INVESTIGATION OF ORGANIC LOSSES IN SOLVENT EXTRACTION CIRCUIT DUE TO SOLUBILITY/DEGRADATION

MD. ALI AZAM

INVESTIGATION OF ORGANIC LOSSES IN SOLVENT EXTRACTION CIRCUIT DUE TO SOLUBILITY/DEGRADATION.

BY

MD. ALI AZAM

A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING IN MECHANICAL ENGINEERING.

FACULTY OF ENGINEERING AND APPLIED SCIENCE

MEMORIAL UNIVERSITY OF NEWFOUNDLAND

JULY 2010

ST. JOHN'S, NL, CANADA

To the most respected and beloved Parents.........

Abstract

Solvent losses in a solvent extraction circuit are some of the most important issues. The losses of solvents may occur in a several ways in any solvent extraction process, which include solubility in the aqueous phase, entrainment, evaporation/volatilization, crud formation and degradation. To prevent the loss of the extractant during metal extraction process the solubility/degradation loss of different organophosphorus acidic extractant were investigated. Two types of extractant candidates such as Cyanex 272 (bis-2, 4, 4-trimethylpentylphosphinic acid) and D2EHPA (Di-(2-ethylhexyl) phosphoric acid) were examined. Sulphuric acid (H_2SO_4) was used in this experiment as an aqueous medium. Phosphorus (P) content in the aqueous phase was measured by inductively coupled plasma spectroscopy (ICP). Initial concentrations of phosphorus in all the reagents were measured before contacting with aqueous phase which acts as a baseline concentration of phosphorus. After contacting with organic phase the solution were transferred to the seperatory funnel for at least 24 hr to attain equilibrium and complete phase separation. The aqueous phase was separated and centrifuged to avoid any kind of entrained organic. To be more accurate SP1 filter paper was used before ICP analysis of the aqueous solution. Based on phosphorus content in the aqueous phase, the effect of different parameters such as acid concentration, extractant concentration, temperature, diluent concentration, metal concentration and impurity concentration were investigated. The kinetics study on the solubility/degradation was also investigated in this research at 25 °C and 50 °C.

Phosphorus in the aqueous phase might come due to the solubility or degradation or phosphorus dissolution of Cyanex 272 and D2EHPA. In order to ascertain the source of phosphorus a gas chromatographic (GC) analysis of the organic sample was performed followed by mass spectrometry (MS). Initially, gas chromatography of each reagent and solution were performed separately before and after contacting with acid. No degraded compound or material was found from the GC-MS analysis. By combining and analyzing the results from ICP-MS or GC-MS, the conclusion is that though there are some solvent losses in the aqueous phase due to the phosphorus dissolution, there is no degradation of Cyanex 272 and D2EHPA in the experimental condition that had been used.

Acknowledgement

The work reported in this paper has been carried out at the Hydrometallurgy Lab, at the Inco Innovation Centre (IIC), Memorial University of Newfoundland, during the period 2008-2010.

I would like to acknowledge my deep indebtedness to my research Supervisor and honorable teacher Dr. Shafiq Alam for his continuous guidance, constructive suggestions, sincere co-operation, and constant encouragement. I am also grateful to him for providing me with the opportunity to get the job done in a relatively independent manner. I am also grateful to Dr. Faisal Khan for his constructive suggestion.

The author gratefully acknowledges the financial supports from the Vale Inco and the ACOA (Atlantic Canada Opportunity Agency) in the form of an AIF grant.

Table of Contents

List of Tables

List of Figures

Nomenclature

A/O	Aqueous/Organic
Cyanex 272	Bis(2,4,4-trimethylpentyl)phosphinic acid.
Co	Cobalt
D2EHPA	Di (2-ethylhexyl)phosphoric acid
K	Kelvin
LIX 63	5,8-diethyl-7- hydroxydodecan-6-oxime
M	Molar
Mg	Magnesium
Mn	Manganese
Ni	Nickel
S930	Amacroporus polystyrene based chelating resin
SX	Solvent Extraction
TP 207	A premium grade weak acid (Ion exchange resin).
TBP	Tri butyl phosphate

Chapter 1

1 Introduction

1.1 Background

There are always some losses of solvent in any solvent extraction process, which is a big concern for any industry. Solvent losses issues play a very vital role on the process efficiency, plant output and environment. The losses of solvents in any solvent extraction process include solubility in the aqueous phase, entrainment, evaporation/volatilization, crud formation and degradation (Rydberg, et al., 1992). A brief description of these processes is given below:

Solubility in the aqueous phase

There are some losses of solvent in water as most solvent extraction reagents are inherently soluble in water to some extent. The conditions prevailing in the system can promote the solubility if the composition and properties of the aqueous phase are not favourable. Solubility depends on temperature, pH and salt concentration in the aqueous phase.

Increase in the temperature of the system can usually enhance the solubility of the solvent in the aqueous phase. The solubility of the polar components is slightly affected with different values of pH. With the increase of the concentration of salt, solubility of the solvent usually decreases because of salting effect (Cox, 2004).

Entrainment

Solvent losses due to entrainment occur in aqueous raffinate, in the strip liquor or in the cruds. Insufficient settling area or time allowed for phase disengagement, poorly designed or operated mixers, too much energy input into the mixing stage, lack of additives to suppress emulsion formation, poor diluent choice, and high extractant concentration in the solvent are responsible for entrainment losses (Cox, 2004).

Volatilization

Generally, solvent losses due to volatilization/evaporation occur when the process runs at high temperatures or in hot climates. Usually, one could expect the most volatile component to evaporate first, and that would probably be the diluent (Cox, 2004).

Crud

A stable mixture resulting from the agitation of an organic phase, an aqueous phase and fine solid particles is defined as the crud. Cruds are usually formed at the interface of the aqueous phase and organic phase and constitute a major solvent loss (Cox, 2004).

Degradation

Degradation of organic material produces organic compounds that alter the quality of the solvent and its effectiveness. Degradation can arise from various sources such as oxidizing properties of the aqueous phase, too high temperature of the system, aging and oxidation by atmospheric oxygen and general stability of the component over prolonged period of use (Cox, 2004). It can also arise from sources like high acidity, sunlight and bacteria (Ritcey, 2006). For the Cyanex 272, the increase in temperature and the presence of an oxidant contribute to the organic degradation (Parker Centre, 2002/2003).

Though solvent losses occur in several ways including solubility, entrainment, evaporation, crud and degradation, the objective of this study is to find out solvent losses due to solubility or degradation. During solvent extraction process poor selection of the appropriate phase ratio of aqueous/organic (A/O) can lead to solvent losses. For example, a higher A/O ratio is responsible for high solvent losses and a lower A/O is responsible for higher consumption of organics resulting in higher inventory costs (Hossain, 2010). The economic advantage of a solvent extraction process over other separation process for metals extraction can be lost if the loss of organic solvent from the process becomes excessive (Cox, 2004). The replacement/make up of organic solvent in a solvent extraction plant plays a significant role in operating cost. Though several factors cause losses in any solvent extraction process, the most significant of them is undoubtedly entrainment. Usually, the loss due to degradation encounters the loss of the extractant component rather than diluent, modifier (Whewell, et al., 1981). Not only the cost involved with extractant loss but there is also zero tolerance for organic transfer to electrowining circuit. If organic component transfers to the electrowining circuit, it may clog the anode bag, which will reduce the current efficiency (Ritcey, 1986). As a result, periodic cleaning of anode bag is necessary, which is a laborious job that also hampers the production operation. So, the solvent loss issue resulting from extractant solubility and/or degradation in this context has become an important issue to select the best solvent extractant.

Organophosphorus extractants are widely used for the extraction and separation of Ni/Co in hydrometallurgical processes. According to Flett, there are more than 40 reagents on offer for hydrometallurgical use and at least twelve of them are in everyday use. The summary of the available types of extractant and their potential application for hydrometallurgical use are given in the "Appendix," Table A1 (Flett, 2005). The extractant Cyanex 272 is a commercial extractant and its active component is bis-2,4,4-trimethylpentylphosphinic acid ($R_2P(O)OH$ where R= 2,4,4-trimethylpentyl group) . The active component is present at 85 – 87% in Cyanex 272 and it also contains trialkyl phosphine oxide impurity (R_3PO, 10- 12%) and the remaining 1-2% are unknown impurities(Sole, et al., 1993). The extractant D2EHPA Di (2-ethylhexyl)phosphoric acid (R_2POOH, Where, R = C_4H_9CH $(C_2H_5)CH_2O$-) is considered to be one of the universal metal extractant because of its extractability of the majority of metal ions (Singh, et al., 2009).

Any chemical reaction that destroys the functional group or that creates an antagonistic or negative catalytic impurity constitutes a degradation process. Both physical solubility and chemical stability can be responsible for solvent loss (Demopolous and Principe, 2003).

1.2 Objective of the Research Work

The foremost rationale of this research work was to investigate the causes of solvent losses in the liquid-liquid extraction process due to solubility or degradation. Two organophosphoric acids Cyanex 272 and D2EHPA were used in this investigation. The reason for the selection of these two solvents was that they were used in the Vale Inco's demonstration plant at Argentia, Newfoundland, Canada.

The organophosphoric acid Cyanex 272 and D2EHPA plays a very significant role in metal extraction process, especially in the nickel extraction process. Any kind of financial advantage of solvent extraction process will be ignored if organic losses become too excessive. In the present work, experiments were carried out to find the solubility/degradation losses by showing the effect of different parameters such as acid concentration, extractant concentration, temperature, diluent concentration, metal concentration and impurity concentration. The kinetic study at different temperatures on extractant degradation/solubility was also investigated.

1.3 Organization of the Thesis

This thesis has been organized as follows

Chapter 1 provides the key research introduction and objectives followed by the organization of thesis.

Chapter 2 provides a details literature review. The literature review starts with a broad point of view like mining, hydrometallurgy and has been narrowed down to solvent extraction and with elaborate description of organophosphorus extractants.

Chapter 3 describes the detailed experimental studies performed in this research with a brief description of the reagents.

Chapter 4 is the most important part of this thesis, which describes the research findings and presents elaborate discussion with comparison of the results of this study.

Chapter 5 describes the research conclusion along with the accomplishment of this work and future recommendations to continue this research.

Chapter 2

2 Literature Review

2.1 Literature Review of Mining and Hydrometallurgy

2.1.1 Mining

Mining is the extraction of metals or minerals from the earth. Generally, valuable minerals or other geological materials are extracted from an ore body, vein or seam. There are many materials, which are recovered by mining such as base metals (Copper, Zinc), precious metals (Gold), diamonds, limestone, oil shale, rock salt, etc. A material that is not possible to produce, created or grown through agricultural, in a laboratory, factory, or any other process is mined (Mining, 2010).

Extractive metallurgy is a specific area in the science of metallurgy that studies mainly the extraction of metals from ores through chemical or mechanical separations. Liberation of minerals from ores by crushing, grinding, and washing that enable the separations of metals is called mineral processing or mineral dressing. It is not possible to extract metal directly from an ore. Metals are usually present in the ore as sulphide or oxide. Metals are reduced in metallic form before separation by chemical means of smelting or through electrolytic reduction.

The Extractive metallurgical process deals with the extraction from ore to pure metal. The usual extractive metallurgical process involves mineral dressing, opening the ore, recovery, preparation of metal, and refining (Habashi, 1970). The schematic metallurgical process is given in Figure 2.1

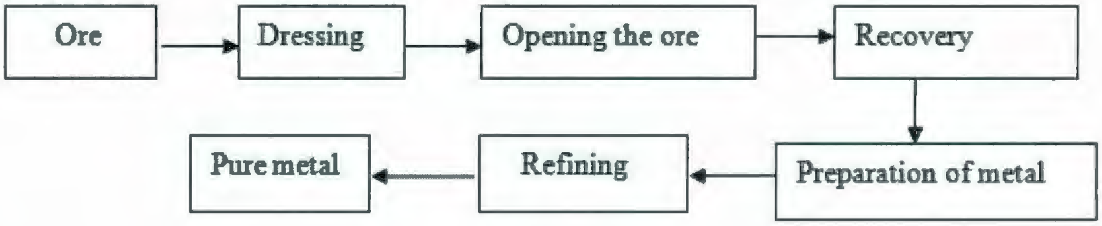


Figure 2.1: General Flow Sheet for Metal Extraction.

In a broad sense, extractive metallurgy can be divided into two groups, pyrometallurgy or dry process, and hydrometallurgy, or wet process. Dry process deals with high temperature and all the reaction completely involves solid material; sometimes melting takes place. Wet process or hydrometallurgy involves reaction in aqueous phases and the reaction usually takes place at low temperatures. Both processes have some advantages and disadvantages. Table 2.1 gives a general idea about the two processes (Habashi, 1970).

Table 2.1: Hydrometallurgical and Pyrometallurgical Processes (Habashi, 1970)

Hydrometallurgy	Pyrometallurgy
	Alkali fusion
Leaching	Roasting
Precipitation form leach solution	Reduction
Ion exchange	Chlorine metallurgy
Solvent extraction	Fluorine metallurgy
Electrolysis of aqueous solutions	Carbonyl metallurgy
	Electrolysis of fused salts

Sometimes metals are extracted by a combination of the two methods that depend on the chemical nature of the metal.

2.1.2 Hydrometallurgy

Hydrometallurgy deals with aqueous metal processing. Hydrometallurgy is a part of the extractive metallurgy. Like other parts of extractive metallurgy, it also deals with the separation process and oxidation-reduction processes (Peters, 1973). Hydrometallurgy is a process that involves aqueous solutions for metal extraction from ore, concentrates, natural or recycled resources and their subsequent recovery into useable products. It is environmentally friendly and cost effective process (Hydrometallurgy, 2010). Hydrometallurgy is generally divided into three broad categories. They are as follows:

a) Leaching

b) Solution concentration and purification

c) Metal recovery

Furnaces have been used for metal recovery from thousands of years ago. But after the invention of alchemist's acid and alkalies, people started using aqueous solutions for ore processing. At the end of 19th century when the cyanidation process for gold and silver extraction and Bayer process for bauxite treatment were discovered modern hydrometallurgy is traced from that time. The Manhattan project in the USA along with uranium extraction made a breakthrough in the later 1940s and made some replacement of the pyrometallurgical process. Now, day by day, it is progressing in its own way. The Canadians role is significant especially in the case of uranium, nickel, cobalt and zinc (Habashi, 2005).

Though the birth of hydrometallurgy can be traced back to 1887, it took a long time to get various leaching and recovery processes. Some of the processes were put into practice immediately, while others had to wait almost fifty years before going to the application stages, and the rest of them never developed beyond the pilot plant. The hydrometallurgical extraction of copper from ore and the precipitation of copper by treatment with metallic ion is an ancient technology (Henry, 2001). However, the hydrometallurgy of copper got significant attention at the beginning of the 20th century.

The First World War created a demand for zinc in order to serve the purpose of cartridge brass and eventually the industry of North America was inspired to provide the extra metal from ore. During the Second World War, when the technology for uranium production was introduced with a purpose to make atom bomb, various new techniques suddenly came into large scale production. At that time, many processes for precipitation from aqueous solution were used and many organic solvent was synthesized as an extractant for uranium. In the middle of the last century, pressure hydrometallurgy was introduced for leaching of different ores and for the direct precipitation of metal solution. This was a new addition to hydrometallurgy, and as a consequence Canadian coin were produced for over forty years using this technique (Habashi, 2005).

Before 1950, the commercial use of hydrometallurgy was limited to very few materials but after that the use of hydrometallurgy has changed dramatically (Burkin, 2001). In the later stage of the 1950s, INCO started a semi commercial plant for low grade ore treating but was shut down after running for a few years, being uneconomical beside the pollution problem associated with sulphur di-oxide exposed to the environment. After a decade, the role of bacteria in leaching was known and its extensive use for the copper extraction was practiced. Now, 20 percent of the world copper production is made by using hydrometallurgical technique. In the 1970s, the pressure leaching of for the extraction of zinc metal was applied industrially and in the 1980s the hydrometallurgical technique was used for the gold extraction. The brief summary of historical development of hydrometallurgical technique is given in the "Appendix", Table A2 (Habashi, 2005).

Advantages of hydrometallurgy (Habashi, 1970)

- Direct metal extraction is done through leaching e.g. precipitation with hydrogen under pressure, cementation or electrolysis in a pure form.
- By applying amalgam metallurgy process it is possible to produce high purity metal though the leach solutions are impure.
- By using hydrometallurgy the siliceous gangue during ore processing is unaffected by most leaching agents. But in the case of pyrometallurgical smelting process gangue material need to be slagged.
- Corrosion is very important in metallurgy. In the case of hydrometallurgy the corrosion problems are relatively less in many aspects like deterioration of refractory linings in furnaces and the number of periodic shutdown and replacement.

- A significant amount of energy is required in the pyrometallugical process. The consumption of fuel is very less in hydrometallurgy compare to the pyrometallurgy.

- Leaching product is easy and cheap to handle whereas handling of molten mattes, slags and metals are not so easy and cheap compared to the pyrometallurgy.

- Treatment of low grade ore is one of the important advantages of hydrometallurgy.

- To build one big furnaces is more economical than multiples small furnaces and for this reason in the case of pyrometallurgical process to design for a large scale production is almost mandatory. This problem can be overcome by using hydrometallurgy because it can be started on a small scale and then it can be expand as required.

- At present, environment is a big concern all over the world. In the case of pyrometallurgical process smelter pollute environment where as hydrometallurgy is an environmentally friendly technology.

2.2 Literature Review of Solvent Extraction and Its Application to Hydrometallurgy

2.2.1 Solvent Extraction

Solvent extraction or liquid–liquid extraction is a separation process used in many chemical processes. It has come to be one of the most important separation processes in hydrometallurgy.

Solvent extraction, specially, has come out to be the work horse of numerous processes because it has versatile and selective class of unit operations, which is used for the recovery and removal of a wide range of materials from both aqueous and organic solutions (Hatton, 2002). This technique is fast, environmentally sustainable, and can be used for diversified composition of solutions and is particularly useful when it is necessary to raise the level of upgrading material (Deep and Carvalho, 2008). Solvent extraction is cost effective, environmentally sound, opening new opportunities for simplicity and is proven to be a powerful tool (Bacon and Mihaylov, 2002).

Solvent extraction is being used in hydrometallurgical processes throughout the world for the processing of Cu, Ni, Co, Zn, U, Mo, W, V, Zr, Hf, Nb, Ta, rare earths, Ga, Ge, and the platinum group metals (Flett, 2005). It is also used in the reprocessing of nuclear fuel, for the recovery of nitric acid and for the purification of wet process phosphoric acid. The application of solvent extraction in hydrometallurgy began in 1942 in the Manhattan project, for the recovery and purification of uranium from nitric acid solution, ether was used as a solvent extracting agent in that project. Alkyl amines and di(2-ethylhexyl) phosphoric acid (D2EHPA) extractants were used for the processing of uranium ore in the 1950s and in this way the phosphorus based extractants are established in the solvent extraction history. In the 1960s, when General Mills Inc. developed hydroxyoxime extractants, the solvent extraction process spreads into more exotic material like Zr/Hf and Nb/Ta. The application of hydroxyoxime extractant used for the recovery of copper added a new dimension in the use of solvent extraction process.

2.2.2 Chemistry of Solvent Extraction

An organic solution is composed of several components. The components to be considered are the extractant, the diluent, the accelerator and the modifier. The extractant is the organic chemical reagent that forms an organic soluble complex with the metal ion in aqueous solutions. During solvent extraction, the organic reagent acts as the convenient shuttle bus between two aqueous phases (Mihaylov, 2009). The diluent is an organic solvent that is used to dilute the extractant concentration to the appropriate level for metal extraction and stripping. An accelerator is added when the kinetics are too slow. A modifier is used to improve the chemical or physical performance (settling behaviour) of the solvent extraction system.

2.2.2.1 Extractant Chemistry

An extractant employed in any commercial separations of metal should have good features. Unfortunately, it is unlikely that any one extractant can meet these sometimes conflicting criteria. Here, some of the features of the extractant are given after Hudson (Hudson, 1982).

- The ability to extract metal at the required pH level.
- To be selective for the required metal and to reject undesired metals.
- High loading (High distribution coefficient)
- To have acceptable rates of extraction, scrubbing and stripping (rapid kinetics).
- To be soluble in the organic phase and to have a limited solubility in the aqueous phase.
- Easy retrieval of the solute.
- Rapid phase separation.
- To be stable throughout the three principal stages of solvent extraction (extraction, scrubbing and stripping.)
- Availability at reasonable price from commercial sources.
- Safety and environment friendliness.

Extractants usually used in the solvent extraction process can be divided into acid extractants, basic extractants, and solvating extractants.

Acidic Extractants

Acidic extractant react with metal cation with suitable anions to form an uncharged species. Organic acids of the sulphonic, phosphoric and carboxyl acid type are used as acidic extractant. The available commercial acidic extractant reagents are given in "Appendix," Table A3 and Table A4 (Cox, 2004).

Basic Extractants

Basic extractant consists of a series of amine extractants, which are used for the extraction of the anionic metal species. High molecular weight amines that are organophilic weak bases are used for solvent extraction. For metal extraction, a certain pH is needed to be maintained for primary, secondary or tertiary amines (Seikine and Hasegawa, 1932). The commercially available basic extractants are given in "Appendix," Table A5 (Cox, 2004).

Solvating Extractants

Generally, neutral metal species are extracted by solvating extractant. Examples include $FeCl_3$ extraction by tributyl phosphate (TBP) and $UO_2\ (NO_3)_2$ extraction with tri–iso-octyl phosphine oxide . Commercially, available some of the solvating extractants are given in "Appendix," Table A6 (Cox, 2004).

2.2.2.2 Diluents

Diluents are organic solutions with no metal extracting ability which dilute the extractant to an appropriate concentration, density and viscosity for metal extraction and stripping. Though most extractant require diluent, some of them are used in full strength. The diluent is usually a combination of aliphatic and aromatic hydrocarbons. An aliphatic diluent has some good criteria which provides better extraction, good separation factor, faster equilibrium and ease of phase separation which makes it preferable over aromatic diluent (Mohapatra, et al., 2007). For example, in copper extraction with hydroxyoxime the rates of extraction are faster in aliphatic diluents but the meal extraction complex has a limited solubility. Aromatic diluents produce slower rates of extraction but have a higher solubility for the complex. In this research Escaid 110 aliphatic kerosene was used as diluent.

2.2.2.3 Modifier

Modifier is additional organic species which is added to solvent to improve its properties. Two examples include increasing the solubility of the meal extractant complex or enhancing the phase separation rates. For example, in the separation of cobalt with D2EHPA, the metal extractant complex becomes insoluble as metal loading increase due to the polymerization of cobalt–D2EHPA complex. Addition of 2-5 % TBP suppresses the formation of the third phase (the insoluble complex). Choice of diluent and modifier will influence the selectivity of the extraction. The selectivity of the extraction can either be enhanced or depressed. In this study 1-Decanol was used as a modifier.

2.2.2.4 Accelerator

Accelerator or catalysts are often added to speed up the rate of transfer. Typically the accelerators are week extractants and their metal extraction rate is very quick. Accelerator form complex with metal and when they arrive in the organic solution, the metal is transferred to the main extractant. Some accelerators which are used for the extraction of copper are given in the "Appendix," Table A7 (Hudson, 1982).

