations for the desired purpose. The same acid was used for pH control purposes.

3.2 Experimental procedure

3.2.1 Extraction

3.2.1.1 Effect of the phase ratio

The experiment was carried out by keeping all other parameters like pH, extractant concentration and contact time constant, and varying the phase ratio. The phase ratio was varied from 0.1 to 10 for both extractants. Hand shaking was used to contact the two phases as the electric shaker was not working properly. The volume for both phases was varied from 27 to 273 ml.

The copper in the raffinate was analysed using the atomic absorption spectroscope (AAS) and the copper in the organic phase was analysed using mass balance calculations. The pH was maintained at 1.4, the extractant concentration was maintained at 22% of the organic volume and the contact time maintained at two minutes.

3.2.1.2 Effect of pH

In these experiments, the parameters such as the phase ratio, extractant concentration and the contact time were kept constant and only the pH was varied. pH adjustments were done with the use of either concentrated sulphuric acid or ammonia solution. To reduce the pH, drops of concentrated sulphuric acid were added to the pregnant leach solution and to increase the pH ammonia solutions was added to the pregnant solution. The pH was varied from an average range of 0.44 to 2.5 and copper in the raffinate was analysed using the AAS. The pH adjustments were made to each measured volume of the pregnant leach solution before the shakeout was done. Thus it was not very easy to use the exact pH for both extractants because the experiment were conducted in such a way that one extractant is used for the whole range and the experiment repeated with another extractant for the whole range. Thus, the experiments were done at not exactly the same pH values but in the same range. This will not affect the conclusion because the experiments were done in the same range for a same pregnant leach solution.

3.2.1.3 Effect of extractant concentration

Extractant concentration as an important parameter in solvent extraction was also investigated. This was done by keeping the pH, contact time and phase ratio constant whilst varying the extractant concentration in the organic phase. The extractant concentration was varied from 10% to 30% for both extractant in the same diluent (Shellsol). For example 10% of the required volume of the organic to give the required phase ratio is the extractant and the remainder is the diluent. The copper in the raffinate was measured and a mass balance gives the copper in the organic.

3.2.2 Stripping

3.2.2.1 Effect of acid concentration

98% sulphuric acid was diluted to required amounts for the experiment. The range of diluted acid was 140 – 210gpl sulphuric acid. The loaded organic solution was prepared in the laboratory by contacting the fresh organic with the pregnant leach solution. The stripping experiments were done with synthetic sulphuric acid. The amount of copper in the two loaded organics may not necessarily be the same because they were just made in the laboratory but what will really matter are the strip efficiencies. The phase ratio and contact time were kept constant in the experiments.

3.2.2.2 Effect of phase ratio variation

The phase ratio was varied whilst keeping the acid concentration at 180gpl and maintaining the contact time at two minutes.

4. Results and discussion

The following were the results from the laboratory bench test works performed.

4.1 EXTRACTION

4.1.1 The effect of volume ratio on copper extraction

Using a pregnant solution which contained 21.5 g/lCu the effect of volume ratio on copper extraction was investigated using Acorga M5774 and Lix 984NC at an extractant concentration of 22%*v/v* and pH 1.4. The results are shown in Figure 4.1 and the data used to plot the graph can be found in the Appendix.
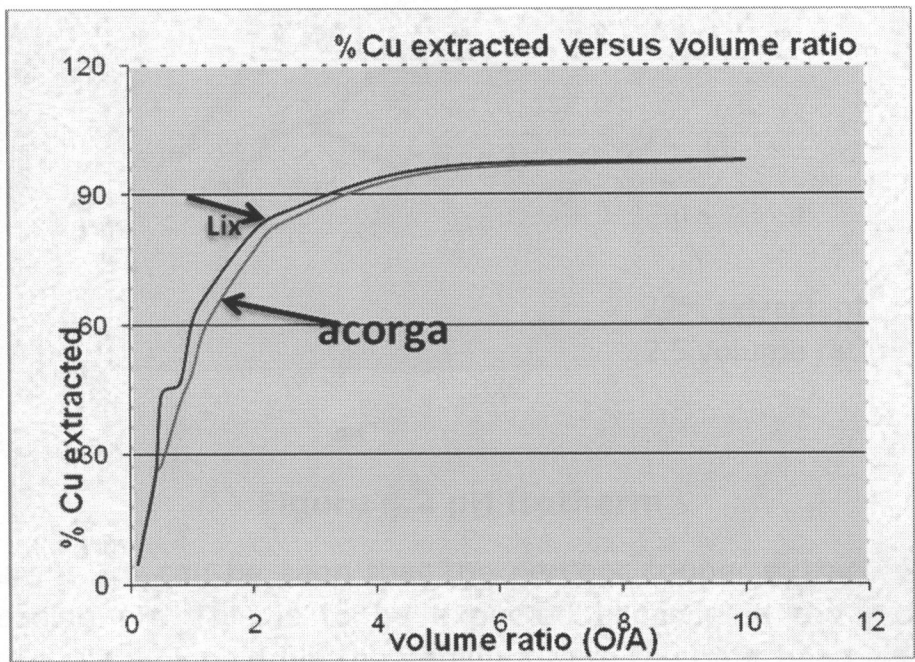

Figure 4.1

From the graph it is clear that at O/A values of about 0.6 to 7.0 Lix 984NC is performing better than Acorga M5774. At values less than 0.6 the performance for both is almost the same.

This can be explained by the fact that Lix 984NC is a very strong extractant with no added modifier. This is what gives it its unoque properties as compared to its counterpart Acorga M5774 which is always used in conjuction with a modifier.