2.3 Literature Review of Organophosphorus Extractants

Organophosphorus extractants cover a significant part among acidic extractants used in the separation process of hydrometallurgy. Phosphorus based extractants have proven to be the reagent of choice especially for the separation of cobalt from nickel. The development of the Cyanex range of reagents, as well as their industrial application is described in this section with flow sheets. In the western hemisphere, around forty percent of the cobalt is produced by using this solvent extraction reagent, including plants throughout Europe, South America, Canada, Africa, China and Australia (Cyanex, 2010).

Phosphine (PH_3) is the first step for the Cyanex range reactants, which has been produced since 1970 by the Cytec Industries Inc. using the technique of conversion of phosphorus via acid process. The commercial production of PH_3, opens up the way for the production of the whole range of Cyanex derivatives. According to Rickleton , the whole range of Cyanex is produced by acid catalyzed addition of phosphine to an aldehyde or free radical addition to olefin (Rickelton, 1996). The reaction of phosphine oxide productions are given below:

$3C_8H_{16} + PH_3 \longrightarrow (C_8H_{17})_3 P$..2.1

$(C_8H_{17})_3 P + H_2O_2 \longrightarrow (C_8H_{17})_3 P (O) + H_2O$..2.2

In the above two reactions, octane reacts with phosphine to produce octayl phosphine.

Octayl phosphine reacts with hydrogen peroxide to produce phosphine oxide.

The use of sterically hindered olefins such as 2,4,4-trimethyl-1-pentene and/or operating the reaction at higher pressure (4 MPa) is favourable for the formation of mono and dialkyl phosphine oxides i.e. $(C_nH_{2n+1})_2POH$.

Mono-dialkyl phosphine derivative mixtures react with hydrogen peroxide to produce phosphinic acid. During the production process, mono acid is removed by caustic scrubbing and the major impurity in the dialkyl phosphinic acid is the corresponding trialkyl phosphine oxide. By treating the dialkyl phosphine derivatives with elemental sulphur and sodium hydroxide the thio analogues of the phosphinic acids can be made. At first, sodium salts are produced and it is converted to acid with reaction with mineral acid. The range of Cyanex solvent extraction reagents are given in the Table 2.2 (Flett, 2005).

Table 2.2: Cyanex Range Extractants.

Cyanex Extractant	Chemical Formula	Use
272	$(C_8H_{17})_2P(O)OH$	Co, Zn and rare earth separation.
301	$(C_8H_{17})_2$ P(S)SH	Extraction of many heavy metals from alkali and alkaline earth metals and manganese.
302	$(C_8H_{17})_2$ P(S)OH	Cyanex 302 acts like Cyanex 272 but the main advantage is extraction takes place at lower pH and Co is separated from Mn.
921	$(C_8H_{17})_3PO$	Recovery of uranium from wet-process phosphoric acid and recovery of acetic acid.
923	R_3PO	Carboxylic acids, phenol and ethanol are recovered from effluent streams, separation and removal of Nb , As, Sb, Bi.
471X	$(C_4H_9)_3PS$	Extraction of Hg, Au and recovery of Ag.

The extraction of metal by acid is done by a cation exchange mechanism. The mechanism is described in equation 2.3.

$$M_{aq}^{p+} + (p + x)(RH)_{org} \longrightarrow (MR_p.\ xRH)_o + pH_a^{+} \qquad 2.3$$

Where M^{p+} is a p-valent metal cation, RH is organic acid and the subscripts 'aq' and 'org' represent aqueous and the organic phase respectively.

Cyanex 272 is one of the well known Cyanex range reagents of Cytec Industries Inc. and has been specifically developed for separation of Cobalt from Nickel. The problem of separation and recovery of Cobalt from nickel sulphate solutions has been overcome by the invention of Cyanex 272. The basis of solvent extraction from the sulphate solution is that nickel does not form sulphato complexes. The commercial operations by Falconbridge Nikkelwerk in Norway, Eramet in France and Summitomo in Japan are based on that knowledge (Flett, and Anthony, 1998). The selectivity of Ni(II) over Co(II) show the marginal selectivity for commercially available extractants like carboxylic acids, hydroxyoximes and β-diketones. The separation of cobalt from nickel in weakly acid sulphate solutions problem remained unsolved until it was realized that the separation factor for cobalt over nickel is a complex function of temperature, cobalt concentration, diluent, modifier and acid type for alkyl phosphorus acids (Flett and West, 1978; Preston, 1982). The order of separation factor is

Phosphinic acids > Phosphonic > Phosphoric

In a specific condition such as 0.1M extractant in shell MSB 210, metal ion concentration $2*10^{-2}$M , temperature 25 °C, pH 4 and a phase volume ratio (1:1), the separation factor comparison for acid alkyl phosphorus extractants are given in Table 2.3.

Table 2.3: Separation Factor Comparison of Cyanex Range Extractants.

Extractant	Type	Co/Ni Separation factor
D2EHPA	Alkyl phosphoric acid	14
PC 88A	Alkyl phosphoric acid	280
Cyanex 272	Alkyl phosphine acid	7000

The stability of the extractant during solvent extraction is an important factor. The presence of degradation product during solvent extraction causes a significant reduction in separation factor and poor phase break. Degradation products may come from the degradation of diluent, modifier or extractant. In South Africa at Rustenburg refiners, at first, D2EHPA was used for the extraction of cobalt in cobalt extraction circuit. But the presence of carboxylic acid in the organic phase was made a concern and it was figured out that cobalt acts as an oxidizing agent to oxidize diluent. In the conversion of the diluent to the corresponding carboxylic acid, the octahedral form of the cobalt complex is found as catalysis. Though this problem was minimized by introducing phenolic antioxidants but other extractants were also. Finally, the study was concluded saying that the solvent Cyanex 272 was more resistant than other solvents. Cobalt catalysed diluent oxidation was further studied by Rickelton, et al., (1991) , where tetradecane was used as the model diluent and the suggested oxidative degradation mechanism steps were as follows:

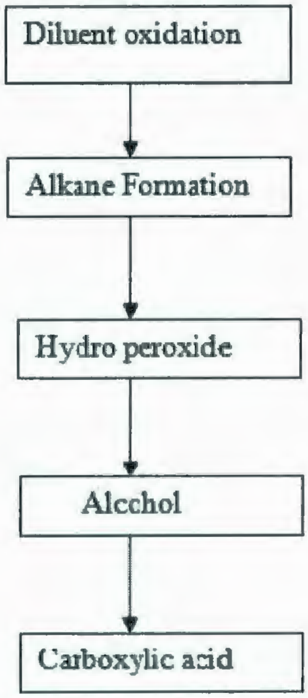


Figure 2.2: Oxidative Degradation Mechanism of Diluent.

Vale Inco, the world's second largest mining company, has chosen Cyanex 272 as a choice of reagent for their Voisey's Bay project. Metals are extracted from nickel sulphide ore in this project. The process starts by atmospheric chlorine leaching of the nickel-cobalt concentrate followed by a pressure oxygen leach. The leach residue is separated from the leach liquor and by removing Cu, Co, Zn and other impurities; leach liquor is purified before sending to the electrowining section, where Ni metal is produced in the Ni Cathode in a chloride electrolyte media. The process flow sheet is given in Figure 2.3 (Flett, 2005). The presence of chloride media helps by being an obstacle to the oxidation of the sulphide sulphur beyond the elemental sulphur. For this reason, elemental sulphur is obtained in the leach residue. Iron precipitates with lime to form gypsum, which actually helps to control excess sulphate. The nickel anolyte from the nickel electrowining section is recycled back to both atmospheric acid chlorine leach step and the oxygen pressure leach step.

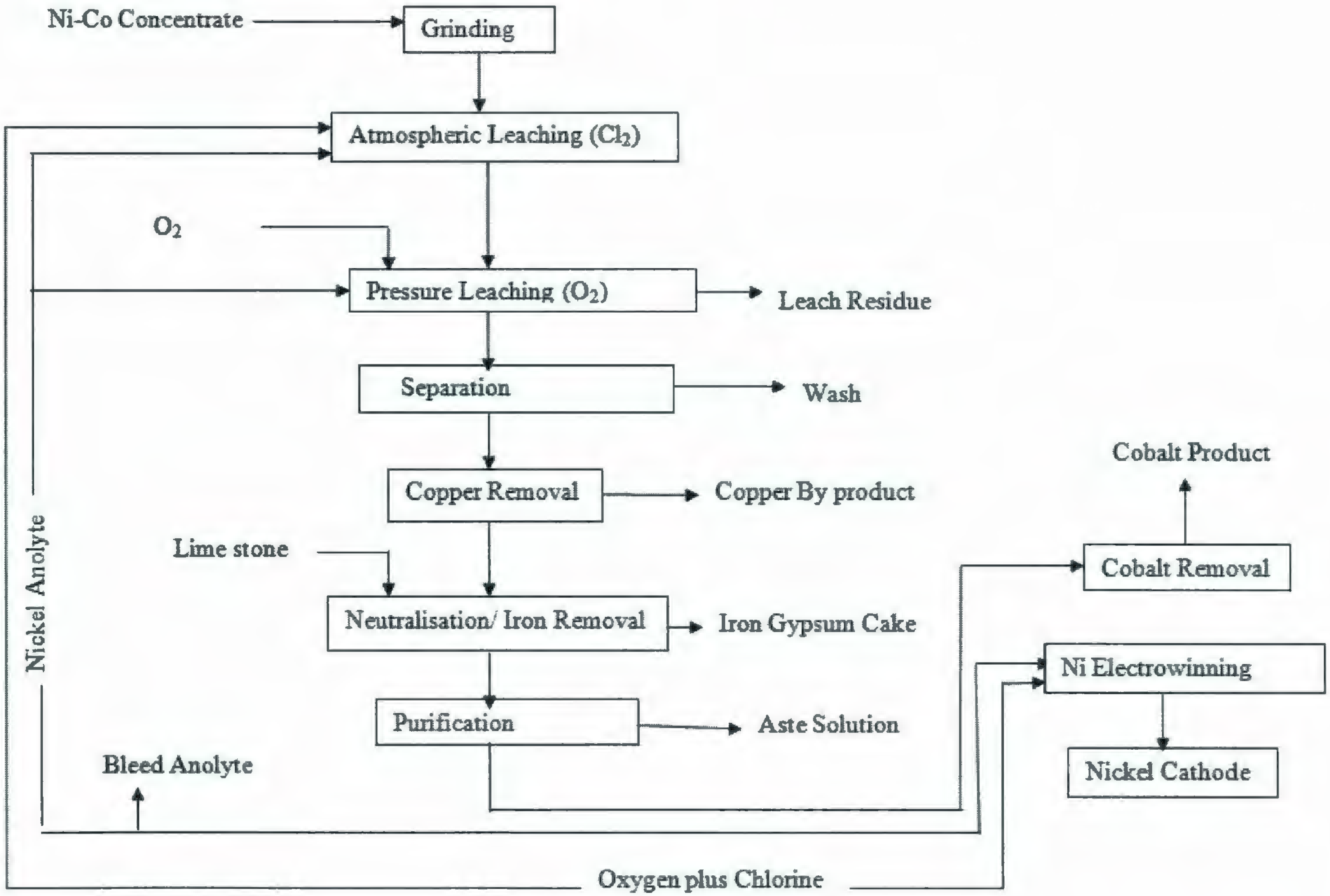


Figure 2.3: Process Flow sheet for INCO's Voiseys Bay Project.

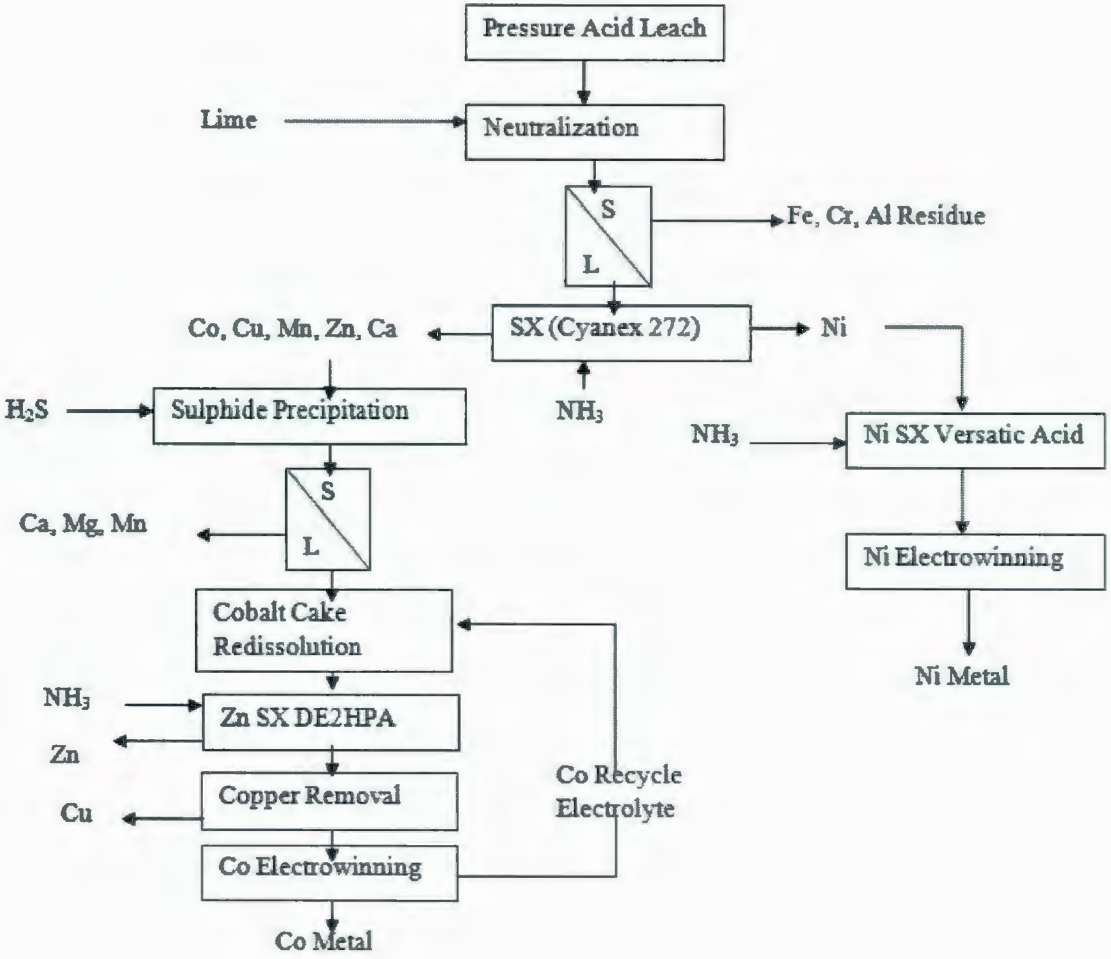


Figure 2.4: Bulong Process Flow sheet.

In the Bulong process (Figure 2.3) in Australia, after leaching the leach liquor is neutralized with lime to precipitate Fe, Cr and Al. After removing the leach residue the leach liquor is contacted with Cyanex 272 to remove Co, Cu, Mn, Zn, and Ca and maximize the nickel rejection. Tri butyl Phosphate (TBP) is also used with Cyanex 272 to inhibit third phase formation. By using carboxylic acid, e.g. versatic 10, nickel is extracted from the raffinate and Ca, Mg are scrubbed using the loaded strip solution and reported to the raffinate. Before electrowining, stripping of nickel is finally done by the recycled electrolyte from the nickel electrowining section. Co-extracted impurities are removed from the cobalt circuit initially by the sulphide precipitation of cobalt, copper and zinc from the loaded strip liquor. Then the sulphide cake is redissolved in acid and Zn is extracted with D2EHPA. The problem is that the Bulong process includes the possibility of cross contamination of the reagents. While DE2HPA was for the removal of Zn followed by cobalt SX with Cyanex 272 the possibility of contamination arises at that time. For this reason it is better to use Cyanex 272 for the selective removal of zinc from cobalt which has been adopted in the Murrin Murrin plant in Western Australia.

The Murrin Murrin process flow sheet is given in Figure 2.5 (Flett, 2005). In this process, following neutralisation with calcrete, sulphide precipitation is used to recover nickel and cobalt effectively from manganese and magnesium. Manganese is rejected effectively at 90 °C by sulphide precipitation.

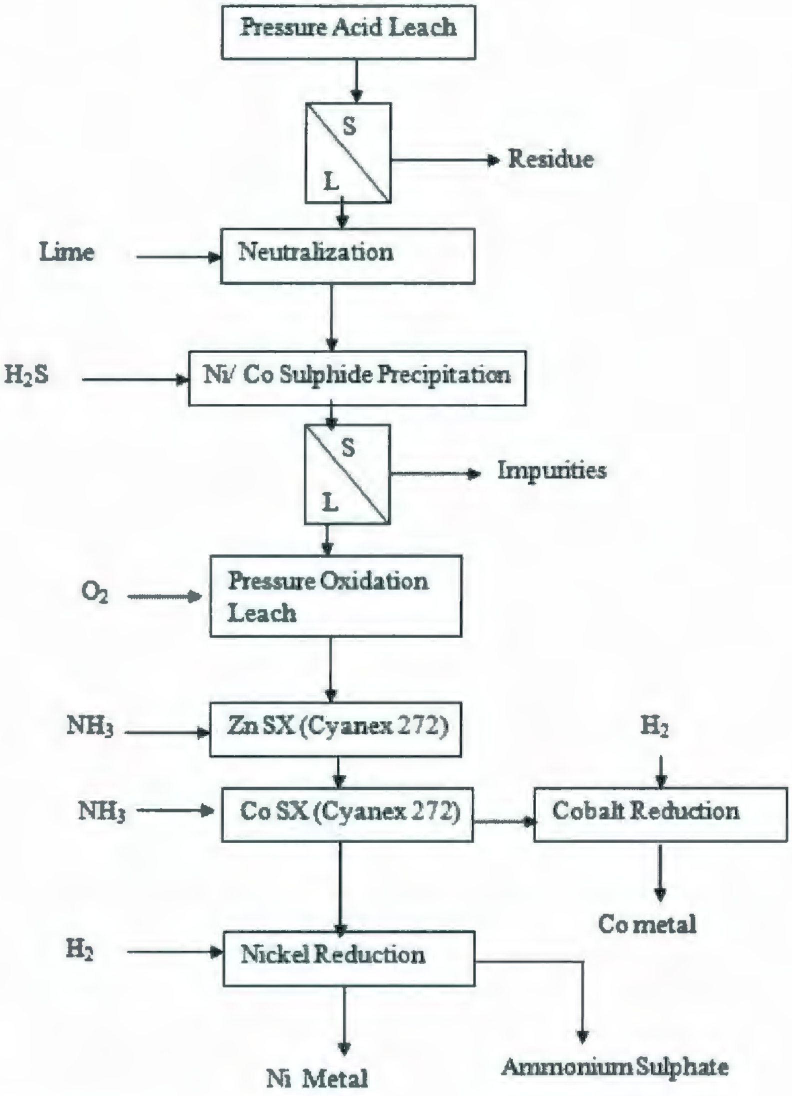


Figure 2.5: Murin Murin Process.

The sulphide is pressure leached and, using Cyanex 272 as the extractant, cobalt is separated from nickel by solvent extraction. The strip liquor and raffinate nickel are separated by pressure hydrogen reduction process.

An important comparison can be made between the Bulong process and the Murrin Murrin process, which is given in Table 2.4.

Table 2.4: Comparison of Bulong and Murrin Murrin Process.

Bulong Process	Murrin Murrin Process
Nickel is recovered by the electrowinning.	Nickel is recovered by Hydrogen pressure reduction.
Co-Extraction circuit is mainly an impurity removal step with a purpose to provide pure nickel stream to the nickel electrowinning section.	Small amount of cobalt in the nickel feed does not affect the quality of nickel powder produced.
Cyanex 272 plant is run to maximise the recovery of cobalt.	Cyanex 272 circuit is run to minimize the amount of nickel to the cobalt strip.

D2EHPA is usually used in commercial plants for extraction and separation of rare earth metals. Other reagents like Ionquest 807 and P507 are also used for this purpose. Though in some cases Cyanex 272 exhibits higher selectivity than its phosphoric and phosphinic counterparts, it has not been used commercially. This is due to the lower loading capabilities and distribution coefficient of Cyanex 272 than alkyl phosphoric or phosphinic acid. But for the heavy rare earth metals, the synergistic mixtures of phosphonic acids and Cyanex 272 provides better distribution, loading and separation factors and also better stripping performances. By using mixture of Cyanex 272, hundred percent stripping of heavy rare earth metal is possible with only 4M hydrochloric acid, whereas using their own acid it requires 6M hydrochloric acid. If HNO_3 is applied for the stripping purpose, then it stripps only 80% of metals. In this way neutralizing cost and chloride contamination of the final product can be minimized by applying a mixture of phosphonic acid and Cyanex 272.

The another di thio analogue of Cyanex 272 has been commercially used for the bulk extraction of nickel and cobalt in INCO's Goro project in New Caledonia. Cyanex 301 is mainly developed for the recovery of zinc but it requires strong sulphuric acid for complete stripping. Cyanex 301 can extract both Co and Ni at a much lower pH than the Cyanex 272. Though the separation factor of Co over Ni is not so good, it can be used for the bulk extraction of Co and Ni and also their separation from Mn, Ca and Mg with less neutralization of leach liquor. However, Cyanex 301 is not stable and decomposes in two steps. The first step is reversible, where formation of disulphide occurs, and the second step is irreversible, where disulphide decomposes to elemental sulphur and Cyanex 272 (Flett, 2005).

The two most important solvating solvent extraction reagents are Cyanex 921 and Cyanex 923. Both of the extractions possess potential in a large range of applications (Cyanex, 2010). The most important applications are the recovery of acetic acid from effluents, recovery of uranium from wet process phosphoric acid and for the treatment of rare earth materials. Particularly, Cyanex 923 is useful for the extraction of rare earth metals from nitrate solutions, and a systematic study about this has already been published.

The commercial application of Cyanex 923 used in Norsk Hydro's Odda process has been discussed Al-shawi et al., (2002). Though Cyanex 923 has a wide range of potential applications Cyanex 921 has some advantage over Cyanex 923 in the case of recovery of acetic acid. The advantages include low solubility losses, high stability during distillation at high temperatures and high extraction coefficient.

The solvating solvent extraction reagent is Cyanex 471, which is based on soft Lewis base. It is an analogue of tributyl phosphine oxide. According to the HSAB principle, it will make complex with metal and exhibit the characteristics of the Lewis acids. Large ionic radius, low oxidation state and ease to be polarized are the specific characteristics of Cyanex 471. The metals that fail those specific criteria are Pd (II), Pt (II), Ag (I), Cd (II), Hg (I), Hg (II) and Au (III). Particularly, the commercial application of Cyanex 471 is in silver recovery. The extraction of silver from chloride solutions by Cyanex 471 has been discussed by Abe and Flett, which showed the higher selectivity from cupric copper rather than cuprous copper (Abe & Flett, 1992). Though the commercial application of palladium by Cyanex 471 has much improved kinetics compared to the dialkyl sulphides, the commercial application of Cyanex 471 has thus far been is so far hindered due to the low solubility of the Pd- Cyanex 471 complex.

2.4 Literature Review of Chemical Analysis Device

Two types of chemical analysis tools were used in this study to analyze the research findings, inductively coupled plasma mass spectrometry (ICP-MS) and gas chromatography-mass spectrometry (GC-MS). A brief description of this chemical analysis devices are given below:

2.4.1 Chemical Analysis by ICP-MS

In this study, for the analysis of the experimental result, ICP-MS device was used. ICP-MS is highly sensitive and capable of determining a range of metals and several non metals. The ion producing ICP and a mass spectrometer are coupled together in this device. It is capable of trace multi element analysis in very lower level, sometimes parts per trillion (10^{12}), concentration level (ICP-MS, 2010).

An inductively coupled plasma-emission spectrometry (ICP) device contains a source that generates and emits high energy plasma. This high energy source is used to excite the atoms in the sample to levels above their ground states. The temperature is so high in plasma state (10,000K) that a significant portion of atoms of many chemical elements are ionized. Finally, every atom loses its loosely bonded electron to form ions. The ions are extracted through a series of cones into a mass spectrometer. On the basis of their mass to charge ratio, the ions are separated and, in proportion to the concentration, the detector receives a signal (ICP Details, 2010)

The ICP-MS device can be described with main five parts. Those are

a) Sample introduction and aerosol generation

b) Ionization by an argon plasma source

c) ICP – MS interface

d) Mass spectrometer

e) Detection system

The schematic diagram and description of an ICP-MS device are given in Figure 2.6 (Description of ICP, 2010)

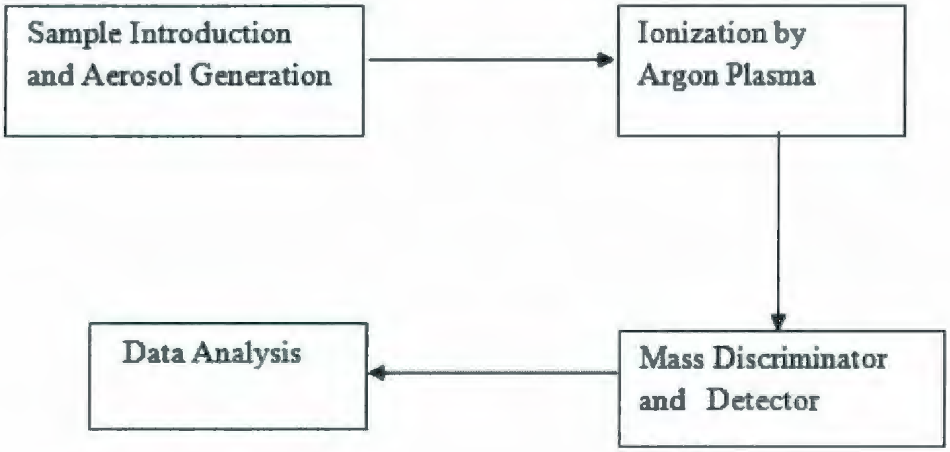


Figure 2.6: Schematic of ICP-MS.

Sample introduction and aerosol generation

The Sample introduction system consists of the peristaltic pump, nebulizer and spray chamber, and provides the means of getting samples into the instrument. It can accept both liquid and solid samples for analysis. There are different approaches for the sample introduction system, and the basic guidelines to select the best sample introduction system according to the sample particularities are discussed by Todoli & Mermet (Todoli and Mermet (2006). Usually, samples are introduced by a nebulizer where aerosol is produced. The droplets then pass through a spray chamber that eliminates all droplets except those that are the right size and velocity for introduction into the plasma.

Ionization by an argon plasma source

When the sample passes through the nebulizer and is partially desolvated, it moves into the torch body and the sample mixes with more argon gasses where plasma is generated. Beuchemin and Craig discussed that instead of only using argon, the mixture of nitrogen – argon plasma may be a better source (Beuchemin and Craig, 1991). The plasma into the torch creates a very hot zone that serves a variety of purpose. During the samples voyage into the plasma, the liquid droplets containing the sample matrix and the elements to be determined are dried to a solid and then heated to a gas. As the atoms travel through the plasma, they absorb more energy from the plasma and eventually release one electron to form a singly charged ion. The singly charged ions exit the plasma and enter the interface region.

ICP MS interface

The plasma operates at atmospheric pressure, but for the MS system it requires vacuum. The interface allows the plasma and the ion lens system to coexist and the ions generated by the plasma to pass into the ion lens region. The interface consists of two inverted funnel-like devices called cones. The sampler cone is located next to the plasma and the skimmer cone is located several millimetres behind the sampler cone. Each cone has an opening of approximately one-millimetre in diameter at the apex that permits the ions to pass through. In order to most efficiently reduce the pressure several pumps are typically used to gradually reduce pressure to 10^{-5} mbar before the ion stream reaches the quadrupole.

Mass Spectrometer

In the mass spectrometer, the ions are initially removed from the plasma and the produced ion beams are focused to the actual unit. A mass analyzer is used to separate isotopes based on their mass to charge ration.

Detection System

The ions exiting the mass spectrometer strike the active surface of the detector and generate a measurable electronic signal. The active surface of the detector, known as a dynode, releases an electron each time an ion strikes it. By counting the pulses generated by the detector, the system counts the ions that hit the first dynode.

Data Measurement Procedure by ICP-MS

To measure the metal concentration in the aqueous solution water sample protocol was used in this study. The procedure is given below

- Count per second (CPS) was measured based on the standard solution.
- Typical sample sequence had five standard solutions followed by blank count, and unknown given sample.
- By using sensitivity of the calibration from the repeated measurement, the concentration of elements in parts per billion (ppb) in the sample was calculated. The sensitivity is defined as CPS/ppb.

- Before further processing, all the counts are averaged and subtracted from the calibration banks.

- Drift was monitored from the internal standard elements like scandium (Sc), indium (In), rhodium (Rh) and corrected for the measurements. Finally, The dilution factor was used to calculate original sample concentration.

2.4.2 Chemical Analysis by GC-MS

The instrument used in this study, to find whether degraded substance exists or not in the test sample, gas chromatography- mass spectrometry (GC-MS) device. GC-MS is an effective instrument which separates chemical mixtures (GC), identifies the compound in molecular level (MS) and provides a representative spectral output. These two components, used together, allow a much finer degree of substance identification than their separate use. By using either gas chromatography or mass spectrometry it is not possible to make an accurate identification of a particular molecule. But the application area of GC is not wide, as the molecules used for GC should be thermally stable and sufficiently volatile (Kaal and Janssen, 2008). A detailed description and a schematic diagram of a GC-MS are described below (GC-MS, 2010). The primary component of a GC includes:

a) Injection port and mobile phase

b) Column

c) Detector

d) Data acquisition system.

Injection port and mobile phase

Mobile phase or the carrier gas is introduced into the injection port where the samples are transformed into gaseous phase. Different types of gas such as argon, helium, hydrogen, nitrogen, or are used as a carrier gas. When gas is chosen the important point to keep in mind that it does not react with the sample or column (Carrier gas, 2010). Many analysts use helium because it does not react. Hydrogen usually is a good carrier gas but it may react and convert the sample into another substance. The ultimate choice for a carrier gas may depend on the type of detector used.

Column

The column is a metal tube, often packed with a sand-like material to promote maximum separation. Capillary columns vary in length from 15 to 100 meters with a diameter ranging between 0.15 – 0.20 millimetres in coiled configuration. As the sample travel through the column, the difference in the chemical properties between different molecules in a mixture will separate the molecules.

Detector

Mass spectrometer is the most common type detector used in the chromatographic system. When molecules from the column come out, it takes some time to allow mass spectrometer downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass to charge ratio.

Data acquisition system

Two basic components together perform data acquisition. The first component amplifies and converts the analog signal from the instrument's detector into digital data. The second component that receives the digitized signal is generally a computer, loaded with a suitable software program. To identify a compound, the computer looks for a match between the results of analysis of the compound and mass spectral data stored in a library.

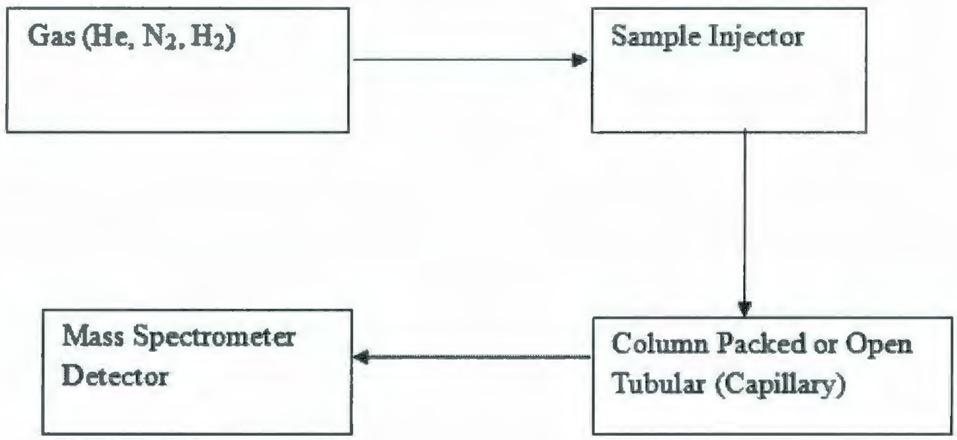


Figure 2.7: GC-MS Schematic.

Chapter 3

3 Experimental Details

3.1 Reagents

3.1.1 Extractant 1

Commercial Name: Cyanex 272

Chemical Name: Bis-2,4,4-trimethylpentylphosphinic acid

Chemical Formula: $C_{16}H_{35}PO_2$

Structural Formula:

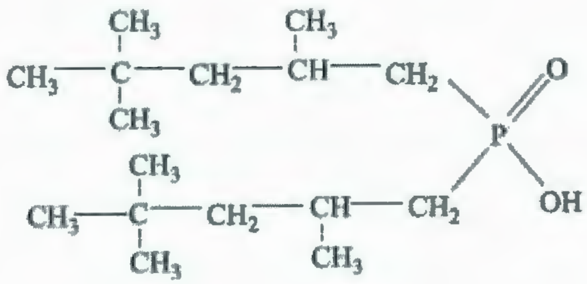


Figure 3.1: Structural Formula of Cyanex 272.

Manufacturer: Cytec Industries Inc.

The extractant, Cyanex 272, is a proprietary but technical grade item of Cytec Industries Inc. (CCI). Its active component is bis-2,4,4-trimethylpentylphosphinic acid. Cyanex 272 extractant has proven to be the reagent of choice for the separation of cobalt from nickel from both sulphate and chloride media. It is totally miscible with common aromatic and aliphatic diluents, and is extremely stable to both heat and hydrolysis. The chemical and physical properties of Cyanex 272 are given in the "Appendix," Table A3 (Technical brochure of Cyanex 272, 2008).

3.1.2 Extractant 2

Commercial Name: D2EHPA

Chemical Name: Di (2-ethylhexyl)phosphoric acid

Chemical Formula: $(C_8H_{17})_2PO_2H$

Chemical Structure:

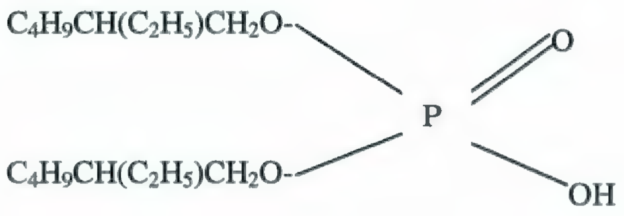


Figure 3.2: Structural Formula of D2EHPA.

Manufacturer: Alfa Aesar

The extractant, D2EHPA is a technical grade (100%) item of Alfa Aesar, A Johnson Mathey Company. It is an effective extractant, which is enormously used in hydrometallurgical processes for separation and purification of divalent transition metals such as copper, cobalt, manganese, and zinc (Flett and Spink, 1976; Sekine and

Hasegawa, 1977; Sato, et al., 1978). In nickel extraction process, it is widely used to remove cobalt. The chemical and physical properties of D2EHPA are given in the "Appendix," Table A4 (D2EHPA, 2010).

3.1.3 Modifier

Chemical Name: Decanol-1-ol

Chemical Formula: $CH_3\ (CH_2)_9OH$

Chemical Structure: $CH_3\text{-}CH_2\text{-}CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ OH$

Manufacturer: Alfa Aesar

1-Decanol is a straight chain fatty alcohol with ten carbon atoms, is colorless viscous liquid and has strong order. It is used as a modifier in the solvent extraction process in order to increase the solubility of the metal extraction complex or enhancing the phase separation rates. The physical and chemical properties of 1-Decanol are given in "Appendix," Table A5 (Decanol, 2010).

3.1.4 Diluent

Commercial Name: Escaid 110

Chemical Name: Hydrocarbon, n-alkanes

Chemical Formula: $(C_{11}\text{-}C14)$

Manufacturer: Univar Canada Ltd.

Escaid 110 is aliphatic kerosene, which is used in the solvent extraction process, to dilute the extractant to the appropriate concentration. It has no metal extracting ability. The chemical and physical properties are given in the “Appendix,” Table A6 (Escaid 110, 2010).

3.2 ICP- MS Analysis Details

The organic solution used in this study, was prepared by diluting extractant in Escaid 110. 1-Decanol was used as phase modifier. All aqueous solutions were prepared using reagent grade chemicals i.e. concentrated acids. The solution preparation and the test conditions for different effects are given as follows:

3.2.1 Effect of Acid concentration on Solubility/Degradation

- Solution Preparation

Several concentrations (0.0001-5) M acid was prepared by using reagent grade sulphuric acid. The reagent grade supplied sulphuric acid concentration was 18.66M. By diluting with pure distilled water desired concentration of sulphuric acid was prepared. For example, the preparation procedure of 1M, 100 mL sulphuric acid was as follows:

V_1 = Volume of reagent grade acid required

S_1 = Concentration of reagent grade sulphuric acid = 18.66M

V_2 = Volume of desired concentration of acid = 100ml

S_2 = Desired concentration of acid = 1M

We have, $V_1S_1 = V_2 S_2$

$V_1 = (V_2 S_2)/S_1$

$= (100 * 1)/18.66$

= 5.3590 ml

For the preparation of 100 mL of 25 vol. % Cyanex 272/D2EHPA solution, 5 mL 1-Decanol and 25 mL Cyanex 272/D2EHPA was taken in a 100 mL volumetric flask and was filled up to its mark by Escaid 110.

- Test Conditions

Equal volume (10 mL) of organic and aqueous phases of known concentration were taken into a 250 mL conical flask and continuously agitated in a programmable air bath shaker (Innova-43 Incubator shaker series from New Brunswick Scientific) for 8 hours to attain equilibrium. The shaking speed and temperature was maintained at 300 rpm and at 25 ^{o}C respectively. After agitation, the solutions were transferred into separatory funnels where they were left for at least 24 h for complete phase separation.

3.2.2 Effect o f Extractant Concentration on Solubility/Degradation

- Solution Preparation

Several concentrations (0-100) vol. % of extractant solution was prepared by diluting with Escaid 110. 1-Decanol was used as a phase modifier. For example, for the preparation of 100 mL of 25 vol. % Cyanex 272/D2EHPA solution, 5 mL 1-Decanol and 25 mL Cyanex 272/D2EHPA was taken in a 100 mL volumetric flask and was filled up to its mark by Escaid 110. The concentration of sulphuric acid was 0.001M.

- Test Conditions

Equal volume (10 mL) of organic and aqueous phases 0.001M concentration was taken into a 250 mL conical flask and continuously agitated in a programmable air bath shaker for 8 hours to attain equilibrium. The shaking speed and temperature was maintained at 300 rpm and at 25 °C respectively. After agitation, the solutions were transferred into separatory funnels where they were left for at least 24 h for complete phase separation.

3.2.3 Effect of Temperature on Solubility/Degradation

- Solution Preparation

For the preparation of 100 mL of 25 vol. % Cyanex 272/D2EHPA solution, 5 mL 1-Decanol and 25 mL Cyanex 272/D2EHPA was taken in a 100 mL volumetric flask and was filled up to its mark by Escaid 110. The concentration of sulphuric acid was 0.001M.

- Test Conditions

Equal volume (10 mL) of organic and aqueous phases of known concentration were taken into a 250 mL conical flask and continuously agitated in a programmable air bath shaker for 8 hours to attain equilibrium. The shaking speed was maintained at 300 rpm. The shaking temperature was maintained at 30 °C, 40 °C, and 50 °C for three different experiments. After agitation, the solutions were transferred into separatory funnels where they were left for at least 24 h for complete phase separation.

3.2.4 Effect of Diluent Concentration on Solubility/Degradation

- Solution Preparation

Several concentrations of extractant solution were prepared. Diluent concentration was varied from 0-100 vol% .1-Decanol was used as a phase modifier. For example, for the preparation of 100 mL of 50 vol. % Cyanex 272/D2EHPA solution, 5 mL 1-Decanol and 50 mL Cyanex 272/D2EHPA was taken in a 100 mL volumetric flask and was filled up to its mark by Escaid 110. The concentration of sulphuric acid was 0.001M.

- Test Conditions

Equal volume (10 mL) of organic and aqueous phases of known concentration were taken into a 250 mL conical flask and continuously agitated in a programmable air bath shaker for 8 hours to attain equilibrium. The shaking speed and temperature was maintained at 300 rpm and at 25 ^{o}C respectively. After agitation, the solutions were transferred into separatory funnels where they were left for at least 24 h for complete phase separation.

3.2.5 Effect of Metal Concentration on Solubility/Degradation

- Solution Preparation

For the metal effect aqueous solution containing different concentration of metal (Ni and Co) was used as aqueous solution. $NiSO_4.6H_2O$ and $CoSO_4.7\ H_2O$ salt was used as a source of metal. 25 vol. % extractant solutions were used as organic phase.

- Test Conditions

Equal volume (10 mL) of organic and aqueous phases of were taken into a 250 mL conical flask and continuously agitated in a programmable air bath shaker for 8 hours to attain equilibrium. The shaking speed and temperature was maintained at 300 rpm and at 25 °C respectively. After agitation, the solutions were transferred into separatory funnels where they were left for at least 24 h for complete phase separation.

3.2.6 Effect of Impurity on Solubility/Degradation

- Solution Preparation

The impurity effect of extractant was studied by comparing Co extraction capacities from synthetic solution of Cobalt. For this reason, 30 g/L synthetic solution of Co^{2+} using Cobalt (II) Sulphate was prepared. The pH of the solution was kept constant at 5 for the maximum extraction of Cobalt by D2EHPA. The Mn^{2+} concentrations were 1.0 g/L, 10 g/L, and 15 g/L. $MnSO_4.H_2O$ salt was used as a source of manganese. A pure aqueous solution was also used without any Mn^{2+} for the comparison of the result. 25 vol.% D2EHPA solution was used as organic phase.

- Test Conditions

Equal volume (10 mL) of organic and aqueous phases of were taken into a 250 mL conical flask and continuously agitated in a programmable air bath shaker for 8 hours to attain equilibrium. The shaking speed and temperature was maintained at 300 rpm and at 25 °C respectively. After agitation, the solutions were transferred into separatory funnels where they were left for at least 24 h for complete phase separation.

3.2.7 Kinetic Study

- Solution Preparation

25 vol. % Cyanex 272/D2EHPA solutions was prepared as a organic phase and 0.001M sulphuric acid was prepared to serve as an aqueous phase.

- Test Conditions

For the kinetic test, equal volumes (100 mL) of the organic and aqueous phases were taken into an 800 mL pyrex beaker and solution was stirred by a magnetic stirrer at 25 °C and 50 °C. The speed of the magnetic stirrer was maintained at 1200 rpm. Solutions were taken out using a pipette at 10 minutes, 1 hr, 2 hr, 5hr, and 24 hr time interval. After that solutions were transferred into separatory funnels where they were left for at least 24 h for complete phase separation.

In all tests, aqueous samples were centrifuged for 15 minutes at 2000 rpm and analyzed for residual phosphorus concentration by inductively coupled plasma mass spectroscopy (ICP-MS; Model: Elan DRII). This served as a means of monitoring solubility/degradation. Samples were centrifuged (Eppendorf Model: 5810) for at least 15 minutes so that analysis results would not consider entrainment. In order to be more accurate phase seperatory filter paper (SP1) was also used to remove an entrained organic from the aqueous solution.

3.3 Gas Chromatography Analysis Details

Gas chromatography was performed on Agilent Technologies series 6890A gas chromatograph coupled with an Agilent Technologies 5973 inert mass selective detector. The experiments were carried out at Centre of Chemical analysis, Research and Training (C-CART), Memorial University of Newfoundland.

The gas chromatography of organic sample before and after contacting with the acid was performed separately. Gas chromatography of each pure reagent was also performed. The chromatographic separation was carried out using a fused silica capillary column. The used column dimension is 0.25mm * 30m * 0.25 μm. Helium was used as a carrier gas at a pressure of 10.69 psi. The oven was programmed to heat the column from 50 ^{o}C to 350 ^{o}C at the rate of 10 ^{o}C per minute. The injector temperature was 290 ^{o}C and the final detector temperature was 300 ^{o}C. A 1 μL sample of the solution was injected manually into the column in split less mode. The total chromatographic conditions are given in section 3.3.1

3.3.1 Chromatographic Conditions

Instrument: Agilent Technologies 6890 N.

Oven Parameters

Initial Temperature: 50 °C

Final Temperature: 310 °C

Maximum Temperature: 350 °C

Rate: 10 °C per minute

Initial Time: 1 min.

Final Time: 10 min.

Run Time: 357min.

Front Inlet Parameters

Mode: Splitless

Initial Temperature: 290 °C

Pressure: 10.69 psi

Purge Flow: 50 mL/min.

Purge time: 2 min.

Total Flow: 54.5 mL/min.

Gas Saver: On

Saver Flow: 20.0 mL/min.

Saver Time: 2 min.

Gas Type: Helium

Column Parameters

Capillary column

Model Number: Agilent 19091S – 433

- 5MS, 0.25mm * 30m * 0.25 µm

Maximum Temperature: 350 °C

Nominal Length: 30 m

Nominal Diameter: 250 µm

Nominal Thickness: 0.25 µm

Mode: Constant flow

Initial Flow: 1.3 mL/min

Nominal Initial Pressure: 10.69 psi

Average Velocity: 41 cm/sec

Inlet: Front inlet

Outlet: MSD

Out let Pressure: Vacuum

Detector Parameters

Type: Flame Ionization Detector (FID)

Temperature: 300 °C

Helium Flow: 8 mL/min.

Hydrogen Flow: 35 mL/min.

Air Flow: 400 mL/min.

Makeup Flow: 35 mL/min.

Makeup Gas Type: Helium

Sample Injection: Volume: 1 μL

Chapter 4

4 Results and Discussion

4.1 Initial Phosphorus Estimation

In this work, the solubility/degradation of the extractants was determined based on the phosphorus (P) dissolution rate or phosphorus content in the aqueous solutions. In order to confirm whether phosphorus (P) is coming from other reagents like diluent (Escaid 110), modifier (1-Decanol) or aqueous sulphuric acid, tests were conducted after washing with hydrochloric acid and the results are shown in Table 4.1 and Figure 4.1

Table 4.1: Concentration of Residual P in Different Chemicals Used in the Experiments.