4.1.2 Effect of pH on extraction of copper

Using a pregnant solution which contained 23.0 g/lCu the effect of aqueous solution pH on copper extraction was investigated using Acorga M5774 and Lix 984NC at an extractant concentration of 22%v/v and the organic to aqueas ratio of 2.5. The results are shown in Figure 4.2 and the data used to plot the graph can be found in the Appendix.
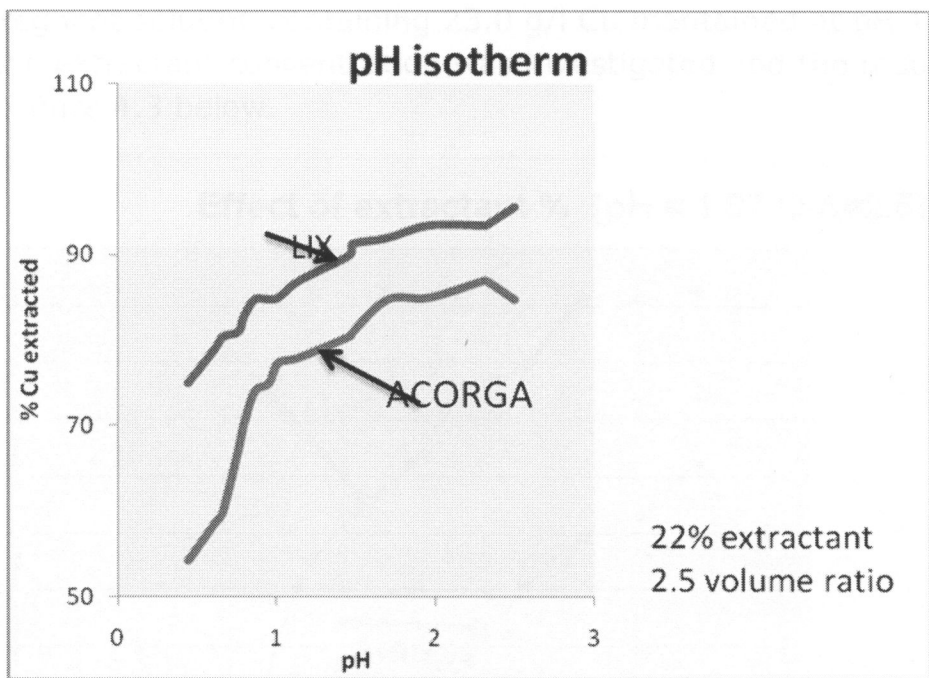
Figure 4.2 pH isotherm

From Figure 4.2 it can be seen that the percent copper extracted increases with increasing pH. This is to be expected because in the reaction, the consumption of Cu^+ ions drive the equilibrium to the right hand side

$$M^{2+} + 2RH = MR_2 + 2H^{2+}$$
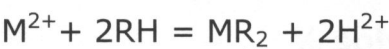
However, due to the luck of selectivity of both extractants for Fe at high pH values (above 1.8), pH values above this value are not desirable. Besides using higher pH values during extraction, the plant would incur large costs in

neutralising the liquor from pH 1.5 during leaching. Therefore, in this pH range Lix 984NC is slightly better than Acorga M5774 by about 10%.

Thus comparing the two extractants, the ranges are;

Lix 984N   80% - 96%

Acorga M5774   54% - 87%

This clearly shows that Lix 984N at any given pH value from the given pH range will have better extraction efficiences than Acorga M5774.

4.1.3 Effect of extractant concentration on copper extraction

Using a pregnant solution containing 23.0 g/l Cu mantained at pH 1.87, the effect of the extractant concentration was investigated and the results are as shown in Figure 4.3 below.
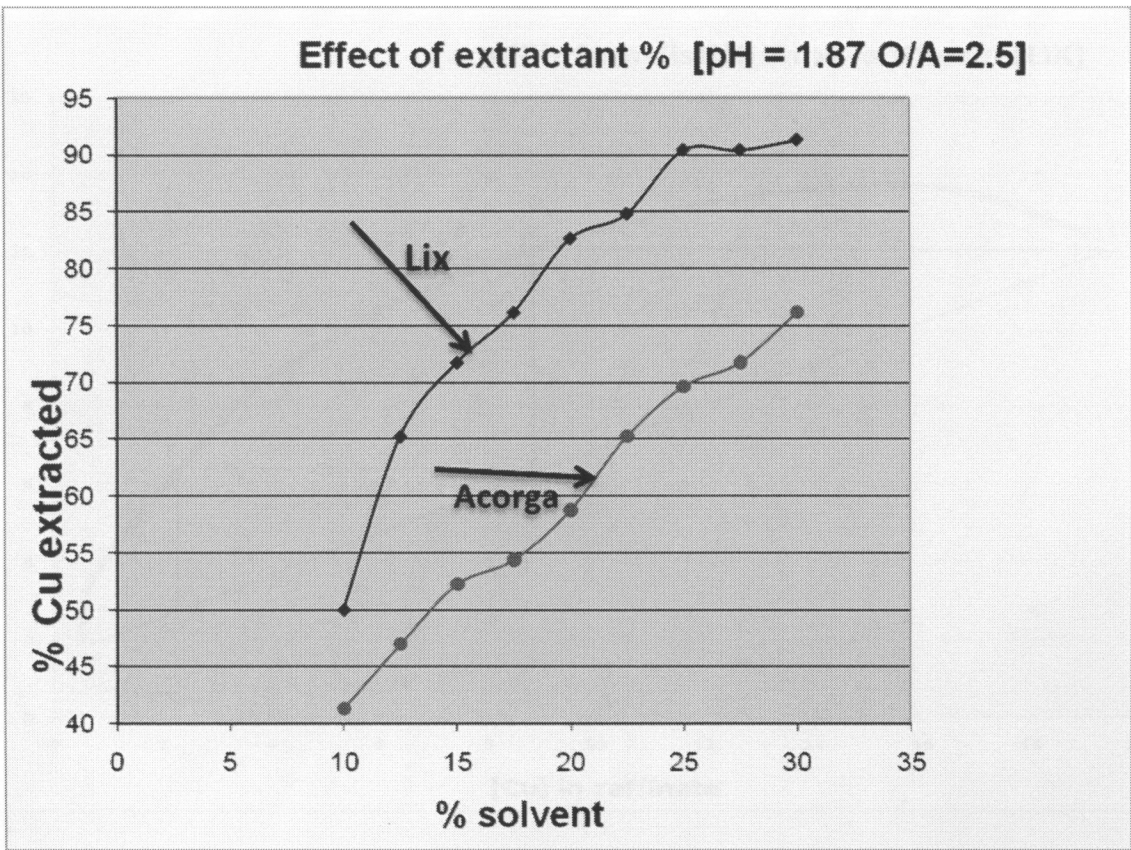

Figure 4.3 Effect of Extractant concentration

Lower extractant concentration leads to low extraction efficiency, too high an extractan concentration leads to high viscosity in the process. The usable range is 17.5 – 25%.Of the two extractants,Lix 984N shows better extraction efficiencies at any given extractant concentration in the diluent. Again this is traced back to the fact that Lix 984NC will strongly extract because it has no added modifier and has rapid copper tranfer kinetics.

4.1.4 Equilibrium distribution isotherm

Extraction distribution isotherms were constructed using the data obtained from the experiment in which different volume ratios (O/A) were used while other solvent extraction parameters are kept constant. From this an estimate of the number of stages for extraction to the required level was done on both extractant using the same operating line. The representation of the two extractant is shown in Figure 4.4.

equilibrium distribution isotherm (LIX)

[Cu] organic

[Cu] in raffinate
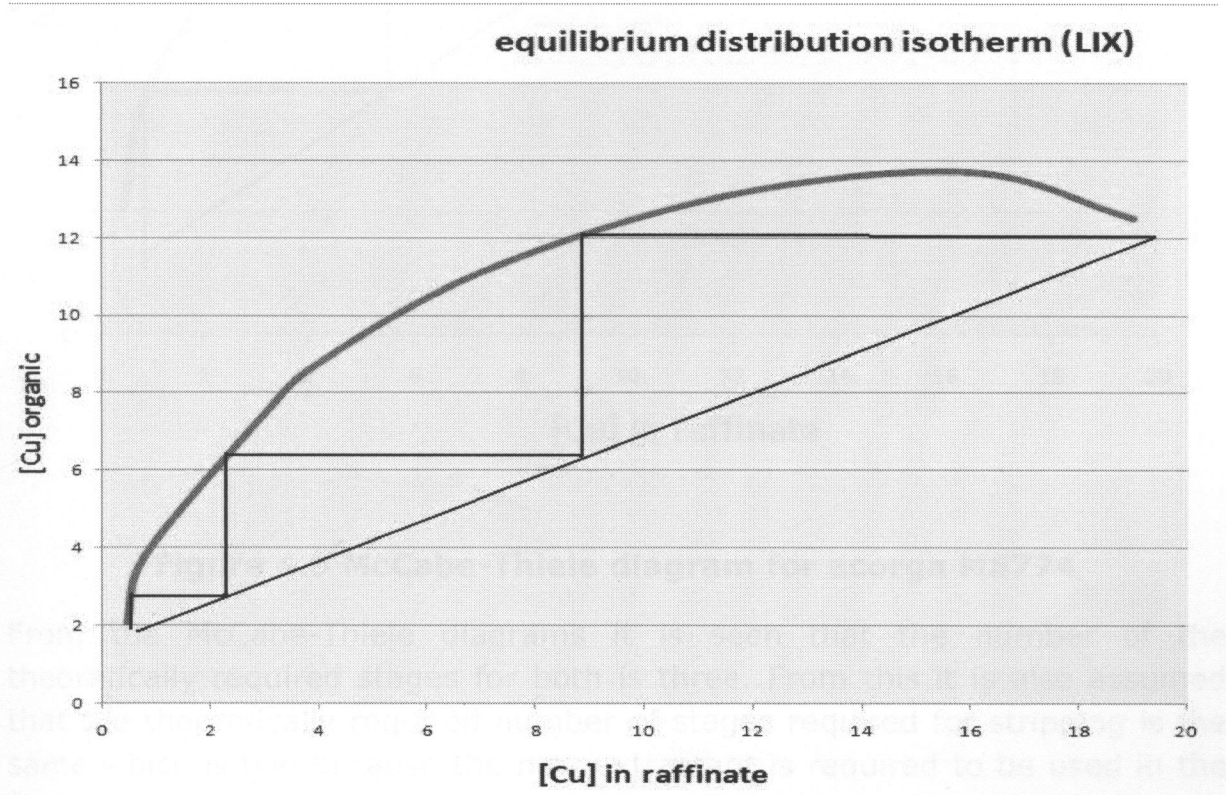
Figure 4.4 McCabe-Thiele diagram for lix 984N