Name of the Chemicals	A/O Ratio	P (ppm) Content
Escaid 110	1	2.76
1- Decanol	1	2.50
0.001 M H_2SO_4	NA	1.84

NA: Not Applicable

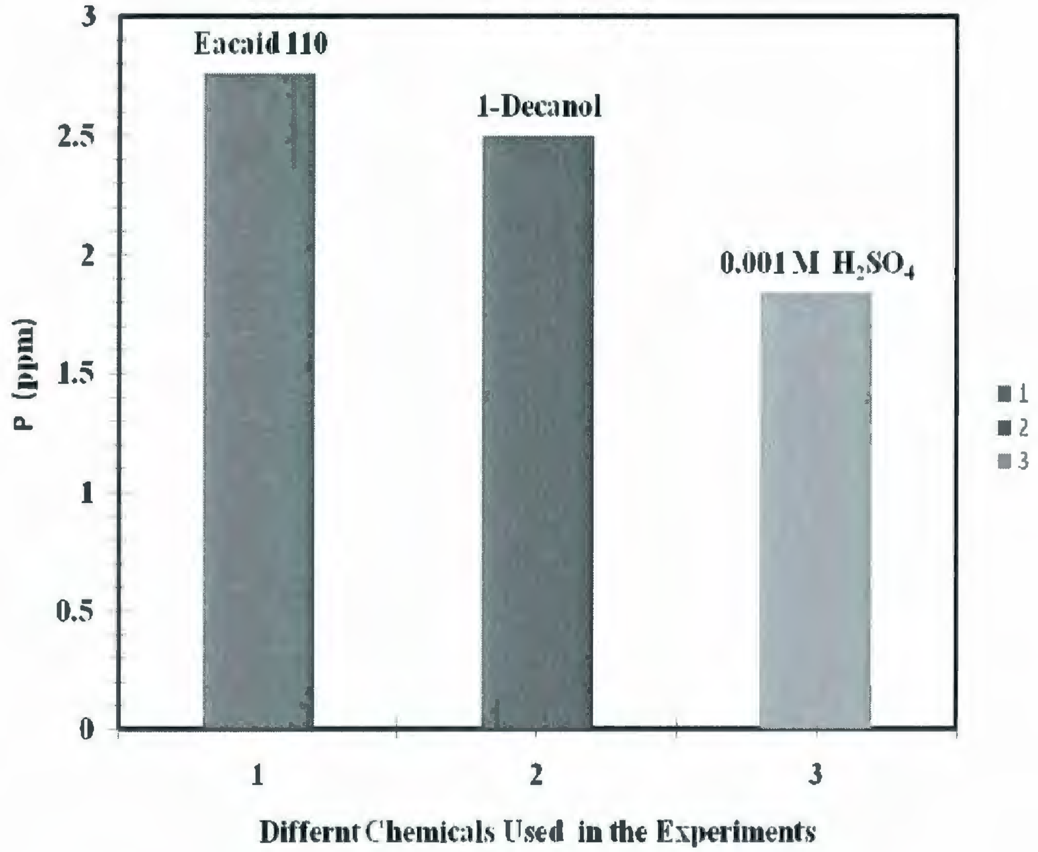


Figure 4.1: Initial P Content of Different Chemicals Used in the Experiment.

From Table 4.1 and Figure 4.1 it is seen that the amount of phosphorus (P) content in the escaid 110, modifier 1-decanol and 0.001 M pure sulphuric acid are very low at the initial stage. This amount of phosphorus worked as a basis for further comparison.

4.2 Effect of Acid Concentration on Solubility/Degradation

Table 4.2: Effect of Acid Concentration in the Range (1-5) M on Phosphorus Dissolution (A/O = 1).

Observation No.	Conc. of H_2SO_4 Acid (M)	P (ppm)
1	1	35.08
2	2	31.95
3	3	30.29
4	5	27.81

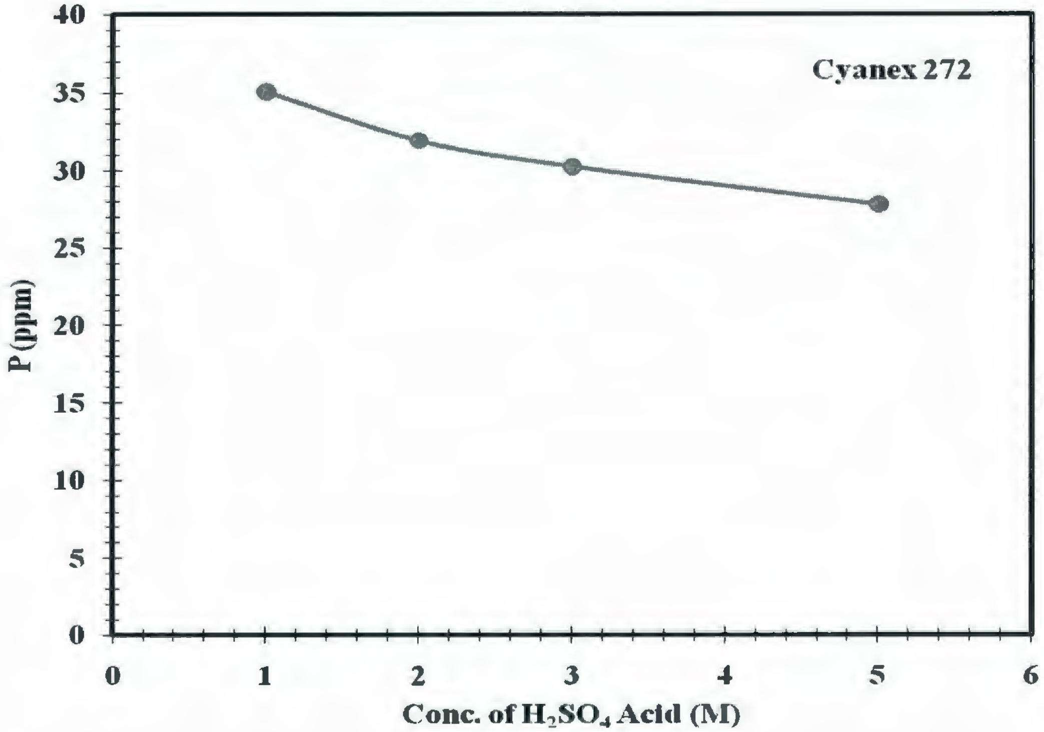


Figure 4.2: Effect of Acid Concentration (1 – 5) M on Phosphorus Dissolution.

Table 4.3: Effect of Acid Concentration in the Range (0.0001- 0.5) M on Phosphorus Dissolution (A/O = 1).

Observation No.	Conc. of H_2SO_4 Acid (M)	P^H	P (ppm)
1	0.05	1.3	29.35
2	0.01	2	39.67
3	0.001	3	45.89
4	0.0001	4	48.86

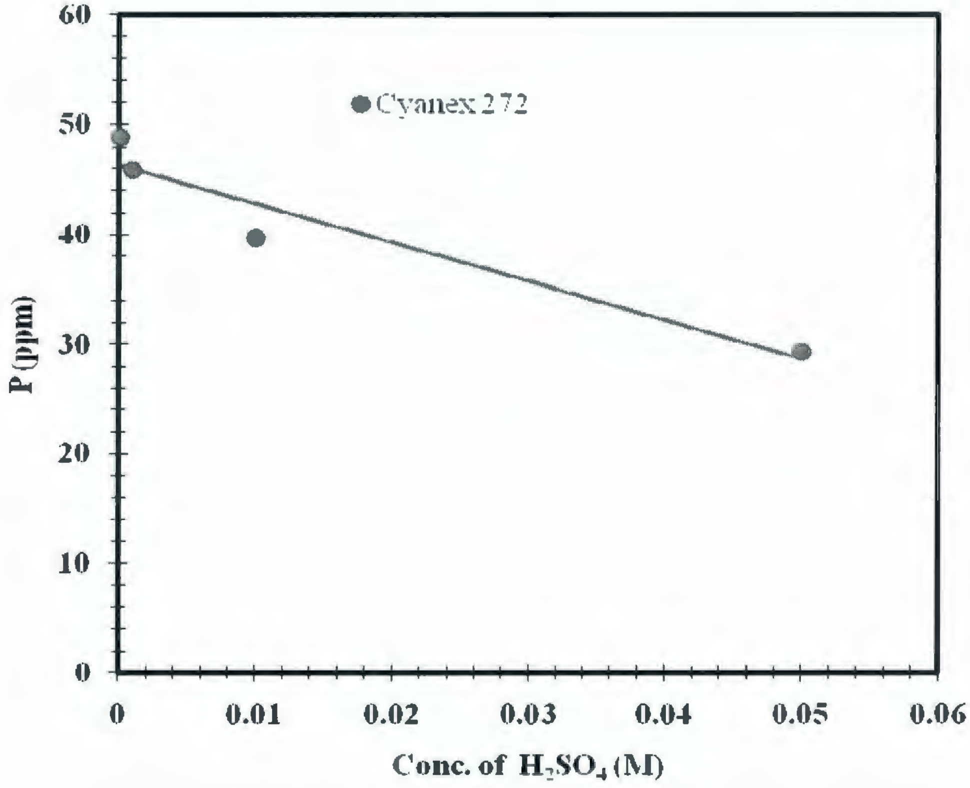


Figure 4.3: Effect of Acid Concentration (0.0001 – 0.05) M on Phosphorus Dissolution.

This experiment was performed in order to investigate, how the dissolution of phosphorus behave with the change in wide range of acid concentration (0.0001–5.0) M. Table 4.2 and Figure 4.2 show the effect in the range (1-5) M, and Table 4.3 and Figure 4.3 show the effect in the range (0.0001–0.05) M on degradation/solubility of Cyanex 272 when exposed to sulphuric acid. From the mentioned figures and tables it is clear that with the increase of sulphuric acid concentration the phosphorus content in the aqueous phase decreases, which indicate that Cyanex 272 is soluble at higher pH range. Though the solubility/degradation is high in the range of pH 4-5 but considering the true plant condition, for the rest of the experiment, pH 3 (0.0001M) was chosen.

4.3 Effect of Extractant Concentration on Solubility/Degradation

Table 4.4: Effect of Extractant Concentration (A/O = 1).

Observation No.	Extractant Vol. (%)	P (ppm) Cyanex 272	P (ppm) D2EHPA
1	5	13.05	54
2	10	16.58	91
3	15	20.21	-
4	50	41.19	199
5	100	86.05	276

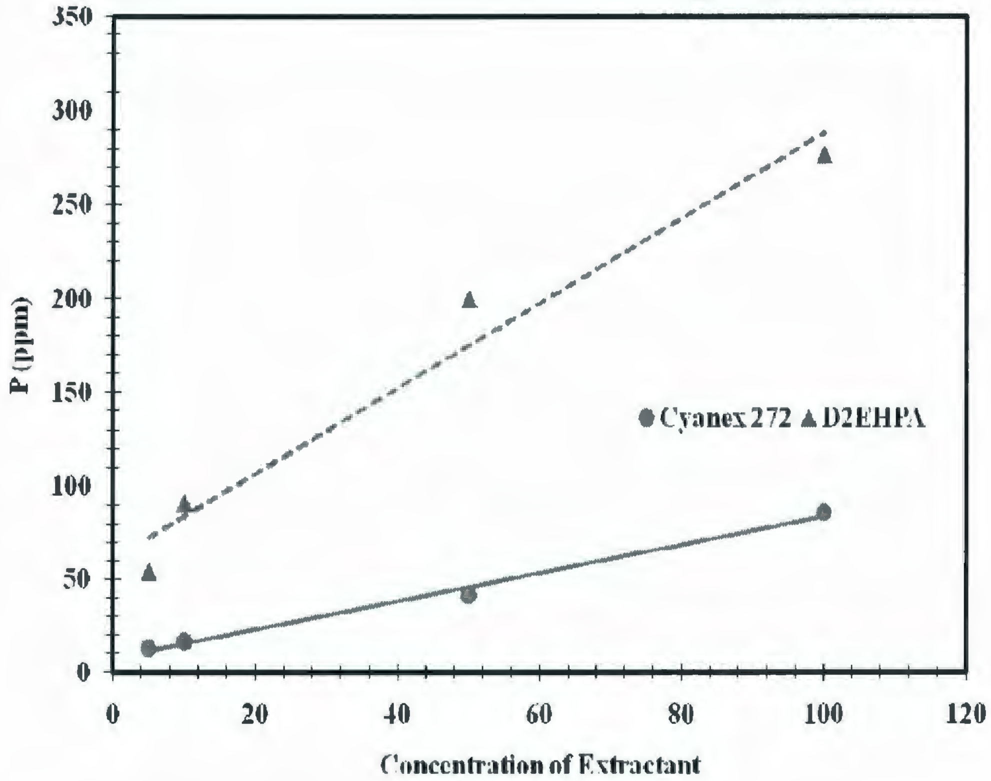


Figure 4.4: Effect of Extractant Concentration.

In this experiment, two organophosphoric acid extractant such as, Cyanex 272 and D2EHPA were contacted separately with 0.001M sulphuric acid and the concentration of the extractant was varied from 5 to 100 vol. %. It is seen from Figure 4.4 and Table 4.4 that both extractants have solubility/degradation in contact with sulphuric acid and the solubility/degradation increases with the increase of the extractant concentration. However, it is clear from Figure 4.4 that the solubility/degradation of D2EHPA is higher than that of Cyanex 272 at the same experimental condition. In this work 25 vol % extractants were used considering the practical point of view. Kuipa and Hughes, (2002) observed that 10 - 40 vol. % of extractant is often optimum in industrial practice.

4.4 Effect of Temperature on Solubility/Degradation

Table 4.5: Effect of Temperature (A/O = 1).

Observation No.	Temperature °C	P (ppm) Cyanex 272	P (ppm) D2EHPA
1	25	23.50	130.50
2	30	25.24	171.81
3	40	29.44	170.64
4	50	28.91	173.87

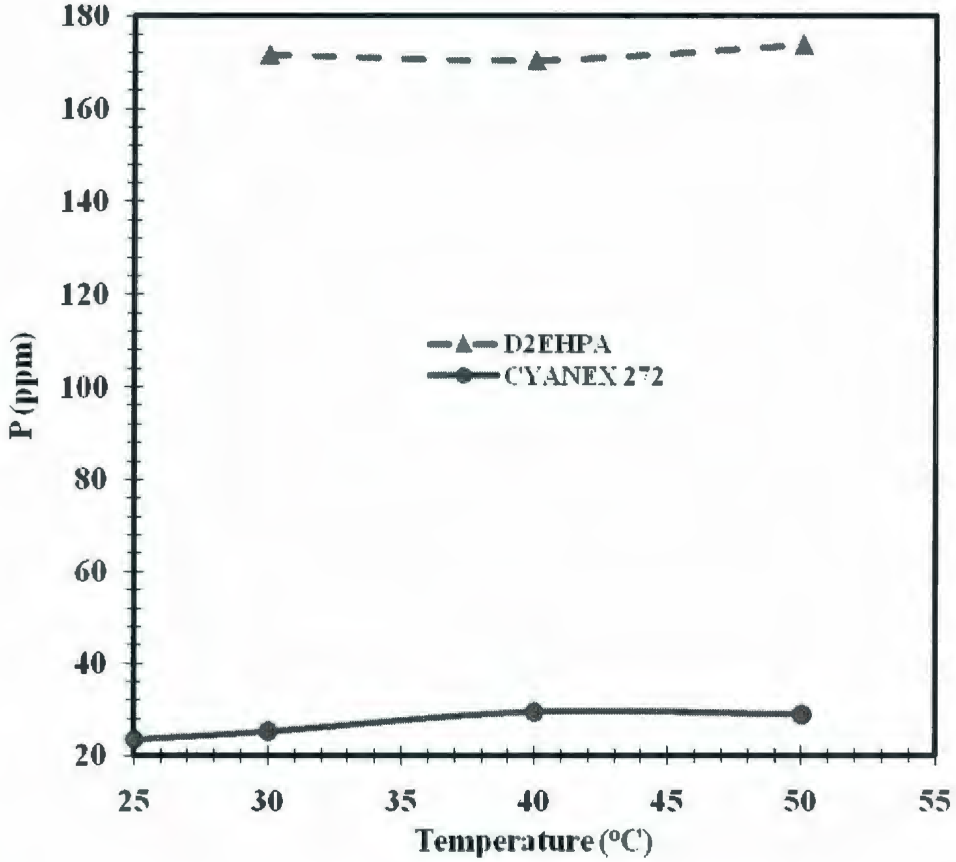


Figure 4.5: Effect of Temperature.

Table 4.5 and Figure 4.5 shows that there is a very little effect of temperature on the solubility of Cyanex 272 and D2EHPA as the concentration of phosphorus in the aqueous solution increases very slightly with the increase in temperature.

4.5 Effect of Diluent Concentration on Solubility/Degradation

Table 4.6: Effect of Diluent Concentration (A/O =1).

Observation No.	Escaid 110 Vol.(%)	P (ppm) Cyanex 272	P (ppm) D2EHPA
1	0	86.05	276
2	45	41.20	199
3	85	16.58	91
4	90	13.05	54
5	100	2.75	2.75

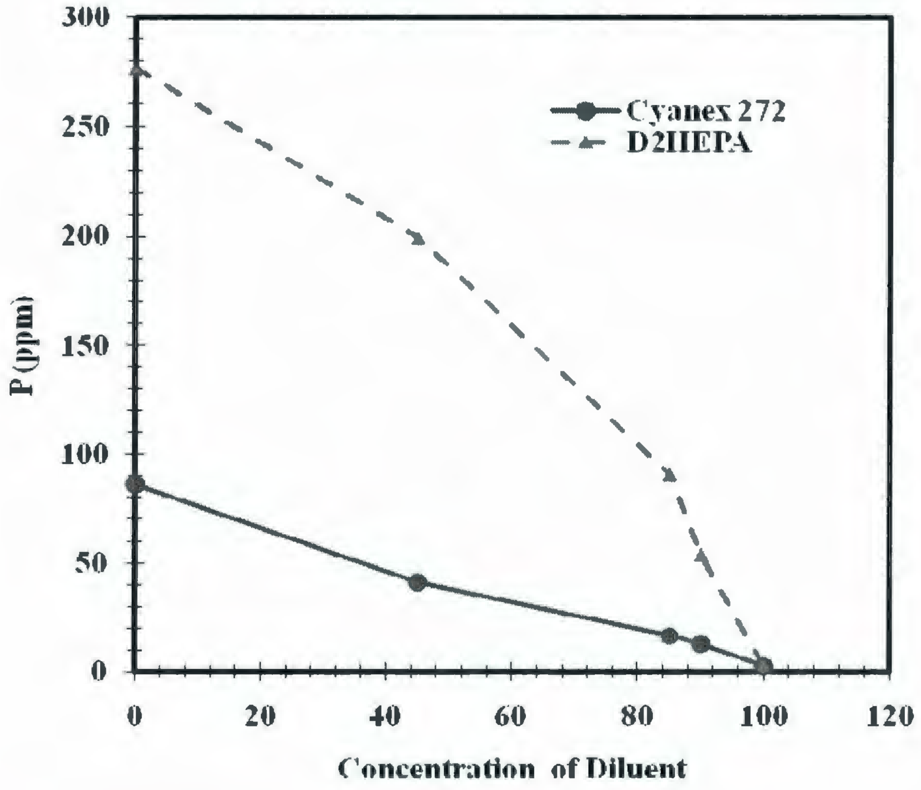


Figure 4.6: Effect of Diluent Concentration.

Table 4.6 and Figure 4.6 show the extent of degradation/solubility undergone by both Cyanex 272 and D2EHPA when diluent concentration was varied. Here, the diluent percentage was changed from 0 - 100 vol. %. The amount of modifier (5 vol. %) was kept constant and the balanced amount was organophosphoric extractant. According to Figure 4.6 the solubility/degradation rate decreases with the increase of diluent concentration. In fact it happened as the diluent concentration in the organic phase increases, the extractant concentration decreases i.e. the less concentration of phosphorus in the organic feed. And at 100% of diluent the amount of phosphorus (P) content was only 2.75 ppm, which was the baseline phosphorus content.

4.6 Effect of Metal Concentration on Solubility/Degradation

Table 4.7: Effect of Metal Concentration (A/O = 1).

Observation No.	Metal(Ni^{2+}& Co^{2+})	P (ppm)	Observation No
1	1	33	1
2	5	46	2
3	10	48	3
4	50	35	4
5	80	31	5

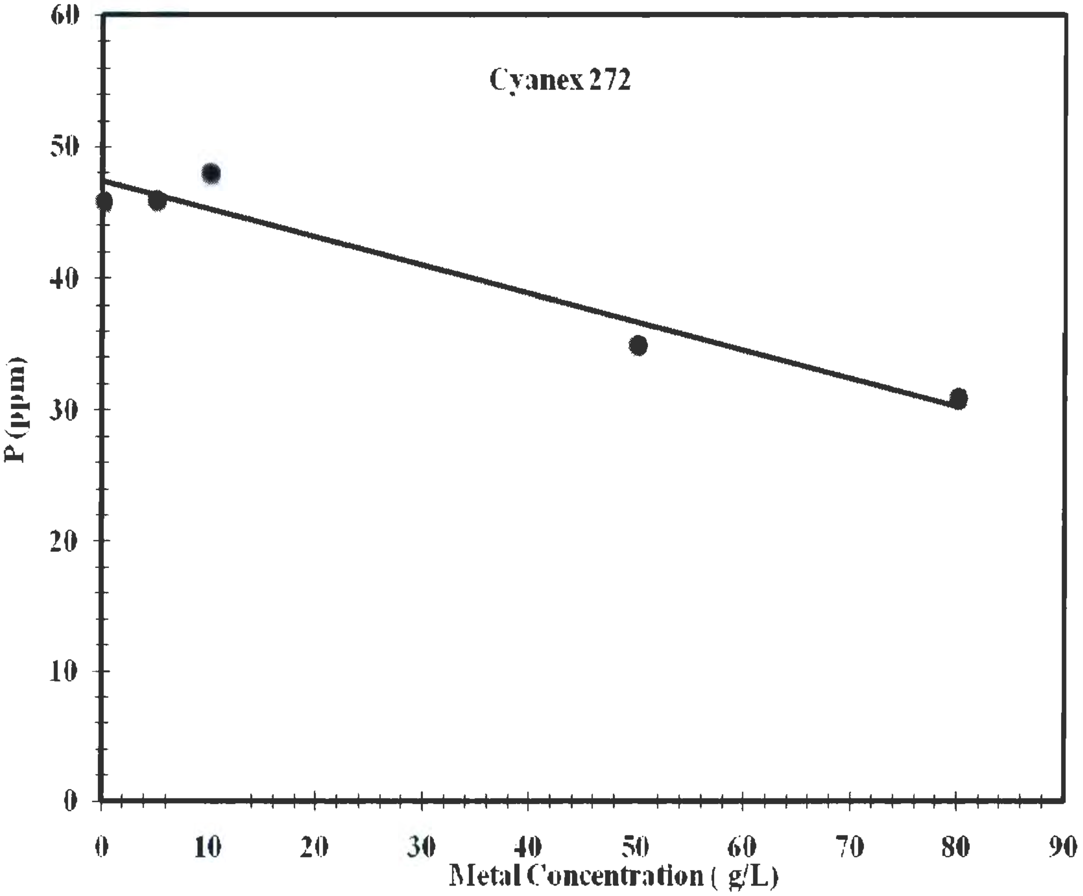


Figure 4.7: Effect of Metal Concentration.