equiliblium distribution isotherm (Acorga)
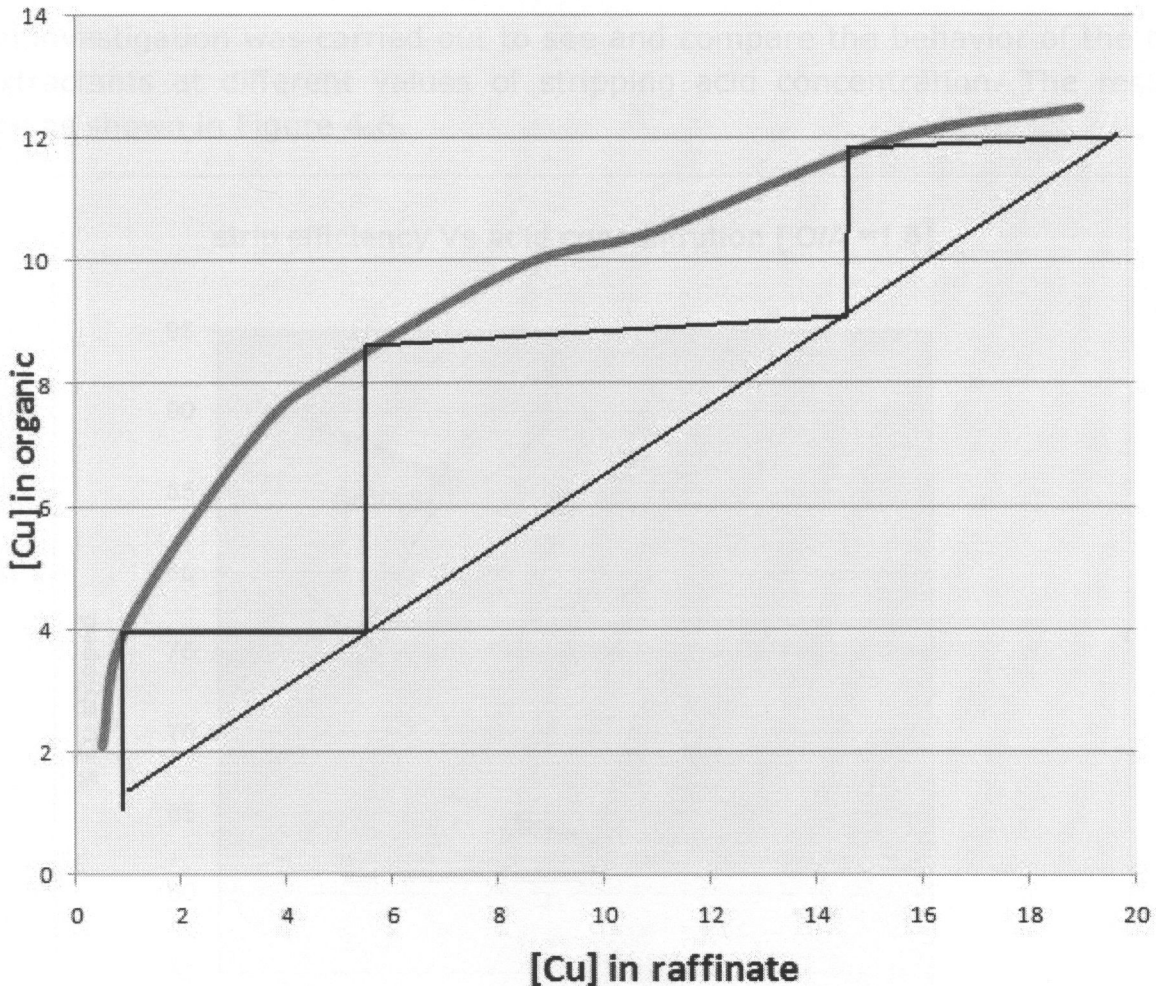
Figure 4.5 McCabe-Thiele diagram for acorga M5774

From the McCabe-Thiele diagrams it is seen that the number of the theoretically required stages for both is three. From this it is also assumed that the theoretically required number of stages required for stripping is the same which is two because the new extractant is required to be used in the same circuit.

4.2 STRIPPING

4.2.1 Effect of acid concentration

An investigation was carried out to see and compare the behavior of the two extractants at different values of stripping acid concentration. The results are as shown in Figure 4.6.

strip efficiency Vs acid concentration [O/A =1.5]
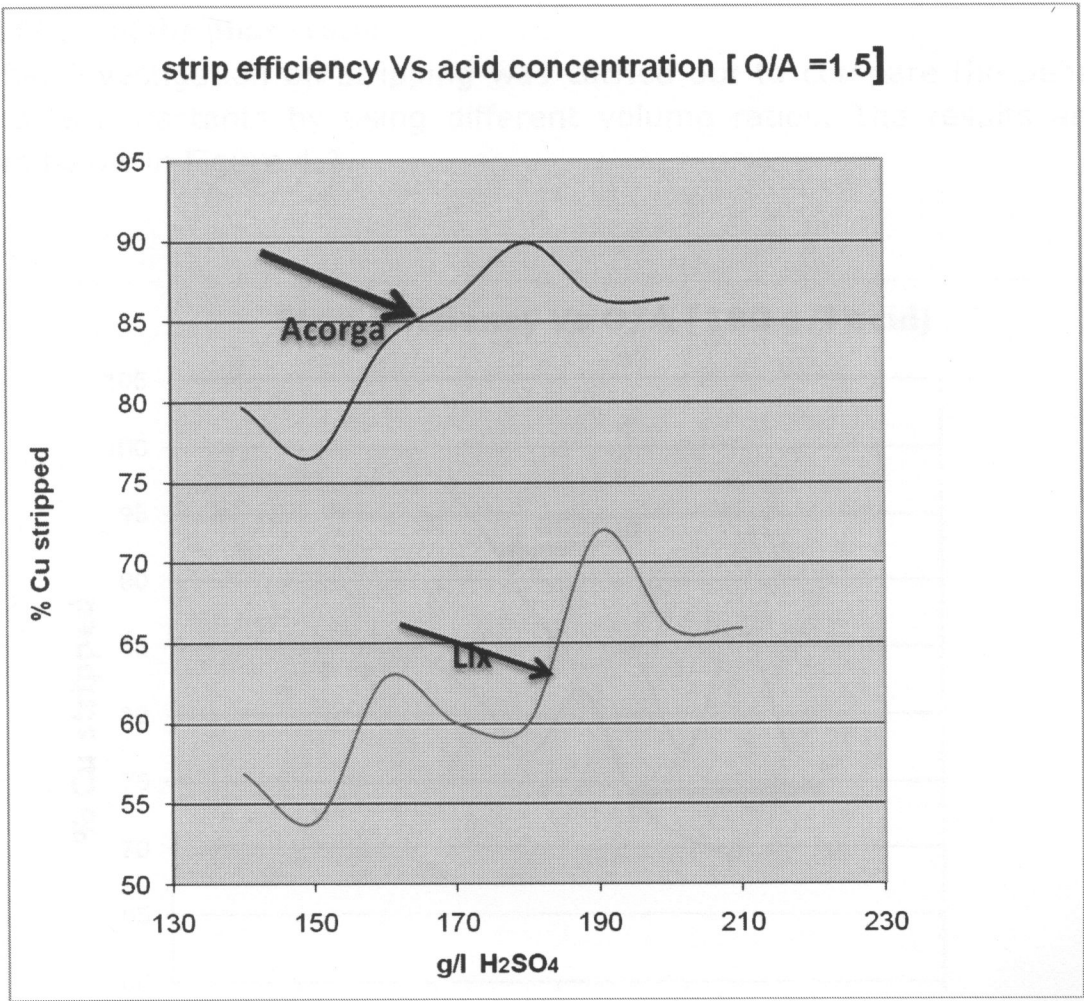
Figure 4.6 effect of acid concentration