In this experiment, metal concentration effect was observed. Different concentration of nickel and cobalt salt was used to prepare the synthetic aqueous phase keeping the pH (3) constant. Table 4.7 and Figure 4.7 show that the phosphorus dissolution rate decreases with the increase in metal salt concentration in aqueous phase.

4.7 Effect of Impurity Concentration on Cobalt Extraction

Table 4.8: Effect of Mn Concentration on Cobalt Extraction (A/O = 1).

Observation No.	Mn Salt Concentration	% Cobalt Extraction
1	0	7.12
2	1	5.35
3	10	4.08
4	15	2.14

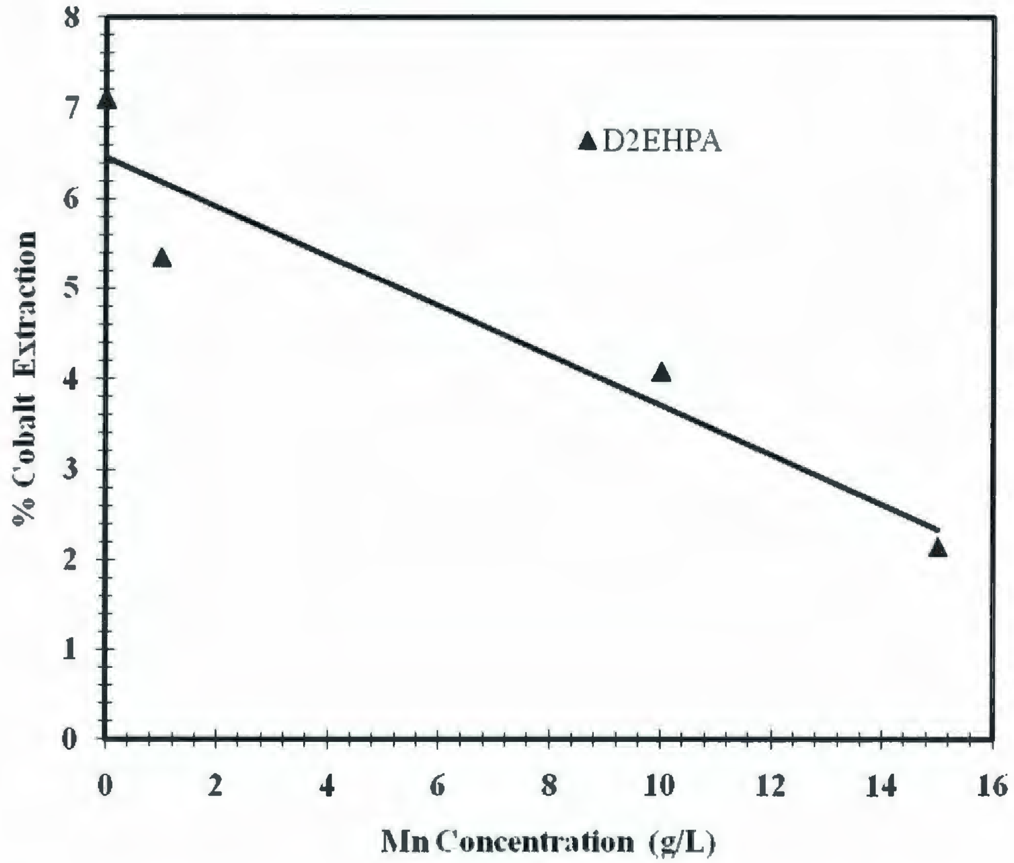


Figure 4.8: Effect of Mn Concentration on Cobalt Extraction.

In this experiment, the impurity or effect of manganese on solubility was observed by comparing the extraction ability of the extractant. Synthetic cobalt solution was prepared and cobalt was extracted with different concentration of manganese in the aqueous phase. By having a careful look on the Figure 4.8 and Table 4.8, it can be said that the extraction ability of D2EHPA decreases almost linearly in the presense of manganese.

4.8 Kinetic Study at Different Temperatures

Table 4.9: Degradation Kinetics of Cyanex272 and D2HEPA at Different Temperatures (A/O = 1).

Observation No.	Temperature °C	Time (Hr) for Cyanex 272	P (ppm) Cyanex 272	Time (Hr)for D2EHPA	P (ppm) D2EHPA
1	25	0.18	26.63	0.18	136.00
2		1.00	28.09	2.00	137.00
3		5.00	27.77	5.00	143.00
4		24.00	32.41	22.00	152.00
5		-	-	24.00	156.00
6	50	0.18	23.60	0.18	159.65
7		3.00	23.60	3.00	157.03
8		22.00	27.10	5.00	155.19

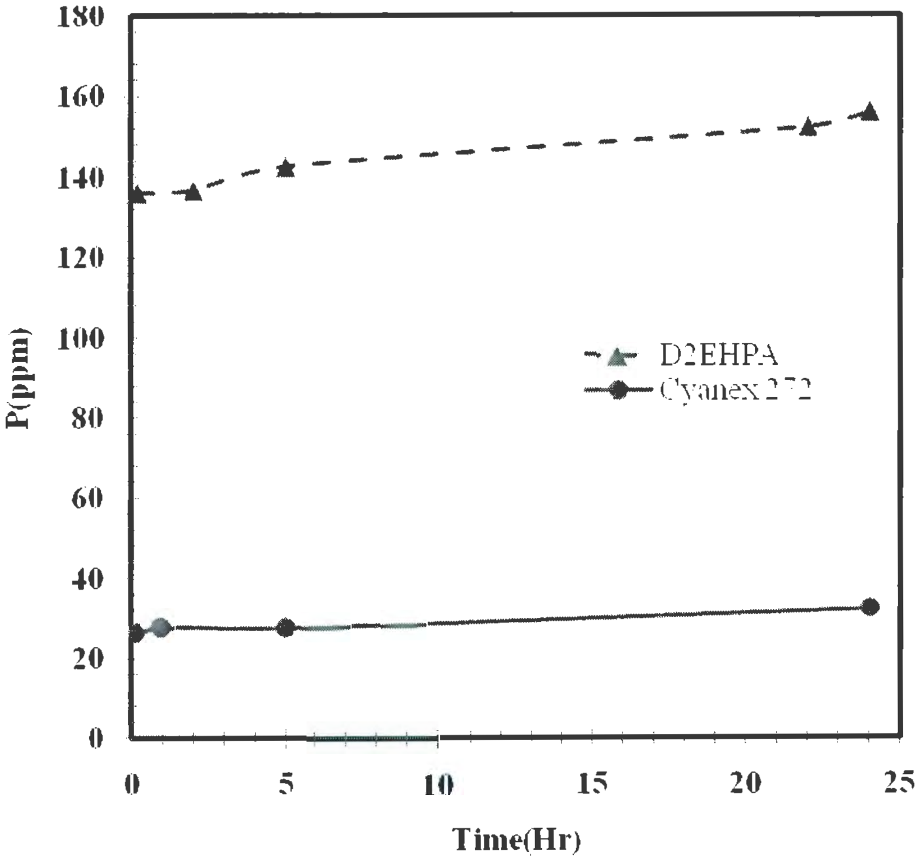


Figure 4.9: Degradation Kinetics of Cyanex272 and D2HEPA at 25 °C Temperature.

Table 4.9 and Figure 4.9 show the kinetics of the phosphorus dissolution at 25 °C and it shows that for Cyanex 272 the phosphorus dissolution is almost same. For D2EHPA it increases slightly with increase in time.

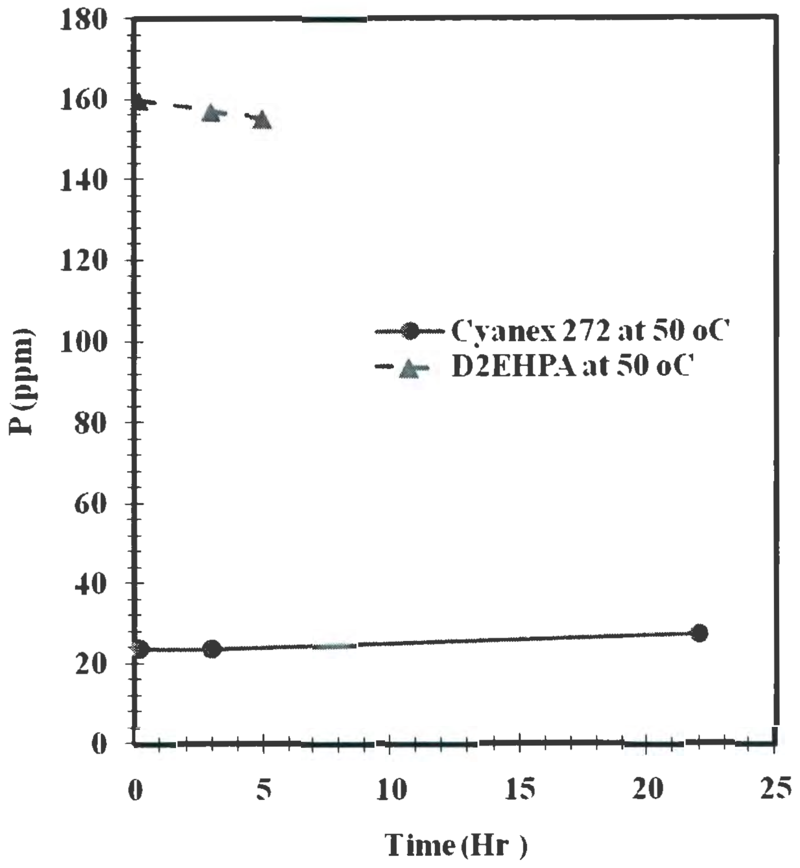


Figure 4.10: Degradation Kinetics of Cyanex272 and D2HEPA at 50 °C Temperatures.

Figure 4.10 shows the kinetics of the phosphorus dissolution at 50 °C and it shows that for Cyanex 272 the phosphorus dissolution is almost same but for D2EHPA it shows a decreases tendency. At high temperature almost all the D2EHPA solution was vaporized for this reason it was not possible to get the sample solution after 5 hr.

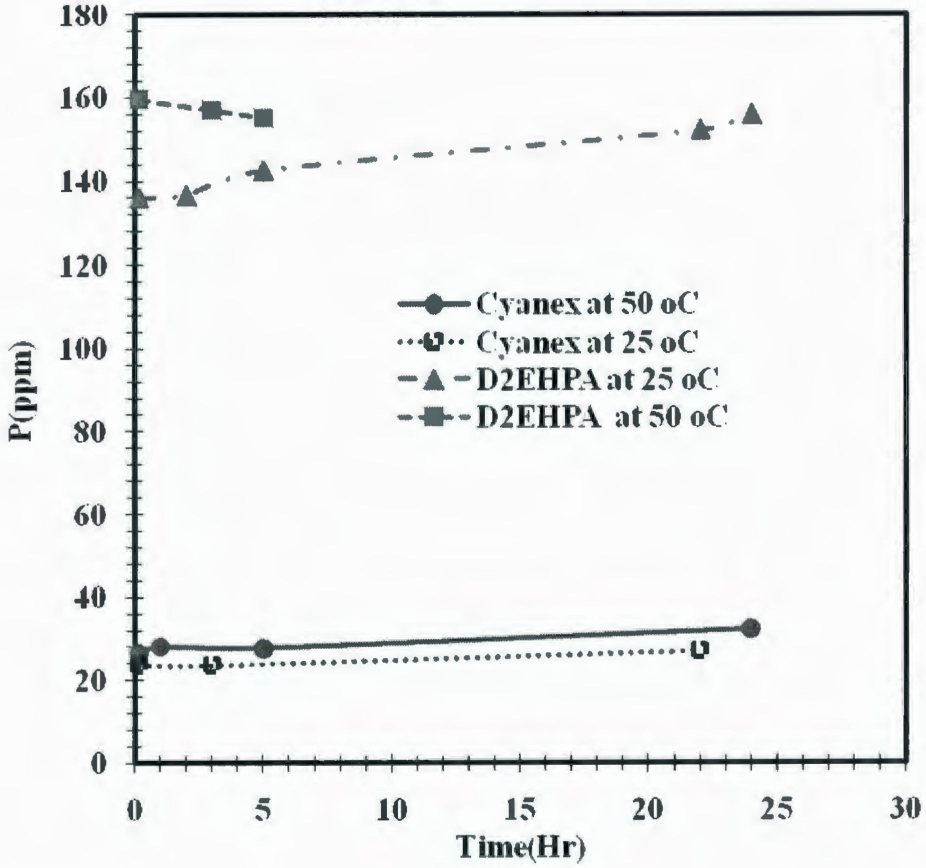


Figure 4.11: Degradation Kinetics of Cyanex272 and D2HEPA at Different Temperatures.

If the data of Figure 4.9 and Figure 4.10 are plotted together then it gives a Figure 4.11, which helps for easy comparison at higher and lower temperature dissolution rate. Figure 4.11 shows the kinetics of dissolution of extractant in single contact with sulphuric acid at 25 °C and 50 °C. The above figure shows that the solubility of D2EHPA increases with time while the solubility of Cyanex 272 remains steady throughout the 24 hr contact with sulphuric acid at 25 °C. However, at 50 °C solubility curve for Cyanex 272 shows an increasing tendency while D2EHPA shows a decreasing tendency. From the kinetic study, it is also evident that the solubility/degradation of D2HEPA is more than that of Cyanex 272. At the same experimental conditions, phosphorus level in the aqueous solution for D2EHPA reached at 156 ppm after 24 hr while for Cyanex 272 it was only 32.41 ppm.

4.9 Comparison of Dissolution of Cyanex 272 with Different Reagents.

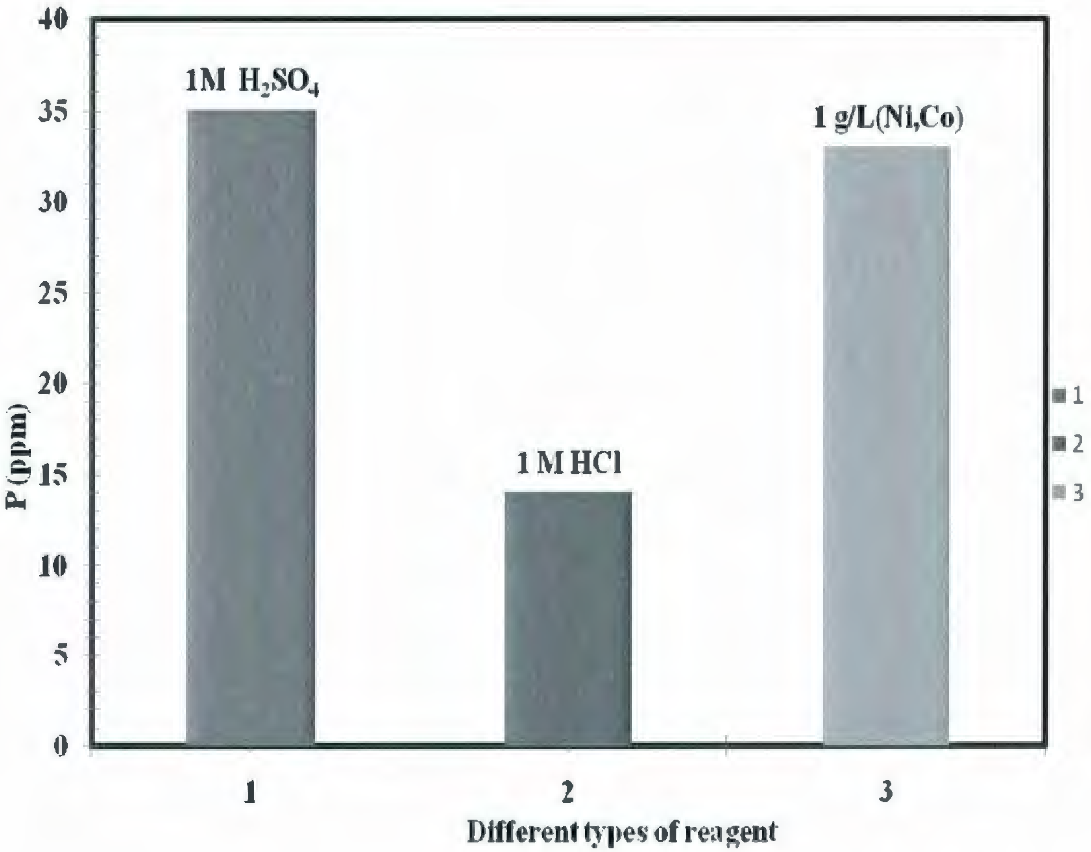


Figure 4.12: Comparison of Dissolution of Cyanex 272 with Different Reagents.

This experiment has been performed to have a look at how phosphorus dissolution rate varies with the change in aqueous phase. It shows the phosphorus dissolution rate at 1M sulphuric acid without any metal is almost same with metal containing 1M sulphuric acid with metal but in case of 1 M HCl the dissolution rate is much low.

4.10 Gas Chromatography Results

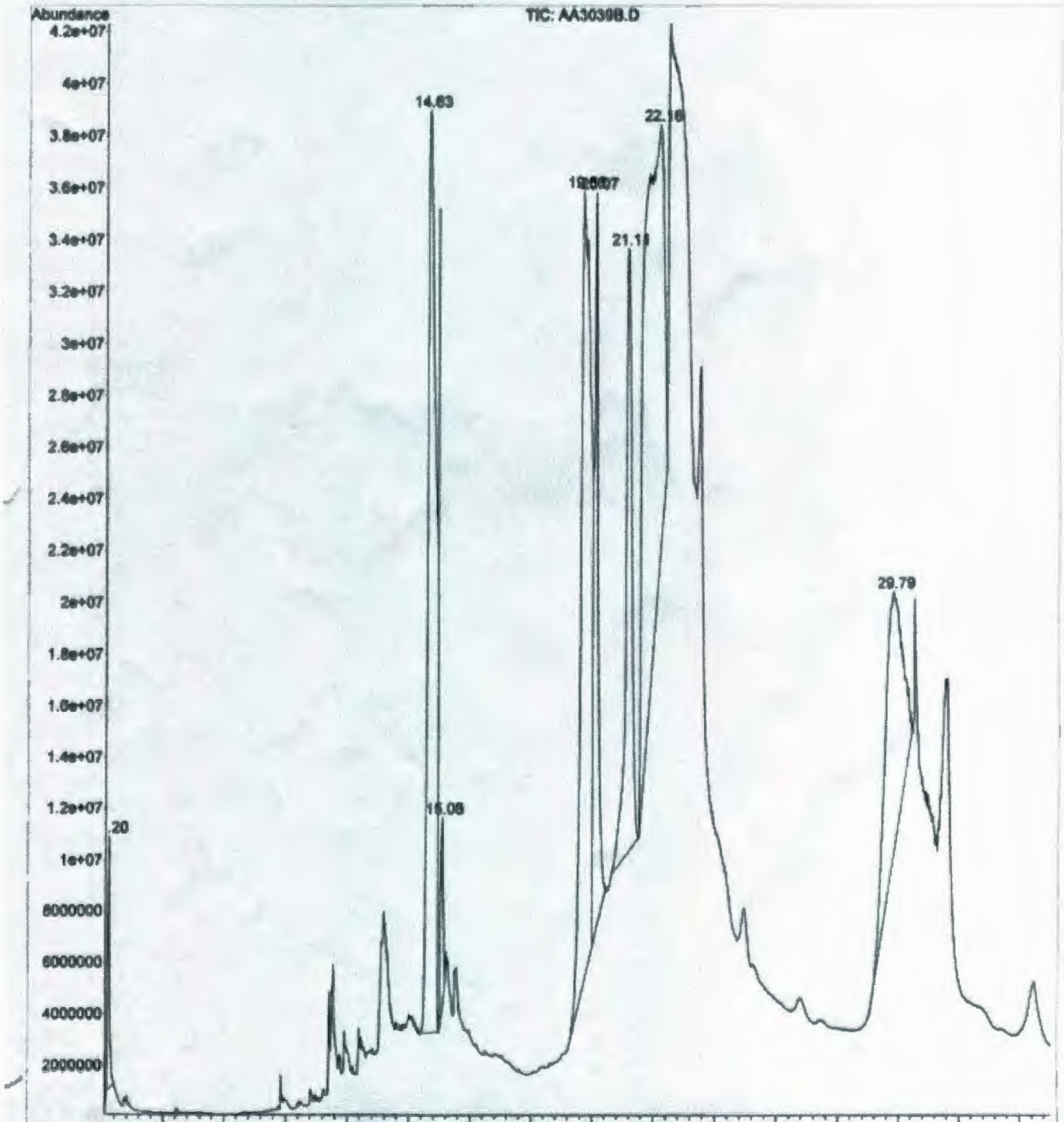


Figure 4.13: Gas Chromatograms of Pure Cyanex 272.

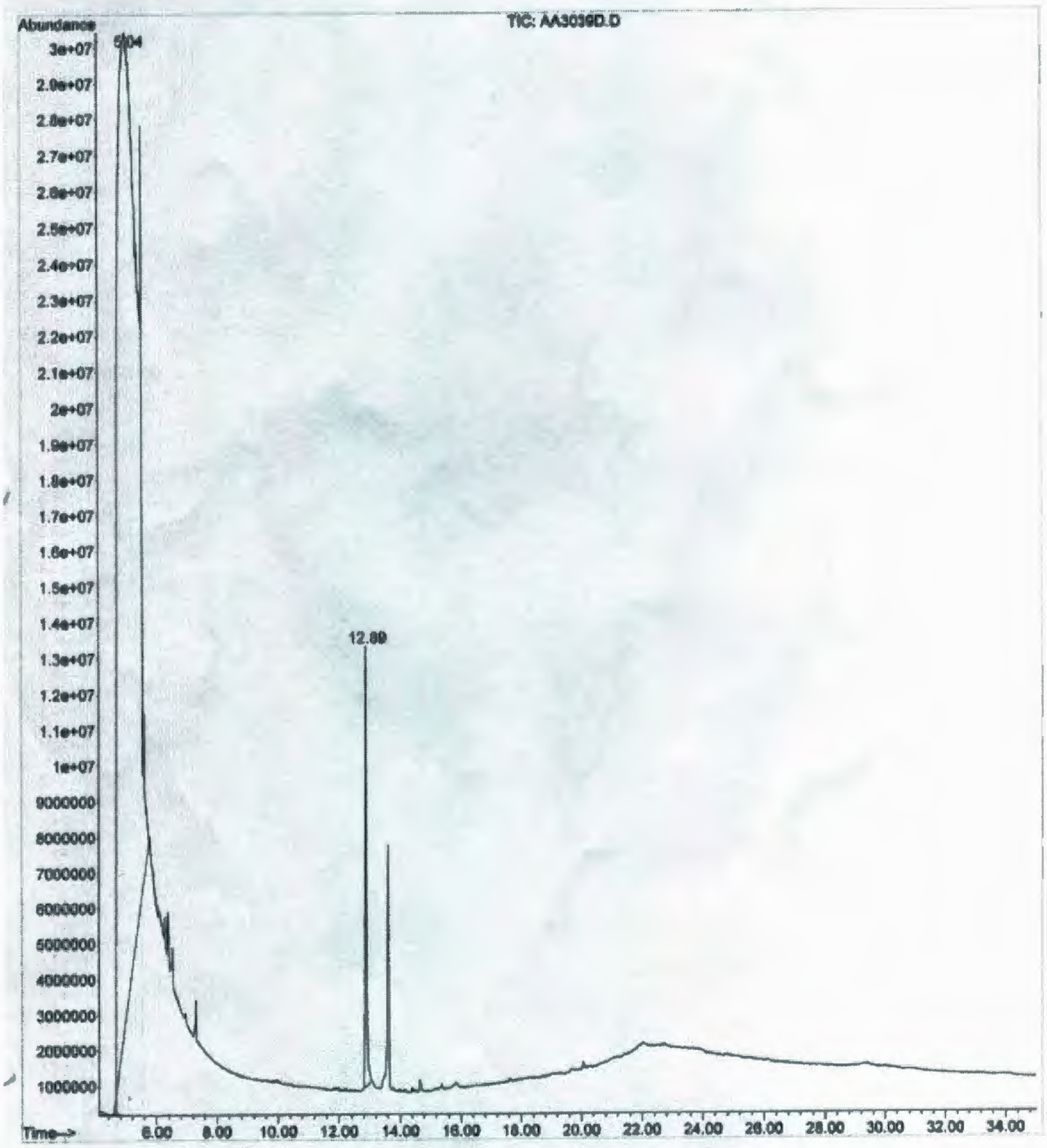


Figure 4.14: Gas Chromatograms of Pure 1- Decanol.

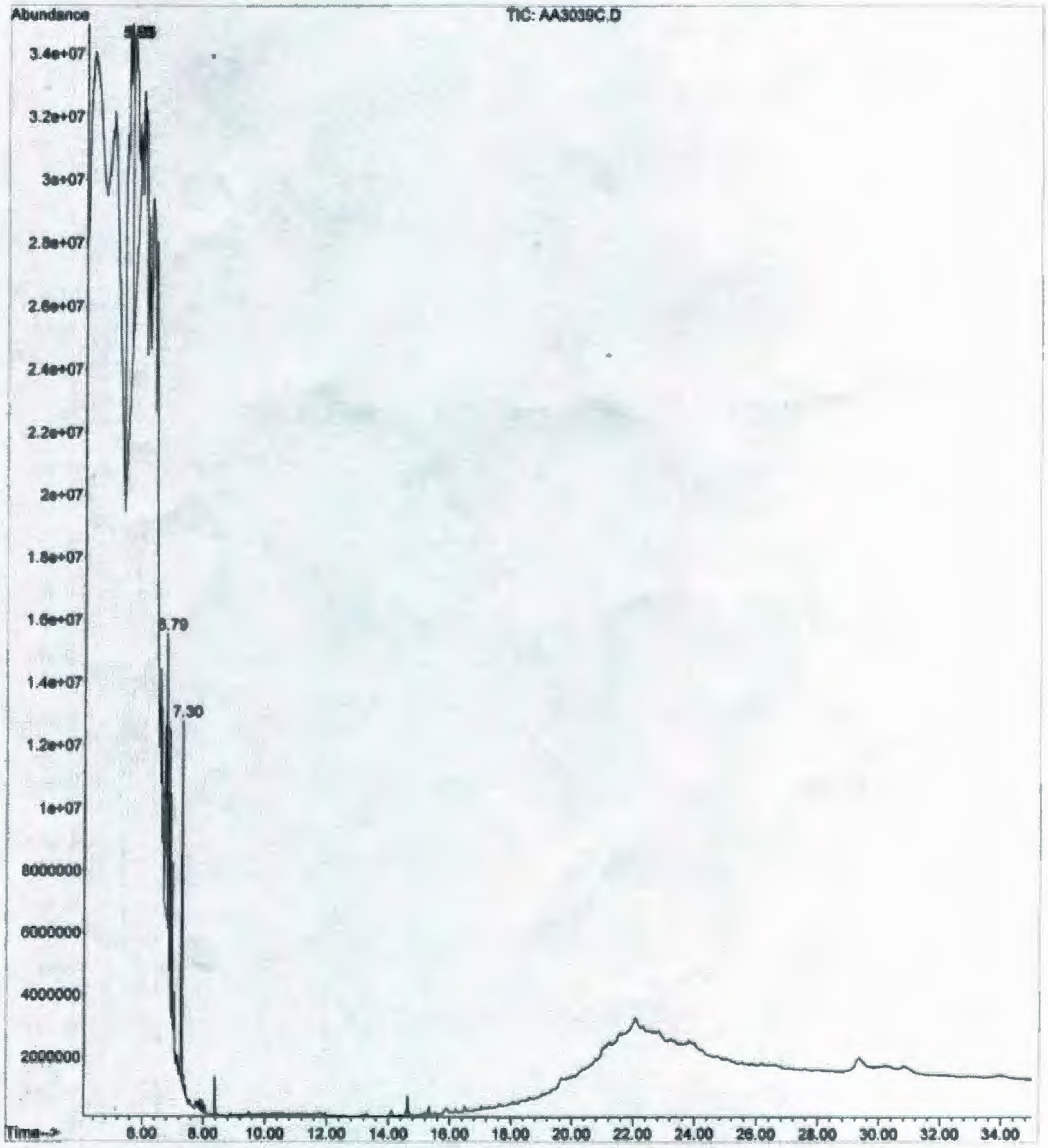


Figure 4.15: Gas Chromatograms of Pure Escaid 110.

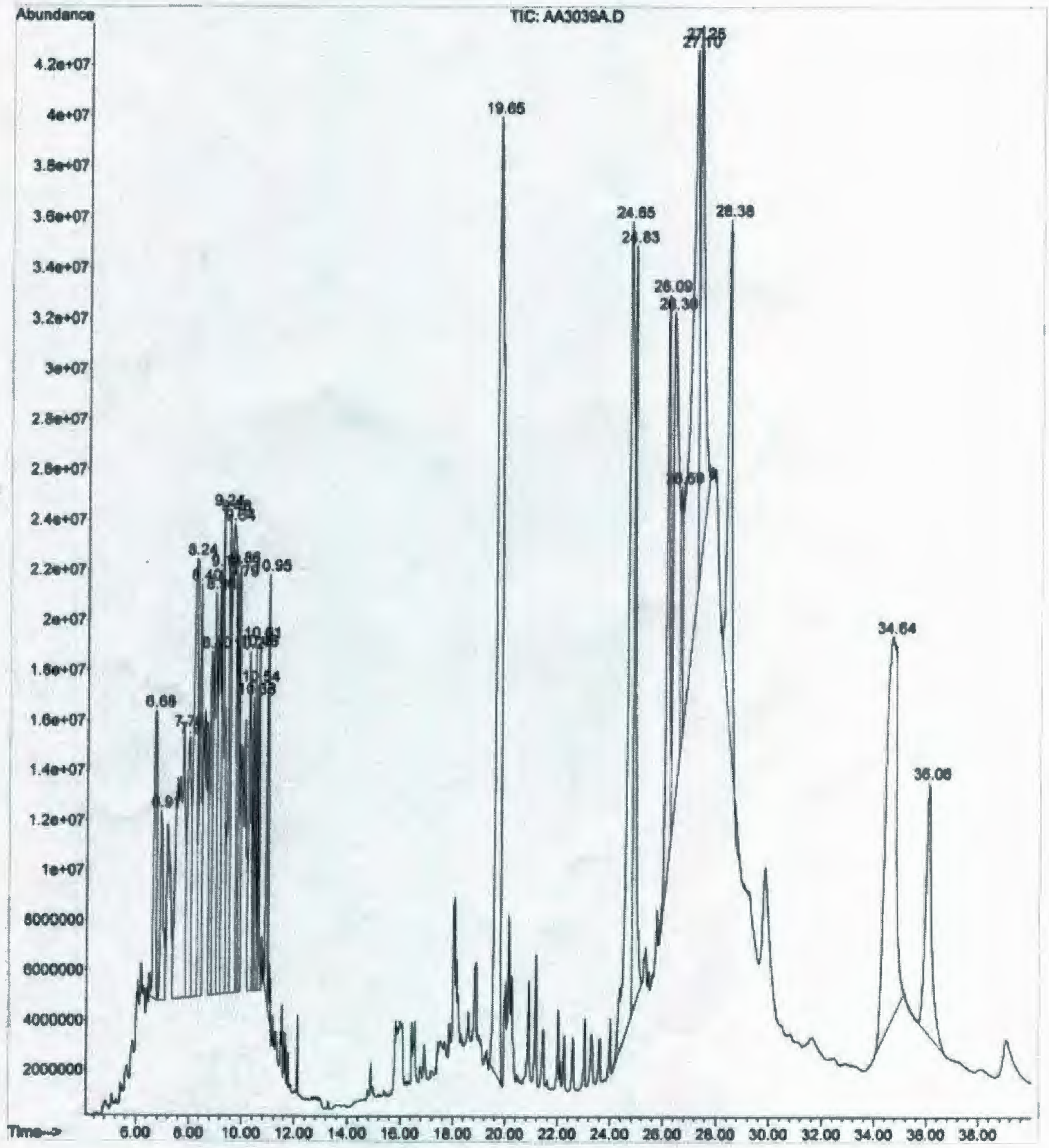


Figure 4.16: Gas Chromatograms of Solvent Solution before Contacting with Acid.

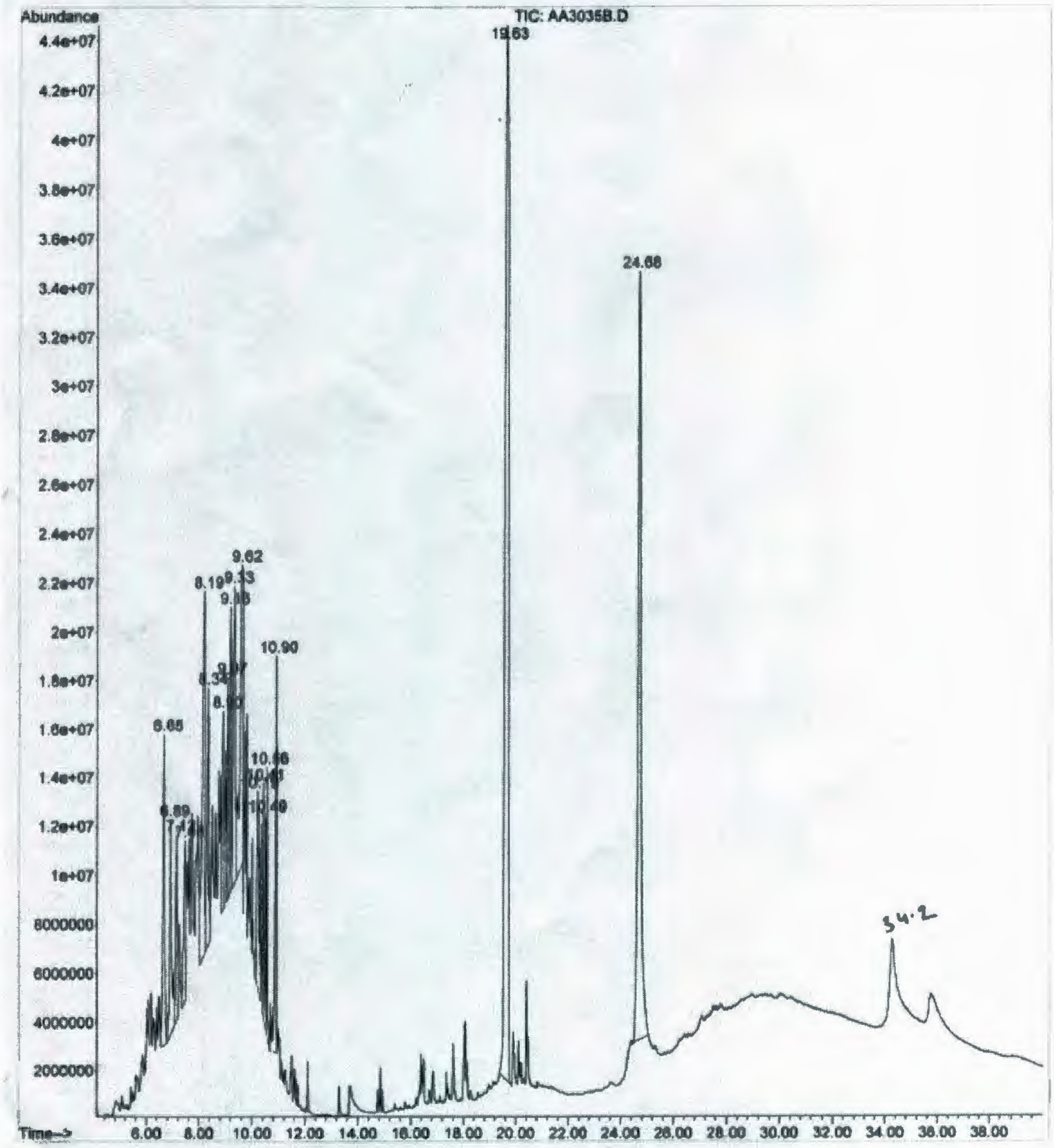


Figure 4.17: Gas Chromatograms of Solvent Solution after Contacting with 1M Sulphuric Acid.

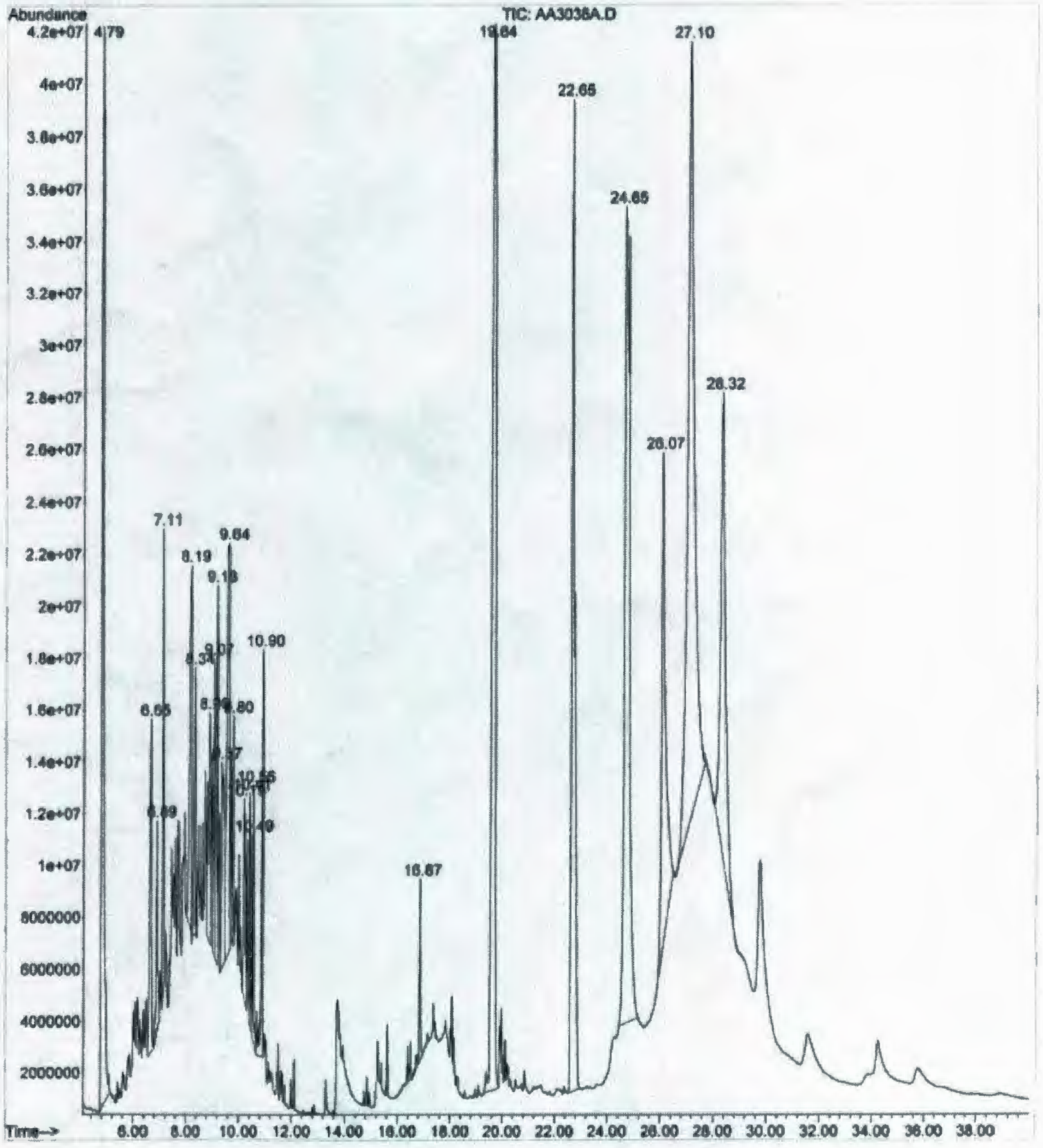


Figure 4.18: Gas Chromatograms of Solvent Solution after Contacting with 8M Sulphuric Acid.

Figures 4.13 - 4.18 show the gas chromatographic results of solvents. To correctly identify any degradation or foreign compound, gas chromatograms of pure solvents were initially performed. After that gas chromatograms of the solvent before and after contact with acid were also performed.

Based on phosphorus content in the aqueous phase the summary of the research findings are given below:

- The order of solubility/degradation of Cyanex 272 and D2EHPA tendencies was found to be D2EHPA> Cyanex 272.
- With the increase of acid concentration, solubility/degradation of both extractant Cyanex 272 or D2EHPA decreases.
- With the increase of extractant concentration, solubility/degradation of both extractants increases.
- The solubility/degradation of Cyanex 272 and D2EHPA increases very slowly with the increase in temperature.
- The solubility/degradation of both Cyanex 272 and D2EHPA decreases with the increase of diluent concentration.
- Kinetic study showed that the solubility/degradation of Cyanex 272 was almost the same, whereas in case of D2EHPA, it increases with time.

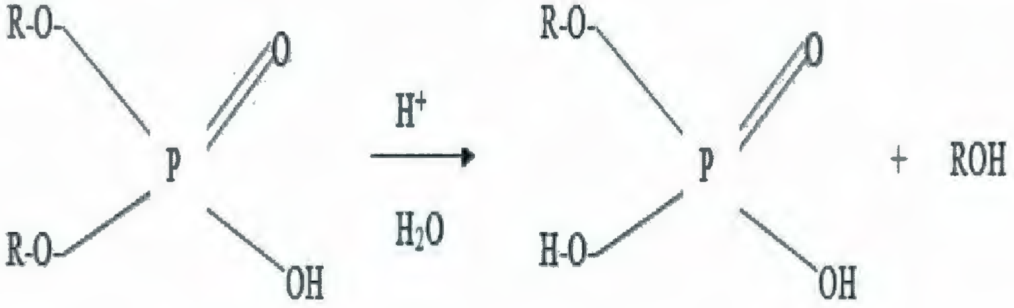
- The solubility/degradation of D2EHPA decreases with the increase of metal (Ni & Co) concentration.

- The efficiency of metal extraction capacity of D2EHPA decreases with the increase of the concentration of manganese in the aqueous phase.

From Table 4.1, it is seen that the initial amount of phosphorus in the aqueous phase is very low, whereas from Table 4.2 through Table 4.9 it is seen that the amount of phosphorus is comparatively very high which indicates that phosphorus is obviously coming from Cyanex 272 or D2EHPA. In every case, it is also noted that for D2EHPA the phosphorus content is much higher than Cyanex 272 in the same experimental condition. Hydrolysis of D2EHPA might be the reason for higher phosphorus content.

Cyanex 272 possesses a very chemically stable configuration where alkyl groups are bound directly to the phosphorus atom (Cotton and Wilkinson, 1980). Hydrolysis of Cyanex 272 at pH 5 and at 50 °C over four weeks has been found very stable (Rickelton, et al., 1984). It has also been found stable by exposing to 5M HCl for 50 days (Gupta, et al., 2007). The oxidation of Cyanex 272 cannot be generated via peroxide oxidation of the corresponding alkyl phosphine (Rickelton, et al., 1984; Rickelton and Boyle, 1990).

According to Beyad et al. (1992) hydrolysis is more likely to occur on phosphorus based extractants containing P-O-R linkages and hydrolysis produces products that are significantly soluble in water. D2EHPA contains P-O-R linkage. The hydrolysis mechanism of D2EHPA are given below



……4.1

Where, R = $C_4H_9CH(C_2H_5)CH_2O$-

The phosphorus in the aqueous phase might come due to the solubility, degradation, or phosphorus dissolution of Cyanex 272 and D2EHPA. So, to ascertain whether the phosphorus is due to solubility or degradation, a gas chromatographic analysis of the organic sample was performed, and then followed by mass spectrometry. However, no degraded compound or material was found from the GC-MS analysis.

By combining and analyzing the results from ICP-MS or GC-MS, it is found that there are some solvent losses in the aqueous phase due to the phosphorus dissolution; there is no degradation of Cyanex 272 and D2EHPA in the experimental condition.

According to the technical brochure for Cyanex 272 from Cytec Industries Inc., analysis by titration and P- NMR failed to detect any degradation of the reagent. Furthermore, they did not find any degradation from a plant that has been operating continuously for as long as ten years (Technical Brochure for Cyanex 272, 2008.)

Very recently K. R. Barnard claimed the chemical degradation of phosphinic acid under solvent extraction operating condition. This is the first example of degradation of Cyanex 272. The Murrin Murrin plant located in the northern goldfields region of Western Australia, is using a combination of Cyanex 272 and tributyl phosphate (TBP) in shellsol 2046. In Murrin Murrin plant, they are sequentially separating zinc and cobalt through solvent extraction. K.R Barand found the degraded Cyanex272 product as n-butyl–bis(2,4,4-trimethylpentyl)phosphinate. The generation of this degraded compound from the phosphine oxide impurity, present in a Cyanex 272 is believed very unlikely, due to the presence of chemically stable P-C bond. Tributayl Phosphate might be a potential source for the presence of phosphinate impurity. The formation of butyl phosphinate impurity from the phosphine acid is believed via two mechanisms (Barnard, 2010):

- TBP and phosphine oxide reacts directly to produce the phosphinate impurity.
- Butanol is generated through the hydrolysis of TBP which subsequently reacts with phosphinic acid.

So, the difference between Barnard and this research is the choice of reagent for solvent extractant. The following Table is presented for easy comparison.

Table 4.10: Comparison of Reagents Used in the Research.

Reagent Type	Barnard's research	Current research
Extractant	Cyanex 272	Cyenex 272
Diluent	Shellshol 2046	Escaid 110
Modifier	TBP	1- Decanol

According to the proposed mechanism for degradation of Cyanex 272 by Barnard, TBP is responsible as a potential source and in this research TBP has not been used at all, which validates this research findings very well.