From Figure 4.6 it is seen that at whatever value of the acid concentration used Acorga M5774 shows better strip efficiencies than Lix 984N. Because Lix 984NC is such a strong extractant with no modifier added which regulates the strength of the bonds, it is not easily stripped and thus the low efficiencies. Both extractants show a gradual rise in efficiency as the acid

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concentration increases. This is to be expected as depicted by the equation below.

$$M^{2+} + 2RH = MR_2 + 2H^{2+}$$
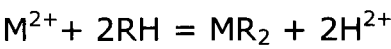
As acid concentration increases more metal is rejected by the extractant but too much acid degrades the extractant.

4.2.2 Effect of the phase ratio

Another investigation on stripping was carried out to compare the behavior of the two reactants by using different volume ratios. The results are as shown below in Figure 4.7.
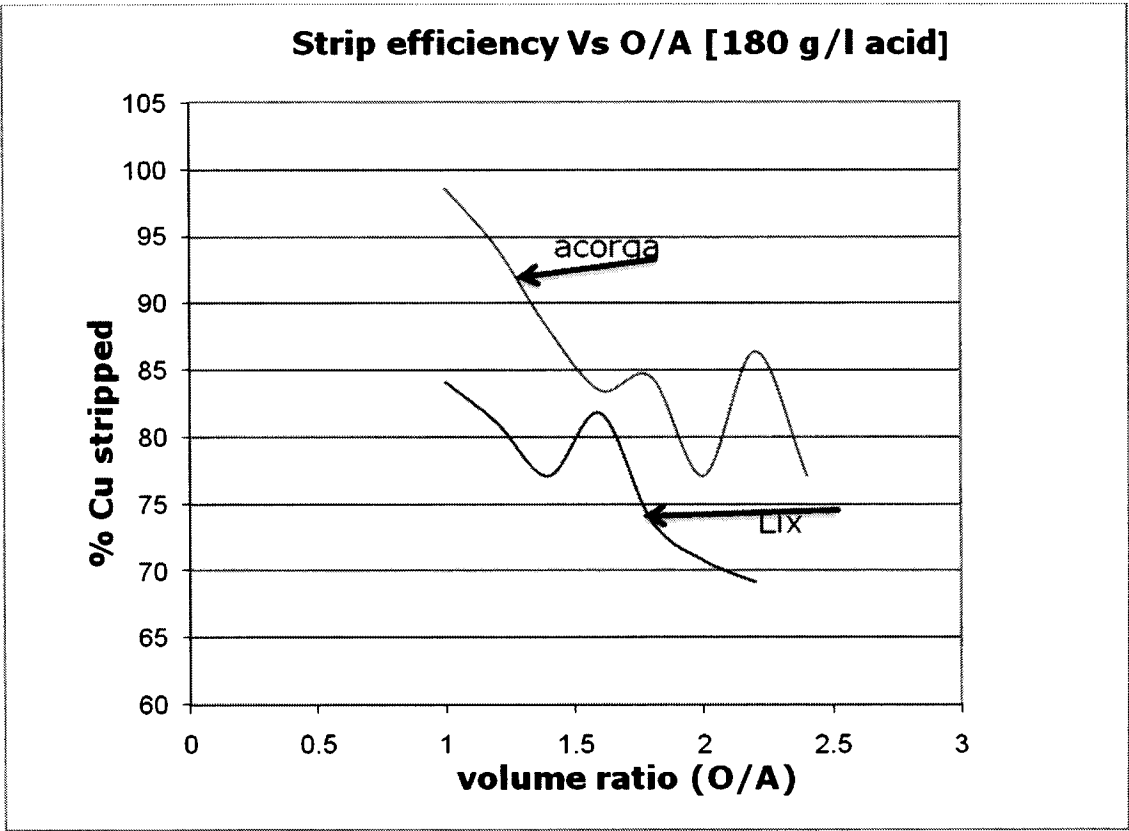

Figure 4.7 phase ratio variation

From the results above it is seen that Acorga M5774 has better strip efficiencies than Lix 984N at the given phase ratio range. Both reagents seam to do better at low phase ratio values.

It can be seen that as the O/A ratio increases the efficiencies drop. This is because at lower O/A ratios there is enough organic to load the aqueous solution and thus more copper is transferred to the electrolyte.

From the results obtained, it is clear that Lix 984N is good at extracting than Acorga M5774 whilst on the other hand; Acorga M5774 is easily striped than Lix 984N.

4.3 Benefit cost appraisal of using lix 984N in preference to acorga M5774

A cost benefit appraisal analysis was done to ascertain the choice of the best extractant on the basis of economics combined with performance. From the above sections it can be seen that Lix 984NC is good at extracting than at stripping. The company is looking for an effective extractant that will perform better than the current one but with low cost.

Thus, by knowing the flow rate of the organic phase and the concentration of the pregnant solution the necessary calculations have been made to come up with Figure 4.8. A sample calculation is included in the Appendix A2 of this report.

The Figure shows the ratio of the additional benefit of using Lix 984NC in preference to Acorga M5774 to the additional cost of purchasing the extractant.