Chapter 5

5 Conclusion

5.1 Research Conclusion

The objective of this study was to find out the solvent losses in solvent extraction process due to solubility/degradation. To find out the losses due to solubility/degradation for Cyanex 272 and D2EHPA an extensive literature review has been performed. A different way to find the solvent losses in terms of phosphorus dissolution has been applied in this research by analyzing the phosphorus using ICP-MS. To make sure whether phosphorus (P) is coming from other reagents like diluent (Escaid 110), modifier (1-Decanol) or aqueous sulphuric acid, tests were conducted initially of those fresh reagent. The amount of initial phosphorus content is 2.76 ppm, 2.50 ppm, and 1.84 ppm respectively. The acid concentration effect was studied first, which showed the increasing tendency of phosphorus dissolution with increase in pH. pH 3 has been selected considering true plant condition. For the extractant concentration effect, the phosphorus dissolution rate was increasing with the increase in extractant concentration for both Cyanex 272 and D2EHPA. The amount of phosphorus content for 100 vol. % of Cyanex 272 and D2EHPA is 86 ppm and 276 ppm respectively. The amount of phosphorus content dictates that the phosphorus dissolution rate. As a result dissolution of D2EHPA is much higher than Cyanex 272. The diluent concentration effect shows a decreasing tendency for both Cyanex 272 and D2EHPA. With the increase in temperature, dissolution rate of phosphorus increases slightly. For the metal concentration effect, it decreases with increasing metal concentration in aqueous phase. Finally, kinetic study has also been performed and at the end of 24 hr amount of phosphorus is 24 ppm and 156 ppm for Cyanex 272 and D2EHPA respectively. In every case, amount of phosphorus content for D2EHPA is much higher than Cyanex 272. So, the phosphorus dissolution rate of D2EHPA is worse than Cyanex 272 in the same experimental condition.

The result from the ICP-MS confirmed that there are some losses of solvent in terms of phosphorus dissolution. In order to find out degraded compound GC-MS analysis of sample also been performed. The result failed to detect any degraded compound. So, from these research findings the conclusion is, there is some loss of solvent in terms of phosphorus dissolution in the aqueous phase, and there is no degradation at all in this experimental condition.

5.2 Significance and Accomplishment of This Work

The study made in this research to find out solvent losses in terms of phosphorus dissolution is very important. The study has concluded saying that in the descried condition there are some losses of solvents in terms of phosphorus dissolution. This study has applied a new approach to describe the organic solvent losses during solvent extraction which may have a vital benefit for the mining industry. It is expected that this research findings will give an opportunity to other graduate and undergraduate students to gather and apply their knowledge in hydrometallurgical process.

5.3 Accomplishment

The accomplishment of this research is that a portion of this thesis has been accepted for publication to the Journal of Chemical Engineering published by The Institute of Engineers, Bangladesh (Azam, et al., 2010).

5.4 Recommendations for Future Work

- Proton and carbon nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR) can also be used for experimental result analysis for more accuracy in identifying degraded compound.

- The diluent and modifier combination can be changed to see the effect of phosphorus dissolution rate. For example, instead of using Escaid 110 and 1-Decanol other diluent shellshol 2046 and modifier TBP can be used or any other combination can be used for preparation of solvent solution.

- The real plant extractant solution, which is being used in the industry, can be used for experiment.

- Aging effect of extractant can also be done to see if there is any change of structure or any other change for long exposure of time.

References

Abe, Y., Flett, D.S., 1992. Solvent extraction of silver from chloride solutions by Cyanex 471X. In: Sekine, T., (Eds.), Solvent Extraction 1990, Part B, Elsevier Scientific Publishers, Amsterdam, pp. 1127 – 1132.

Al-Shawi, A.W., Engdal, S.E., Jenssen, O.B., Jorgensen, T.R., Rosaeg, M., 2002 .The integrated recovery of rare earths from apatite raw material in the odda process of fertilizer production by solvent extraction. A plant experience. In: Sole, K. C., Cole, P. M., Preston, J. S., Robinson, D. J., (Eds.), Proceedings of the International Solvent Extraction Conference 2002, (ISEC 2002). Chris van Rensburg Publications (Pty) Ltd., Cape Town, South Africa Vol. 2, pp. 1064–1069.

Azam, M.A., Alam, S., Khan, F.I., 2010. The solubility/degradation study of organophosphoric acid extractants in sulphuric acid media. Journal of Chemical Engineering, IEB (Accepted).

Barnard, K.R., 2010. Identification and characterisation of a Cyanex 272 degradation product formed in the Murin Murin solvent extraction circuit. Hydormetallurgy 103, 190-195.

Bacon, G., Mihaylov, I., 2002. Solvent Extraction as an Enabling Technology in the

Nickel Industry. In: Sole, K.C., Cole, P.M., Preston, J.S., Robinson, D.J., (Eds.).Proceedings of the International Solvent Extraction Conference 2002 (ISEC 2002). Chris van Rensburg Publications (Pty), Ltd. Vol. 1(1), Cape Town, South Africa, pp. 1-13.

Beauchemin, D., Craig, J.M., 1991. Investigations on mixed-gas plasmas produced by adding nitrogen to the plasma gas in ICP-MS. Spectrochimica Acta Part B: Atomic Spectroscopy 46 (5), 603–614.

Beyad, M.H., Lyman, D.E., Zarnegar, B.M., (1992). Effect of Temperature and Acidity on Various Phosphorus Containing Extractants. In: T. Sekine (Eds.), Solvent extraction 1990 Proceedings of the International Solvent Extraction Conference 1990 (ISEC '90). Elsevier. Kyoto, Japan, pp. 339-344.

Burkin, A.R., 2001. Chemical hydrometallurgy theory and principles. Imperial College Press, London, 5.

Carrier gas: Retrieved May 15, 2010 from websitehttp://clu in.org/characterization/technologies/gc.cfm

Cotton, F.A., Wilkinson, G., 1980. Advanced Inorganic Chemistry, 4th Edition. John Wiley and Sons, New York, 466.

Cox, M., 2004. Solvent extraction in hydrometallurgy. In: Rydberg, J., Cox, M., Musikas, C., & Choppin, G.R., (Eds.). Solvent extraction principals and Practice. Marcel Dekker Inc., New York, 475.

Cyanex: Retrieved May 5, 2010, from Website: http://www.cytec.com/specialty-chemicals/cyanex.htm#PAE.

Deep, A., Carvalho, J. M. R., 2008. Review on the Recent Developments in the Solvent Extraction of Zinc. Solvent Extraction & Ion Exchange 26 (4).

Decanol: Retrieved May 11, 2010. Website : www.alfa.com/contents/msds/USA A17288.pdf.

Demopoulos, G.P., Principe. F., 2003. The solubility and stability of organophosphoric acid extractants in H_2SO_4 and HCl media. Hydrometallurgy 68, 115 – 124.

D2EHPA: Retrieved May 11, 2010. Website : www.alfa.com/contents/msds/USA A17723.pdf

Description of ICP : Retrieved May 12, 2010 from website http://www.cee.vt.edu/ewr/environmental/teach/smprimer/icpms/icpms.htm

Escaid 110: Retrieved May 11, 2010. Website : http://msds.univarcanada.co/wercswv.asp

Flett, D.S., 2005. Solvent extraction in hydrometallurgy: the role of organophosphorus extractants. Journal of Organometallic Chemistry, 690 (10), 2426-2438.

Flett, D.S., Anthony, M.T., 1998. International Mining and Metallurgy 1, 29.

Flett, D.S., Spink, D.R., 1976. Solvent Extraction of Non-Ferrous Metals: A Review 1972-1974. Hydrometallurgy 1, 207.

Flett, D.S., West, D.W., 1978. Complex Metallurgy'78. The Institution of Mining and Metallurgy, London.

GC-MS: Retrieved May 12, 2010 from website http://en.wikipedia.org/wiki/Gas_chromatography-mass_spectrometry

Gupta, B., Mudhar, N., Singh, I., 2007. Separations and Recovery of Indium and Gallium using bis (2,4,4-trimethyl)phosphinic acid (Cyanex 272), Separation and Purification Tech. 57, 294-303.

Habashi, F., 1970. Principles of extractive metallurgy, Science publisher, London, Vol.2, 1.

Habashi, F., 2005. A brief history of hydrometallurgy. Hydrometallurgy 79 (1-2), 15-22.

Hatton, T.A., 2002. Tailored solvents and colloids for green processing of chemicals and biochemical's. In: Proceedings of the International Solvent Extraction Conference 2002 (ISEC'2002). Elsevier, Cape Town, South Africa, Vol. 1, pp. 15-23.

Henry, L.E., 2001. Past present and future of biohydrometallurgy. Hydrometallurgy 59 (2-3), 127-134.

Hossain, M.R.M., 2010. Removal of impurities from electrolyte solution to produce pure metals. A thesis submitted to graduated studies office of Memorial University of Newfoundland, Canada, for the partial fulfilment of the requirements of the degree of Master of Engineering in Mechanical Engineering.

Hudson, M.J., 1982. An Introduction to Some Aspects of Solvent Extraction Chemistry in Hydrometallurgy. Hydrometallurgy 9, 149-168.

Hydrometallurgy (2010.). Retrieved May 5, 2010, from Wikipedia, free encyclopaedia. Website: http://www.hydrometallurgysection.org.

ICP Details: Retrieved May 12, 2010 from website http://en.wikipedia.org/wiki/Inductively_coupled_plasma_mass_spectrometry

ICP-MS: Retrieved May 12, 2010 from website http://www.cee.vt.edu/ewr/environmental/teach/smprimer/icpms/icpms.htm

Kaal, E., Janssen, H., 2008. Extending the molecular application range of gas chromatography. Journal of Chromatography A. 1184 (1-2), 43-60.

Kuipa, P.K., Hughes, A.M., 2002. Diluent effect on the solvent extraction rate of copper. Separation Science and Technology 37 (5), 1135-1152.

Mihaylov, I., 2009. Purification process, In Ni/Co Hydrometallurgy (Short course), Conference of Metallurgist (COM'09), Sudbury, Ontario, Canada.

Mining: Retrieved May 5, 2010, from Wikipedia, free encyclopaedia. Website: http://en.wikipedia.org/wiki/Mining.

Mohapatra, D., Hong-In, K., Nam, C.W., Park, K.H., 2007. Liquid liquid extraction of aluminium (III) from mixed sulphate solutions using sodium salts of Cyanex 272 and D2EHPA. Separation and Purification Technology 56 (3), 311-318.

Parker Centre (2002/2003). Cooperative research centre for hydrometallurgy. Annual Report 2002/2003.

Peters, E., 1973. The physical chemistry of hydrometallurgy. International Symposium on Hydrometallurgy, Chicago, Ilinois, U.S.A

Preston, J.S., 1982. Solvent extraction of cobalt and nickel by organophosphorus acids I. Comparison of phosphoric, phosphonic and phosphonic acid systems. Hydrometallurgy 9, 115.

Ritcey, G.M., 2006. Solvent extraction in hydrometallurgy: Present and future, Tsinghua Science & Technology 11 (2), 137-152.

Rickelton, W.A., 1996. Kirk–Othmer Encyclopedia of Chemical Technology, 4th Edition. John Wiley and Sons. New York, 18, 656–668.

Rickelton, W.A., Boyle, R.J., 1990. The Selective Recovery of Zinc With New Thiophosphinic Acids, Solvent Extraction and Ion Exchange 8, 783-797.

Rickelton, W.A., Flett, D.S., West, D.W., 1984. Cobalt-Nickel Separation by Solvent Extraction with a Dialkylphosphinic Acid, Solvent Extraction and Ion Exchange 2 (6), 815.

Rickelton, W.A., Robertson, A.J., Hillhouse, J.H., 1991. The significance of diluent oxidation in cobalt nickel separation. Solvent Extraction and Ion Exchange 9, 73.

Ritcey, G.M., 1986. Iron-an overview of its control in solvent extraction of metals. Iron Control in Hydrometallurgy. Ellis Horwood, Chichester, England, 247–281.

Rydberg, J, Musikas, C., Choppin, G.R., 1992. Principles and practice of solvent extraction. 1st Edition. Marcel Dekker Inc., New York.

Sato, T., Kawamura, M., Nakamura, T., Ueda, M., 1978. The Extraction of Divalent Manganese, Iron, Cobalt, Nickel, Copper and Zinc from Hydrochloric Acid Solutions by Di-(2-Ethyl hexyl)phosphoric Acid. Journal of Applied. Chem. Biotechnology 28, 85.

Sing, S.K., Misra, S.K, Sudersanan., Dakshinamoorthy.A., 2009. Studies on the Recovery of Uranium from Phosphoric Acid Medium by D2EHPA/n-Dodecane Supported Liquid Membrane, Separation Science and Technology 44 (1), 169–189.

Sekine, T., Hasegawa, Y., 1977. Solvent Extraction Chemistry: Fundamentals and Applictions, New York, Marcel Dekker. 217

Sole, K.C., Hiskey, J.B., Ferguson, T.L. (1993). An Assessment of the Long-Term Stabilities of Cyanex 302 and Cyanex 301 in Sulfuric and Nitric-Acids, Solvent Extraction and Ion Exchange 11 (5), 783-796.

Todoli, J.M., Mermet, J.M., 2006. Sample introduction systems for the analysis of liquid microsamples by ICP-AES and ICP-MS. Spectrochimica Acta, Part B: Atomic Spectroscopy 61 (3), 239–283.

Technical Brochure of Cyanex 272, 2008.

Whewell, R. J., Foakes, J. H., Hughes, A. M., 1981. Degradation in hydroxyoxime solvent extraction systems. Hydrometallurgy 7, 7-26.

Appendix

Table A1: Summary of the Extractants Available for Hydrometallurgical Use.

Different category of extractant	Type	Examples	Commercial uses
Acid extractants	Carboxylic acids	Naphthenic acids, Versatic acids	Nickel, yttrium extraction and Copper/nickel separation.
	Alkyl phosphoric acids	Dialkyl phosphoric acids and sulphur analogues	Uranium, Zn, rare earth extraction and cobalt/nickel Separation.
	Alkylphosphonic acids	2-ethylhexyl phosphonic acid 2-ethylhexyl ester	Cobalt/nickel and rare earth separation.
	Alkyl phosphinic acids	Dialkyl phosphinic acids and sulphur analogues	Cobalt/nickel and rare earth separation,zinc and iron extraction,

Table A 1: (Contd.)

	Aryl sulphonic acids	Dinonyl naphthalene	Magnesium extraction
Acid chelating extractants	Hydroxyoximes	Alpha alkaryl hydroxyoximes, LIX 63, LIX 64N, LIX 65N	Copper and nickel Extraction
	Beta diketones	LIX 54	Copper extraction.
	Hydroxamic acids	LIX 1104	Fe, As, Sb and Bi extraction, Proposed for nuclear fuel reprocessing.
Basic extractants	Primary amines	Primene JMT, Primene 81R	Commercial use un-kown.
	Secondary amines	LA-1, LA-2.	Uranium extraction, proposed for vanadium and tungsten extraction

Table A1: (Contd.)

	Tertiary amines	Various Alamines, in particular Alamine 336.	Uranium, cobalt and tungsten extraction.
	Quaternary amines	Aliquat 336	Vanadium extraction, other possible uses for chromium, tungsten, uranium, etc.
	Mono N-substituted Amide Trialkyl guanidine	LIX 79	Gold extraction from cyanide Solution
Solvating extractants	Phosphoric, phosphonic and phosphinic acid esters and thio analogues	Tributyl phosphate , TOPO, CYANEX 921, CYANEX 923, CYANEX 471X.	Uranium oxide refining , nuclear fuel reprocessing, Iron extraction, Zirconium-Hafnium separation, Niobium-tantalum separation, rare earth separation, gold

Table A1: (Contd.)

	Various alcohols, ketones, esters, ethers,etc.	Butanol – pentanol Diisopropyl ether MIBK etc	Phosphoric acid extraction. Phosphoric acid extraction Nb/Ta separation, Zr/Hf separation
	Alkyl and aryl sulphides	di-n-hexyl sulphides	Palladium extraction.

Table A2: Summary of Historical Development in Hydrometallurgy

Early period	
(7 – 18)th century	In this time period the apparent transmutation of iron into copper by alchemists. Aqua regia was discovered by the Arab alchemist Jabir Ibn Hayyan (720–813 AD). Heap leaching was introduced for copper-containing pyrite in the Harz mountains in Germany and in Río Tinto in Spain. By leaching ashes after burning wood production of potash for soap and glass industries was started.
Modern Era	
1887 - 1930	In this time period cyanidation process and Bayer's process was invented and recovery of copper from leach solution in Chile by electrolysis was started. Development of the hydrometallurgical electrowinning zinc process at Trail and Anaconda and Caron process for nickel production by reducing laterites was started. Henglein process for pressure leaching of ZnS at high temperature in the presence of oxygen and sullivan process for ambient leaching of copper sulfides by ferric chloride solution.

Table A2: (Contd.)

Development during World War II	
1940s	Uranium technology was developed in connection with the US Manhattan Project aimed at producing an atomic bomb. Sodium carbonate as a leaching agent for uranium, the widespread use of ion exchange and solvent extraction for uranium recovery, and the separation of the lanthanides by ion exchange was introduced in this time period
Recent advances	
1940 - 1980	Introduction of pressure hydrometallurgy for nickel extraction from sulphide ores and the discovery of the microorganisms role in leaching process for extraction of copper from low-grade material. Uranium recovery from waste leach solutions and and galvanic action in leaching sulphide minerals was also introduced. Finally the hydrometallurgy of gold greatly advanced in this time period.

Table A3: Commercial Acidic Extraction Reagents.

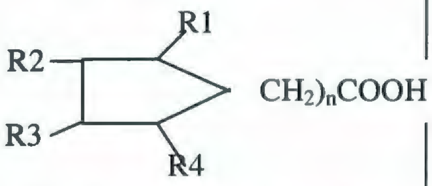
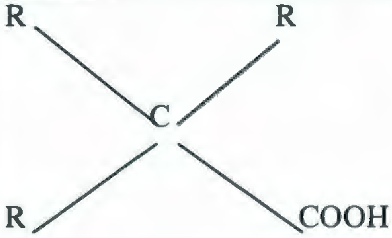
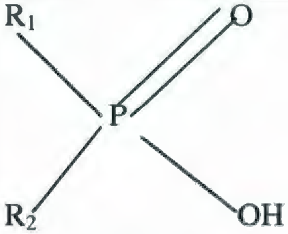
Reagent Class		Extractants
Carboxylic acid		Naphthenic acid
		R_1 = R_2= C_5= Versatic 10 R_1 = R_2= C_4 -C_5 =Versatic 911
Phosphorus acid		
Phosphoric acids	R_1 = OH R_2= $C_4H_9CH(C_2H_5)CH_2O$-	Mono-2-ethylhexylphos-phoric acid
	R_1 = R_2= $C_4H_9CH(C_2H_5)CH_2O$-	Di-2-ethylhexylphos-phoric acid (DE2HPA)
	R_1 = R_2=P- $CH_3(CH_2)_6CH_2C_6H_5O$-	Di-p-octylphenylphosphoric Acid (OPPA)

Table A3: (Contd.)

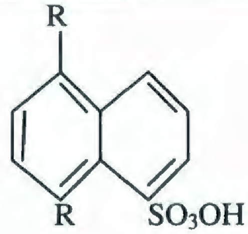
Phosphonic acids	$R_1 = C_4H_9CH(C_2H_5)CH_2$- $R_2 = C_4H_9CH(C_2H_5)CH_2O$-	2- ethylhexylphosphonic acid mono-2- ethyl ester(PC88A)
Phosphinic acid	$R_1 = C_4H_9CH(C_2H_5)CH_2$- $R_1 = R_2 =$ $CH_3(CH_2)_3CH_2CH(CH_3)CH_2$-	Di-2-ethylhexylphos-phinic acid (P - 229) Di -2,4,4-trimethylpentyl phosphinic acid.(Cyanex 272)
Thiophosphorus acid	$R_1R_2P(S)SH$ $R_1 = R_2 =$ $CH_3(CH_2)_3CH_2CH(CH_3)CH_2$-	Di -2,4,4-trimethylpentyl monothiophophinic acid.(Cyanex 302)
	$R_1R_2P(S)OH$ $R_1 = R_2 =$ $CH_3(CH_2)_3CH_2CH(CH_3)CH_2$-	Di -2,4,4-trimethylpentyl dithiophophinic acid.(Cyanex 301)
Sulphonic acid	 $R = C_9H_{19}$	5,8-dinonylnaphthanenesulphonic acid DNNSA

Table A4: Commercial Chelating Acidic Extractants.

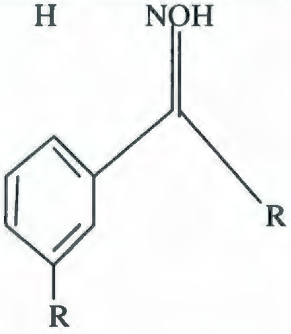
Reagent class	Structure	Extractants.
α – Hydroxyoxime	$R^1C(NOH)CH(OH)R^2$	5,8-diethyle-7-hydroxydodecan-6-oxime(LIX 63)
β- Hydroxyaryloximes		
	R^1= Phenyl; $R^2 = C_9H_{19}$	LIX 65N
	R^1= CH_3 ; $R^2 = C_9H_{19}$	LIX84
	R^1= H; $R^2 = C_9H_{19}$	P1
	R^1= H;P1 + Nonoyl phenol	P5000 series
	R^1= H;P1 + tridecanol	PT 5050
	R^1= H; P1 + ester modifier	M5640
	R^1= H; $R^2 = C_{12}H_{25}$	LIX860
	LIX84 + LIX860	LIX984

Table A4: (Contd.)

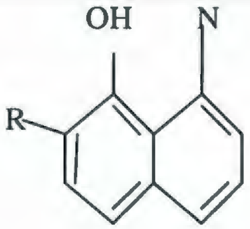
	LIX 984+ tridecanol	LIX622
8 – Quinolinol		
	R= 4-ethyl-1-methyloctyl	Kelex 100
	R= unknowns side chain	Kelex 108
	R= Unknown saturated alkyl	LIX 26
β- Diketones	$R^1COHCH_2COR^2$	
	R^1= R-C_6H_5 R^2= $CH_3(CH_2)_5$	LIX54

Table A5: Commercial Basic Extractants.

Reagent Class	Structure	Extractants
Primary amines	RNH_2 $R= (CH_3)_3C(CH_2(CH_3)_2)_4$	Primene JMT
Secondary amines	$R^1 R^2NH$	
	$R^1 = C_9H_{19}CH =CHCH_2$ $R^2 = CH_3C(CH_3)_2(CH_2C(CH_3)_2)_2$	Amberlite LA -1
	$R^1 = CH_3(CH_2)_{11}$ $R^2 = CH_3C(CH_3)_2(CH_2C(CH_3)_2)_2$	Amberlite LA -2
	$R^1 = R^2 = CH_3(CH_2)_{12}$	Adogen 283
	$R^1= R^2\ CH_3CH(CH_3)CH_2(CH_2)_6$	HOE F2562
Tertiary amines	$R^1= R^2 = R^3N$	
	$R^1= R^2 = R^3 = CH_3(CH_2)_7$	Trioctyl amine Alamine 300
	$R^1= R^2 = R^3= C_8$-C_{10} mixture	Alamine 336, Adogen 364 Hostarex A 327
	$R^1= R^2 = R^3= (CH_3)_2CH(CH_2)_5$	Tri isooctylamine. Adogen 363, Alamine 308, Hostarex A 324

Table A5: (Contd.)