It is very important to extract as much copper as possible from the cobalt circuit to minimize copper losses. Lix 984NC just does it right if compared to acorga M5774. With acorga M5774 the copper losses will be so high with time because it will extract less and this would add cost to the plant operations because more lime would be required to help precipitate the copper out in the cobalt solution (raffinate) prior to cobalt concentration whilst at the same time loosing copper to the tails.
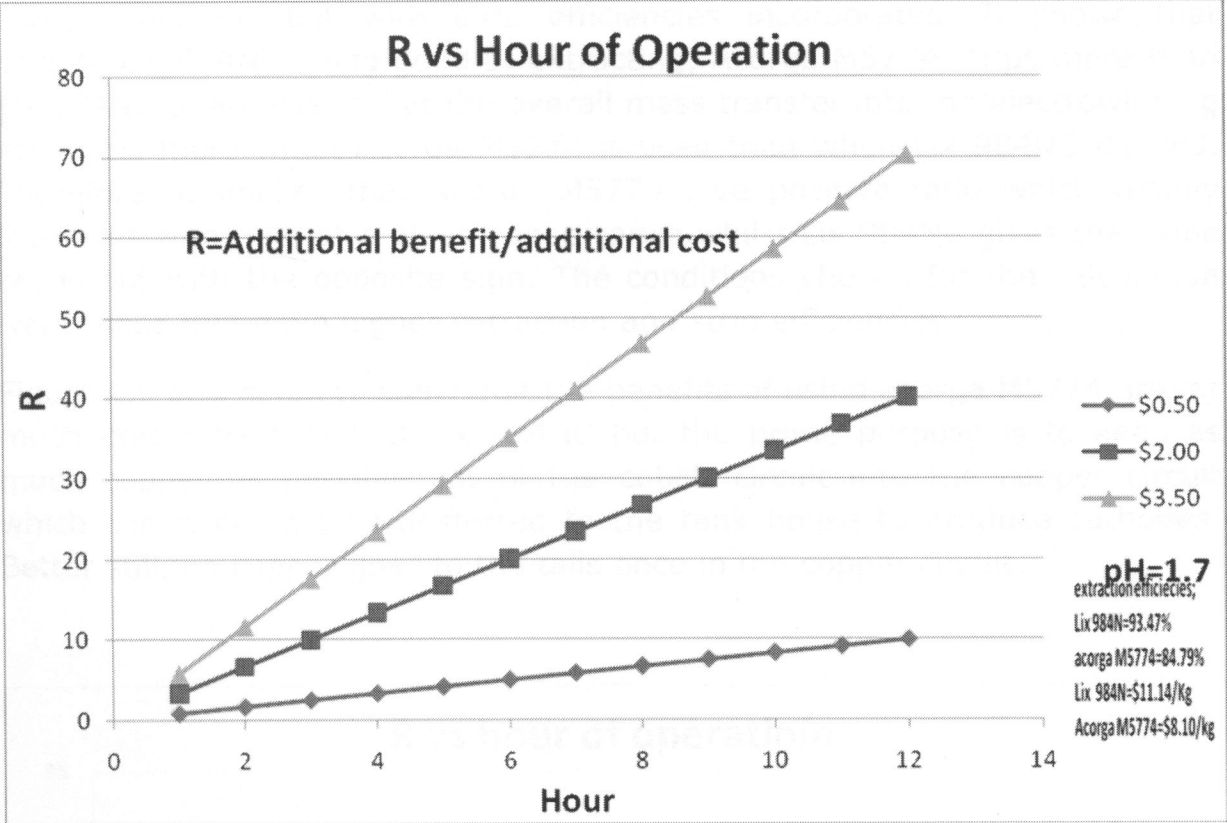
Figure 4.8 benefit cost appraisal of using Lix 984NC in preference to Acorga M5774

Therefore, to minimise the copper losses as well as cost, the selection of the best extractant will be done on the basis of the extraction stage which is more critical. Figure 4.8 shows the plot of the additional benefit to additional cost ratio (R) against the hour of operation and a ratio greater than one implies that Lix 984NC is not just a better extractant than Acorga M5774 but also cost effective. Even though strip efficiencies of Lix 984NC are lower as compared to Acorga M5774, Lix 984NC reduces copper losses and increases the circulating load of the copper in the circuit, at least not to the tails. The figure also shows that after few minutes the ratio exceeds the value one and there after the ratio keeps on increasing each hour at a price of copper/kg given. The graph is sensitive to the copper price such that a small increase in metal price reduces the time at which the ratio R exceeds the value one. The price of metal changes now and again and that of the extractant is fairly constant over a long period of time.

Figure 4.9 also show the benefit cost appraisal of the two extractant at the same conditions but with strip efficiencies incorporated. It shows that despite Lix 984NC being good at extracting, Acorga M5774 strips more than Lix 984NC to an extent that the overall mass transfer into the electrowinning section is more when Acorga M5774 is used than when Lix 984NC is used. Therefore, it implies that Acorga M5774 give positive ratio which rapidly increases with time at a given copper price whilst Lix 984NC gives the same ratios but with the opposite sign. The conditions chosen for the calculation were those that gave higher extraction and strip efficiencies.

Figure 4.9 also seem to show that the benefits of using acorga M5774 are far much better than that of Lix 984NC but the prime purpose is to keep as much copper as possible out of the cobalt circuit into the copper circuit which can later on be transferred to the tank house to produce cathodes. Better still, no copper goes to the tails once in the copper circuit.

R vs hour of operatioin

R=Additional benefit/additional Cost

Legend:
- $0.50
- $2.00
- $3.50

pH=1.7
strip efficience
acorga=94.2
lix=81.1
extraction efficiecies;
Lix 984N=93.47%
acorga M5774=84.79%
Lix 984N=$11.14/Kg
Acorga M5774=$8.10/kg

X-axis: Hour
Y-axis: R
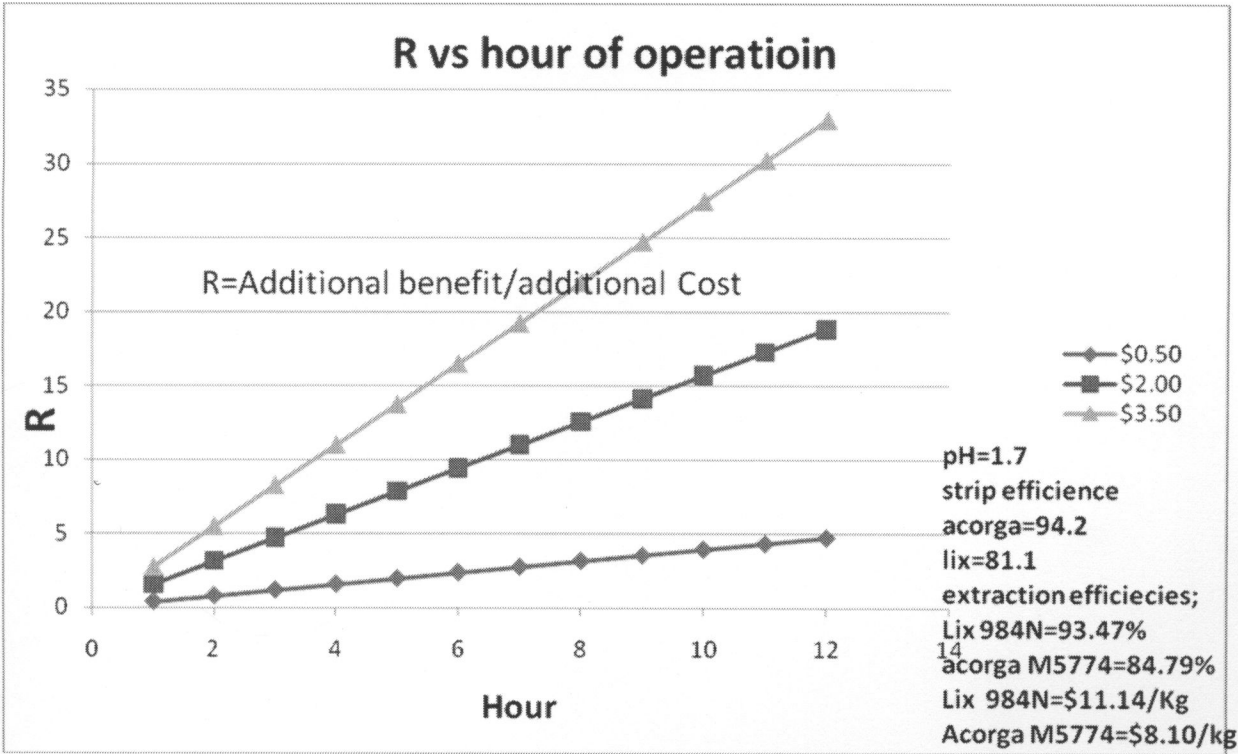
Figure 4.9 benefit cost appraisal of using Acorga M5774 in preference to Lix 984N

If we compare Figure 4.8 and Figure 4.9 which incorporates both extraction and stripping we see that the graph of extraction has higher ratios than that of the graph which incorporates both extraction and stripping. The above two figures (4.8 and 4.9) also show that it is more beneficial to use Lix 984N because of its higher ratios than it would be if stripping was to be incorporated in the selection basis.

The behaviour exhibited by Lix 984NC owes to the fact that it is a very strong copper extractant, so strong that it is always used in conjunction with an equilibrium modifier or with a ketoxime in order to increase the strip efficiency. The down side of Equilibrium modifiers is that they often increase crud formation and entrainment probably via hydrogen bonding to solids in the pregnant leach solution. They can increase or decrease oxime stability depending on the modifier.

5 Conclusion and Recommendations

5.1 conclusion

From the analysis shown in section 4, it is evident that solvent extraction as a very important by process in the purification of the cobalt metal requires careful consideration in the manner in which the extractant to be used is selected. Much attention should be paid to the manner in which the extractant extracts, the easy with which it is stripped and the cost.

Putting all these factors together, it has thus been concluded that despite Lix 984NC being more expensive in terms of price and having lower strip efficiencies than Acorga M5774, it has proved to be more cost effective and more cheaper in the long run. It also has the advantage of not just minimizing cost but also copper losses to the tails which is the sought metal in this by process.

5.2 Recommendations

Owing to the facts discussed above, I therefore recommend that Lix 984NC should at the moment continue to be used until at such a time when a better extractant is found which will have superior properties than it.

I further recommend that since Acorga M5774 is better at stripping than at extracting, the company should try to synergise the two extractant and see what effects this will bring.

I also recommend that further test works should be carried out to see the effect of selectivity of the two extractant on iron and other metals, crud formation and phase disengagement time should also be investigated.

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APPENDIX A1

Extraction results

Effect of phase ratio on extraction

O/A	A(ml)	O(ml)	Cu g/l in raffinate (lix)	Loaded org Cu g/l (lix)	Extraction efficiency % (lix)	Cu g/l in raffinate (acorga)	loaded org Cu g/l (acorga)	Extraction efficiency % (acorga)	
10	27	273	0.475	2.08	98.0	0.5	2.1	97.7	
5.0	50	250	0.80	3.79	96.3	1.0	4.1	95.3	
2.5	86	214	3.00	7.43	86.0	3.5	7.23	83.7	
2.0	100	200	4.0	8.75	81.4	5.0	8.25	76.7	
1.25	130	170	7.0	11.1	67.4	8.5	9.94	60.5	
1.0	150	150	8.5	13.0	60.46	11.0	10.5	48.8	
0.8	170	130	11.5	13.08	46.5	12.5	11.77	41.86	
0.5	200	100	14.0	15.0	43.9	15.5	12.0	27.9	
0.4	214	86	16.0	13.69	25.6	16.0	13.68	25.6	
0.2	250	50	19.0	12.5	11.6	19.0	12.5	11.6	
0.1	273	27	20.5	10.1	4.65	20.5	10.1	4.65	

Extractant conc 22%, extraction pH = 1.4, pregnant solution contain 21.5gpl CU

Table 1

Effect of reagent concentration

pH =1.87,   O/A = 2.5   pregnant solution = 23.0 g/l Cu

Lix %	Cu in raff g/l	% efficiency	Acorga %	Cu in raff g/l	% efficiency
10.0	11.5	50.0	10.0	13.5	41.3
12.5	8.0	65.2	12.5	12.2	46.96
15.0	6.5	71.7	15.0	11.0	52.2
17.5	5.5	76.1	17.5	10.5	54.35
20.0	4.0	82.6	20.0	9.5	58.7
22.5	3.5	84.8	22.5	8.0	65.2
25.0	2.2	90.4	25.0	7.0	69.6
27.5	2.2	90.4	27.5	6.5	71.7
30.0	2.0	91.3	30.0	5.5	76.1

Table 2

Effect of pH on extraction

O/A = 2.5,   pregnant solution = 23.0 gpl Cu   22% extractant concentration

pH	Extraction efficiency % (acorga)	Extraction efficiency % (lix)
0.44	54.3	75
0.61	58.7	79
0.66	60	80.4
0.76	67.39	81
0.79	70	82.61
0.86	74	84.78
0.95	75	84.78
1.01	77.4	85
1.14	78	86.96
1.46	80.5	90
1.48	81	91.3
1.7	84.78	92
1.96	85	93.47
2.3	86.96	93.47
2.32	87	93.47
2.5	84.78	95.65

Tables 3

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Tables used to plot the McCabe-Thiele diagrams

Cu g/l in raffinate (acorga)	loaded org Cu g/l (acorga)
0.5	2.1
1	4.1
3.5	7.23
5	8.25
8.5	9.94
11	10.5
15.5	12
19	12.5

Table 4

Cu g/l in raffinate (lix)	Loaded org Cu g/l (lix)
0.475	2.08
0.8	3.79
3	7.43
4	8.75
7	11.1
11.5	13.08
16	13.69
19	12.5

Table 5

STRIPPING RESULTS

Effect of acid concentration

O/A = 1.5

H$_2$SO$_4$ g/l	Cu in advance electrolyte g/l (acorga)	Strip efficiency % (acorga)	Cu in advance electrolyte g/l (lix)	Strip efficiency % (lix)	
140	11.5	79.7	9.5	56.9	
150	11.0	76.6	9.0	53.9	
160	12.0	83.6	10.5	62.9	
170	12.5	86.4	10.0	60.0	
180	13.0	89.9	10.0	60.0	
190	12.5	86.4	12.0	71.9	
200	12.5	86.4	11.0	65.9	
210			11.0	65.9	
Concentration of loaded organic	9.63 g/l		11.3 g/l		

Table 6

Effect of phase ratio

Acid concentration = 180 gpl

O/A	Cu g/l in advance electrolyte (lix)	Strip efficiency % (lix)	Cu g/l In advance electrolyte (acorga)	Strip efficiency % (acorga)
1.0	9.5	84.1	9.6	98.6
1.2	11.0	81.1	11.0	94.2
1.4	12.2	77.1	12.0	88.1
1.6	14.8	81.8	13.0	83.5
1.8	15.0	73.7	14.8	84.5

2.0	16.0	70.8	15.0	77.1
2.2	17.2	69.2	18.5	86.4
2.4			18.0	77.1
Cu in loaded organic	11.3 g/l			9.73 g/l

Table 7

Tables for cost benefit appraisal

Hour	$0.50	$2.00	$3.50
1	0.836749	3.346997	5.857245
2	1.673498	6.693994	11.71449
3	2.510248	10.04099	17.57173
4	3.346997	13.38799	23.42898
5	4.183746	16.73498	29.28622
6	5.020495	20.08198	35.14347
7	5.857245	23.42898	41.00071
8	6.693994	26.77598	46.85796
9	7.530743	30.12297	52.7152
10	8.367492	33.46997	58.57245
11	9.204242	36.81697	64.42969
12	10.04099	40.16396	70.28694

Table 8 for extraction only

Hour	$0.50	$2.00	$3.50
1	0.392155	1.568619	2.745084
2	0.78431	3.137239	5.490168
3	1.176465	4.705858	8.235252
4	1.568619	6.274478	10.98034
5	1.960774	7.843097	13.72542
6	2.352929	9.411717	16.4705
7	2.745084	10.98034	19.21559
8	3.137239	12.54896	21.96067
9	3.529394	14.11758	24.70576
10	3.921549	15.68619	27.45084
11	4.313704	17.25481	30.19592
12	4.705858	18.82343	32.94101

Table 9 for both extraction and stripping

APPENDIX A2

SAMPLE CALCULATION OF BENEFIT COST APPRAISAL OF USING LIX 984N IN PREFERENCE TO ACORGA M5774

Concentration of pregnant solution = 23g/l

Flow rate of organic solution = 380m^3/hr, **phase ratio** = 2.5, 22% extractant, **pH** = 1.7, **extraction efficiencies** for Lix 984N = 93.47%, Acorga M5774=84.79%

Basis; hour of operation

Volume of organic = 380m^3

Volume of aqueous = $V_o \times \frac{A}{O} = 380 \times \frac{1}{2.5} = 152$ m^3

Mass of Cu going in = $152 \times \frac{23}{0.001} = 3496000 kg$

Volume of extractant used = $0.22 \times 380 = 83.6$ m^3

Mass of Lix 984N used = $volume \times density = 83.6 \times 900 = 75240 kg$

Mass of Acorga M5774 = $volume \times density = 83.6 \times 970 = 81092 kg$

Cost of lix 984N used = $11.14 \times 75240 = US\ 838173.6$

Cost of Acorga M5774 used = $8.1 \times 81092 = US\ 656845.2$

Additional cost = $838173.6 - 656845.2 = US\ 181328.4$

Copper extracted by Lix 984N = $3496000 \times .9347 = 3267711.2 kg$

Copper extracted by Acorga M5774 = $3496000 \times 0.8479 = 2964258.4 kg$

Mass difference = $3267711.2 - 2964258.4 = 303452.8 kg$

Price of copper = U$ 3.50/kg (assumed)

Total Cu price = $3.50 \times 303.452.8 kg = US\ 1062084.8$

$$R = \frac{additional\ benefit}{additional\ cost} = \frac{1062084.8}{181328.4} = 5.86$$

This ratio is then plotted against time and increases with the same amount each hour.