	$R^1 = R^2 = R^3 =$ $(CH_3)_2CH(CH_2)_5$	Tri isooctylamine Adogen 363 Alamine 308 Hostarex A 324
	$R^1 = R^2 = R^3 =$ $(CH_3)_2CH(CH_2)_5$	Tri isooctylamine Alamine 310
	$R^1 = R^2 = R^3 = CH_3(CH_2)_{11}$	Adogen 363 Alamine 304
	$R^1 = R^2 = R^3 = CH_3(CH_2)_{11}$	Adogen 383
	$R^1 = R^2 = R^3 = C_{28}H_{57}$	Amnerlite XE 204
	$R^1 = CH_3(CH_2)_7$ $R^2 = CH_3(CH_2)_9$ $R^3 = CH_3(CH_2)_{11}$	Adogen 383
Quaternary amines	$R^1 R^2 R^3NCH_3(CH_2)_{12}$	Aliqut 336 Adogen 464 HOE W 2706

Table A6: Commercial Solvating Extractants.

Reagent class	Structure	Extractants
Carbon oxygen extractants amides	R^1CONR^2 $R^1 = CH_3$ $R^2 = CH_3(CH_2)_5CH(CH_3)$ $R^1 = R^2 =$ Unknown	N503 A101
Ethers	$CH_3(CH_2)_3OCH_2CH_2O$ $CH_2CH_2O(CH_2)_3(CH_3)$	Dibutyl carbitol (Butex)
Ketones	$(CH_3)_2CHCH_2COCH_3$	Methyl isobutyl ketone (MIBK)
Phosphorus –oxygen extractants	$R^1R^2R^3PO$	
Phosphorus esters	$R^1 = R^2 = R^3 = CH_3(CH_2)_2$ CH_2O	Tri –n – butyl phosphate (TBP)

Table A6: (Contd.)

	$R^1 = R^2 = CH_3(CH_2)_2 CH_2O$; $R^3 = CH_3(CH_2)_2 CH_2$	Dibutylbutylphophonate(DBBP)
	$R^1 = R^2 = CH_3O$, $R^3 = CH_3$	Dimethylmethylphosphonate
Phosphine oxides	$R^1 R^2 R^3 PO$	
	$R^1 R^2 R^3 = CH_3(CH_2)_6CH_2$	Tri-n- octylphosphine oxide (TOPO) Cyanex 921X
Phosphorus-sulphur extractants	$R^1 R^2 R^3 PS$	
	$R^1 = R^2 = R^3 = CH_3(CH_2)_6 CH_2$	Cyanex 471X
Carbon – sulphur extractants	$R^1 R^2 S$	Di hexyl sulfide
	$R^1 = R^2$	Diheptylsulphide

Table A7: Commercially Available Accelerator for Copper.

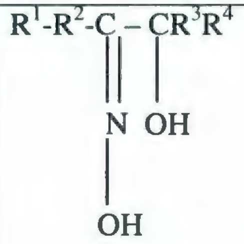
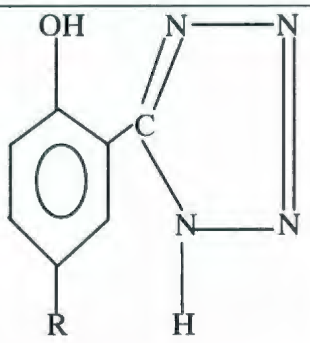
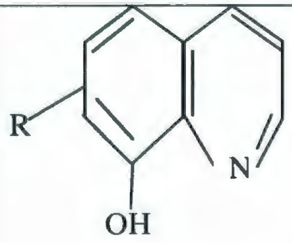
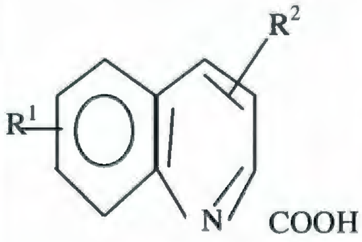
Type	General Formula	Comments
Aliphatic α- hydroxyoximes (LIX63)	 $R^1\text{-}R^2\text{-}\underset{\substack{\| \\ N \\ \| \\ OH}}{C} - \underset{\substack{\| \\ OH}}{C}R^3R^4$	Chelate (N,O) forming six membered rings
O- hydroxyarayl tetrazoles		Chelate (N,O) forming six membered rings
Alkylated hydroxyl-quinolines		Chelate (N,O) forming five membered rings
Alkylquinaldic acids		Acid and chelating (N,O) Properties five membered ring

Table A7: (Contd.)

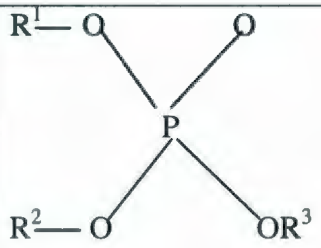
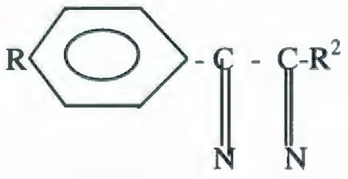
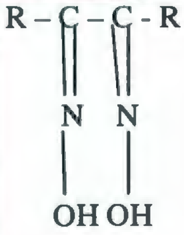
Alkyl phosphoric acids	 R^1, R^2, R^3 = H or alkyl	Acid
Sulphonic acids	$ROSO_2H$ R = alkyl or arayl	Acid
Carboxylic acid	RCO_2H R = Alkyl or aryl	Acid
Vicinal di oximes	 $R^2 = H> CH_3>C_7H_{15}$	
Vicinal dioxime	 $R-C(=N-OH)-C(=N-OH)-R$ $R = C_7H_{15}$	Not as good as 8

Table A7 (Contd)

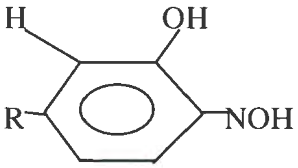
Substituted 2-hydroxycyclohexane		Unsatisfactory

Table A8: Typical Properties of Cyanex 272.

Properties	Description
Bis(2,4,4-trimethylpentyl)phosphinic acid	85%
Appearance	Colourless to light amber liquid
Specific Gravity at 24°C	0.92
Viscosity, Brookfield at 25°C at 50 °C	142cp 37 cp
Solubility in distilled H_2O at pH 2.6 at pH 3.7	16 µg/mL 38µg/mL
Boiling Point	>300 °C
Flash Point, closed cup	>108 °C
Specific Heat @ 52°C	0.48 cal/gm/oC
Thermal Conductivity	2.7 x 10-4 cal/cm/sec/°C

Table A9: Typical Properties of D2EHPA.

Properties	Description
Appearance	Colourless
Form	Liquid
Odor	Not determined.
Density	0.965 g/cm^3
Solubility/miscibility in water	<1 g/L
Boiling Point/Boiling range	48 ^{o}C
Flash Point, closed cup	>110 ^{o}C
Vapor pressure	Not determined.

Table A10: Chemical and Physical Properties of 1-Decanol.

Properties	Description
Form	Liquid
Appearance	Colourless
Odor	Sweet
Density	0.8287 g/cm^3
Viscosity, dynamic at 20^oC	13.8 mpas
Solubility /miscibility in water at 25^oC	0.037 g/L
Boiling Point/Boiling range	(230 - 232) ^oC
Flash Point	82 ^oC
Melting point/ Melting range	7 ^oC

Table A11: Physical and Chemical Properties of Kerosene.

Properties	Description
Form	Liquid
Appearance	Colourless
Odor	Mild petroleum
Density	0.80 g/cm^3
Viscosity,	1.05 cp
Solubility /miscibility in water	Negligible
Boiling Point/Boiling range	(165 - 204) ^oC
Flash Point	82 ^oC
Melting point/ Melting range	< - 5.4 ^oC

Table A12: Washing of Extractant Solution With 1M HCl.

Contact No.	P (ppm) Cyanex272
1	14
5	5
6	1.65
7	1.65

Table A13: ICP Result for Pure H_2SO_4.

file =		0								
run =		waters								
owner =		AliAzam/MHossain								
date =		Jun 17 09	12:45 pm							
calculated:		17-Jun-09	15:31:54							
waters (w), biol. (b):		w								
avg diln g/g:		0.353385								
conc given in:		ppb								
conc in:		wet								
interference correction?										
intf. factor										
ppm intf.										
lld - intf.										
lld - ppb/ppm										
lld - blank		0.362	0.837	0.73	50680		0.295	9.249	84.473	3.09
bk average					133939	6468				
Sample		Li 7	Be	B	C	N	Mg	Al	Si	P
name		ppb	ppb	Ppb	ppb	cps	ppb	ppb	ppb	ppb
blanknano-1		<0.84	<1.95	2.98		6313	2.4	<21.6	<197	<7
t171		5.47	<2.91	12.1		6194	2574.1	<32.1	1193	95
t155		32.91	0.03	91.48		6001	10980.3	52	4282	<10
t153		49.9	<2.91	90.87		6151	8276	<32.2	2238	<11
0.001M H2SO4 1st dil		<10.85	34.98	166.91		8106	59	<277.5	7331	1842
CF-1 2nd dil		<1100.56	<2546.00	61994.33		6829	8547516	<28136.7	<256975	<9401
SXR-1 2nd dil		<964.83	52.98	49283.32		6548	6395201	<24666.7	<225284	18042

Table A14: ICP Result for Decanol and Escaid.

file =		0								
run =		waters								
owner =		M.AliAzam								
date =		Oct 14 09 11:55 am								
calculated:		15-Oct-09	10:38:39							
waters (w), biol. (b):		w								
avg diln g/g:		0.054162								
conc given in:		ppb								
conc in:		wet								
interference correction?										
intf. factor										
ppm intf.										
lld - intf.										
lld - ppb/ppm										
lld - blank		1.042	4.879	4.623	0.435	1.037	80.95	14.107	17527.5	1906.894
bk average										
Sample		Li 7	Be	B	Mg	Al	Si	P	S	Cl
name		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
blanknano1		<0.57	<2.66	<2.52	0.6	1.9	153	<8	<9541	<1038
t171		6.97	<2.56	19.34	2797	20.5	1684	104	<9212	11095
t155		37.89	<2.32	93.22	12061	75.5	5124	<7	25063	24153

Table A14: (Contd.)

t153		54.72	<2.75	107.82	9154	42.3	2879	<8	17418	35645
t191		4.24	<2.63	38.57	3819	57.5	1925	<8	18759	14295
t193		2.93	2.92	38.27	4586	45.7	6056	<7	<8345	33378
blanknano2		<3.34	<15.62	<14.80	5	<3.3	<259	<45	<56106	<6104
m32755o	C1	<3.13	<14.64	23.51	45	<3.1	<243	23061	55686	<5722
m32756a	C2	<3.47	<16.22	21.62	18	<3.4	<269	10752	73034	<6341
m32757m	C3	<3.47	<16.24	183.49	45	11.5	<269	9568	56278	<6346
m32758y	C4	<3.49	<16.34	35.34	8	<3.5	274	8017	57585	<6386
m32759k	D1	<3.48	<16.27	60.13	86	<3.5	831	131662	36466	<6359
m32760y	D2	<3.41	<15.95	70.61	65	<3.4	637	103686	50198	<6235
m32761o	D3	5.49	<16.63	91.02	55	<3.5	1350	91079	72132	<6500
m32762e	D4	<3.46	<16.18	59.64	31	<3.4	389	77900	51672	<6323
m32763u	Decanol	<3.84	<17.97	65.84	136	48	759	2499	69093	<7022
m32764e	Escaid 110	<3.39	<15.85	175.45	262	77	<263	2757	36570	<6194
m32755o dup		<3.41	<15.98	55.55	45	<3.4	<265	22177	38867	<6245
m32762e dup		<3.40	<15.92	63.18	30	<3.4	<264	74712	44047	<6222

Table A15: ICP Result for Washing.

file =		0								
run =		waters								
owner =		M.AliAzam w2273								
date =		Oct 23 09	10:34 am							
calculated:		23-Oct-09	14:28:38							
waters (w), biol. (b):		w								
avg diln g/g:		0.057366								
conc given in:		ppb								
conc in:		wet								
interference correction?										
intf. Factor										
ppm intf.										
lld - intf.										
lld - ppb/ppm										
lld – blank		0.848	3.659	12.543	1.034	3.935	758.374	39.619	9929.322	143.981
bk average										
Sample		Li 7	Be	B	Mg	Al	Si	P	S	Cl
Name		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
blanknano1		5.841	<9.52	<32.63	13.18	<10.2	<1973	<103	<25831	<375
t171		6.431	<2.04	19.791	2828.09	18.97	1569	109	<5527	10419
t155		34.971	<1.85	105.092	12202.12	72.4	4988	<20	22753	24084

Table A15: (Contd.)

t153		54.435	<2.18	102.411	9271.4	41.82	2677	<24	15739	35852
t191		4.66	<2.09	43.296	3955.85	59.5	2020	<23	20045	15151
t193		2.772	2.564	35.411	4495.38	42.84	5534	<20	<5007	31333
m32824u	C-5	<3.47	<14.97	63.379	40.59	<16.1	<3102	7651	<40614	<589
m32825x	C-6	<3.40	<14.66	<50.24	19.14	<15.8	<3038	7004	62149	<577
m32826b	C-7	<3.63	<15.69	66.335	24.91	<16.9	<3251	5968	60920	<617
m32827f	C-8	<3.43	<14.81	63.573	45.81	<15.9	<3070	25876	52532	<583
m32828j	D-5	<3.35	<14.48	54.562	27.99	50.12	<3001	64310	42205	<570
m32829m	D-6	<4.00	31.092	<59.15	34.38	<18.6	<3576	48850	73923	<679
m32830v	D-7	<3.77	<16.27	<55.77	20.63	<17.5	<3372	35490	47446	<640
m32831t	D-8	<3.71	<16.00	<54.85	43.85	<17.2	<3316	6401	60677	<630
m32831t dup		<3.53	<15.25	<52.27	40.22	<16.4	<3161	6099	58492	<600
m32824u dup		<3.39	<14.65	55.077	14.68	<15.7	<3035	7920	49702	<576

Table A16: ICP Result for Acid Effect 1.

file =	0									
run =	waters									
owner =	Md Ali Azam									
date =	Jun 04 09 15:18 pm									
calculated:	05-Jun-09	13:00:27								
waters (w), biol. (b):	w									
avg diln g/g:	0.427913									
conc given in:	ppb									
conc in:	wet									
interference correction?										
intf. Factor										
ppm intf.										
lld - intf.										
lld - ppb/ppm										
lld – blank	0.002	0.007	0.007	0		0.001	0	0	0.008	0.057
bk average				313902	7233					
Sample	Li 7	Be	B	C	N	Mg	Al	Si	P	S
Name	ppb	ppb	ppb	ppb	cps	ppb	ppb	ppb	ppb	ppb
Blanknano	<0.00	<0.00	<0.00	<0	2672	0.1	<0.0	<0	<0	<0
t155	30.64	<0.03	86.08	<0	5851	10282.8	55.7	4276	<0	19505
t153	47.34	<0.03	88.73	<0	6014	7870.1	31.4	2195	<0	12771
0.05M	<0.06	<0.23	20.29	1068524	6917	50	1164.4	<0	29348	2409167
0.5M	3.72	<0.25	295.5	1638397	7657	42	1414.2	1768	31185	9545518
1.0M	5.79	15.6	485.14	3161848	8484	93	1637.2	2878	35085	21924351
2.0M	1.52	10.82	223	4438989	8569	52	1425	2432	31946	35147605

Table A17: ICP Result for Acid Effect 2.

file =		0								
run =		waters								
owner =		MdAliAzam								
date =		Jul 23 09 12:05 pm								
calculated:		23-Jul-09	14:46:13							
waters (w), biol. (b):		w								
avg diln g/g:		0.350795								
conc given in:		ppb								
conc in:		wet								
interference correction?										
intf. Factor										
ppm intf.										
lld - intf.										
lld - ppb/ppm										
lld – blank		0.129	0.248	1.749	14253		0.145	0.388	54.832	2.618
bk average					197278	9205				
Sample		Li 7	Be	B	C	N	Mg	Al	Si	P
Name		ppb	ppb	ppb	Ppb	cps	ppb	ppb	ppb	ppb
Bnano		<2.15	<4.15	<29.26		9150	11.1	7.9	<917	<44
t143		16.11	9.39	31.43	55474	9068	9664.2	18.5	9703	17
t145		23.41	8.95	40.45	<41869	8777	7757.2	49.5	4566	11
t155		32.55	1.11	95.79	<43972	8756	10922.8	57.8	4495	<8
0.00001M		<3.08	<5.95	171.05		9152	178	39.9	<1314	49822
0.0001M		<2.86	<5.53	78.83		9201	110	24.8	<1222	48859
0.001M		<2.87	7.82	54.02		9136	1151	320.1	<1225	45885
0.01M		<2.91	4.66	105.84	345477	9609	162	181.4	<1240	39676

Table A18: ICP Result for Extractant Concentration and Kinetic Study.

file =			0								
run =			waters								
owner =			A.Bertin(w2258)/M.Azam(2259)								
date =			Aug 27 09 16:16 pm								
calculated:			40053.39	40053.39							
waters (w), biol. (b):			w								
avg diln g/g:			0.060844								
conc given in:			ppb								
conc in:			wet								
interference correction?											
intf. factor											
ppm intf.											
lld - intf.											
lld - ppb/ppm											
lld - blank		12.34153	0.515514	5.603485	5.987701	1.293774	3.44778	1469.78	70.83012	41625.54	1187.3
bk average											
Sample		Li 6	Li 7	Be	B	Mg	Al	Si	P	S	Cl
name		ppb	ppb	ppb	ppb	Ppb	ppb	ppb	ppb	ppb	ppb
blank-nano-1		<7.12	<0.30	<3.23	<3.46	1.1	<2.0	<848	<41	<24027	<685
t171		<7.29	6.71	0.24	18.06	2663.5	18.1	880	103	-3591	10211
t143		14.12	16.28	9.25	31.49	10218	21.9	12184	<42	<24719	23230
t145		17.11	24.21	7.11	41.57	8305.1	61.1	5325	<36	332	40224
t155		32.74	34.26	<3.00	100.37	12175	74.9	5764	<38	22951	25386

Table A18: (Contd.)

t153		44.38	52.9	<3.54	96.27	8770.8	39.8	2472	<45	8089	35107
t191		<7.50	3.79	<3.41	43.36	3770.9	58.2	1923	<43	<25297	14495
t193		<6.60	2.76	3.84	39.22	4450.5	44.5	6997	<38	<22266	33584
blank-nano-3		<54.85	<2.29	<24.90	<26.61	28.1	<15.3	<6532	<315	<184995	<5277
m32570f	5%	<50.99	3.3	<23.15	131.86	75.6	<14.2	<6073	53662	<171992	<4906
m32571r	10%	<50.92	10.12	<23.12	88.2	90.4	<14.2	<6064	90739	<171736	<4898
m32572d	25%	<50.82	<2.12	<23.07	146.14	179.8	65.1	<6052	152516	<171410	<4889
m32573p	50%	<49.68	<2.08	<22.56	112.86	123.6	<13.9	<5916	199388	<167558	5256
m32774c	100%	<48.91	<2.04	<22.21	83.03	157.2	26.9	<5825	276463	<164965	<4705
m32575o	10 min	<49.64	<2.07	<22.54	69.89	171.3	26	<5912	136103	<167428	<4776
m32576a	1 hr	<49.19	<2.05	<22.34	144.28	186.5	<13.7	<5859	143684	<165924	<4733
m32577m	2 hr	<49.32	<2.06	<22.39	375.23	121.5	<13.8	<5874	136763	<166346	<4745
m32578y	5 hr	<48.85	<2.04	<22.18	2072.42	97	<13.6	<5817	142613	<164745	<4699
m32579k	22 hr	1364.34	1347.26	<22.51	4289.6	192	27.6	<5904	152228	<167198	<4769
m32580c	24 hr	<49.03	<2.05	<22.26	107.18	283.2	18.7	<5839	155928	<165364	<4717
m32580c dup		<48.77	<2.04	<22.14	76.35	275.1	15.2	<5808	156557	<164495	<4692
m32570f dup		<50.52	<2.11	<22.94	133.93	66.2	<14.1	<6017	54503	<170399	<4860

Table A19: ICP Result for Extractant Concentration Study.

file =		0									
run =		waters									
owner =		M.Ali Azam (w2254)									
date =		Aug 07 09 10:52 am									
calculated:		07-Aug-09	15:04:10								
waters (w), biol. (b):		w									
avg diln g/g:		0.05504									
conc given in:		ppb									
conc in:		wet									
interference correction?											
intf. factor											
ppm intf.											
lld - intf.											
lld - ppb/ppm											
lld - blank		1.311	5.107	51.556	3.444	11.059	541.566	221.396	56186.09	10583.25	1962.389
bk average											
Sample		Li 7	Be	B	Mg	Al	Si	P	S	Cl	Ca 43
name		ppb	ppb	ppb	ppb	ppb	ppb	ppb	Ppb	ppb	ppb
bnano-1		<2.62	<10.22	<103.17	<6.9	<22.1	<1084	<443	<112435	<21178	<3927
t171		5.91	<2.73	<27.54	2392	15.5	1158	<118	<30010	9302	6006
t143		16.48	7.11	<27.70	9390	13.3	8845	<119	<30183	21977	49339

Table A19: (Contd.)

t145		24.79	8.35	35.71	7709	46.8	4235	<102	6703	38202	27551
t155		31.32	<2.47	85.92	10657	52.1	4043	<107	20254	22253	40381
t153		50.41	<2.92	83.79	8151	27.9	2236	<127	15481	33490	25751
t191		4.36	<2.80	33.05	3366	40.6	1730	<121	17135	13328	27198
t193		2.71	3.6	31.36	4068	29.2	5141	<107	<27185	30986	16367
bnano-2		<2.70	<10.51	<106.10	<7.1	<22.8	525	83	15709	1496	456
m32543l	1%	<5.93	<23.11	21.67	88	<50.0	587	16581	128073	6801	1522
m32544c	5%	<6.04	6.47	387.23	102	<50.9	<2495	13054	112887	4345	1678
m32545t	15%	<6.08	4.94	14.46	120	<51.3	228	20209	132227	7485	3047
m32546k	50%	<7.33	<28.57	23.57	191	<61.9	<3029	41196	100369	5226	1957
m32547c	100%	<6.23	<24.26	3.07	291	<52.5	234	86047	84226	<50269	<9321
diw		<7.22	0.22	<283.77	105	<60.9	<2981	395	<309251	<58251	<10801
diw		<7.22	<28.11	<283.77	112	<60.9	<2981	<1219	<309251	<58251	<10801

Table A20: ICP Result for Metal Effect Study.

file =		0								
run =		waters								
owner =		M.AliAzam w2279 rerun								
date =		Nov 09 09 11:30 am								
calculated:		09-Nov-09	15:46:26							
waters (w), biol. (b):		w								
avg diln g/g:		0.03735								
conc given in:		ppm								
conc in:		wet								
interference correction?										
intf. factor										
ppm intf.										
lld - intf.										
lld - ppb/ppm										
lld - blank		0.002	0.018	0.004	0.001	0	0.937	0.148	35.048	4.261
bk average										
Sample		Li 7	Be	B	Mg	Al	Si	P	S	Cl
name		ppm	ppm	ppm	ppm	ppm	ppm	Ppm	ppm	ppm
bnano1		<0.00	<0.01	<0.00	0	<0.0	<0	<0	<10	<1
t191		0.004	<0.01	0.044	3.77	0.05	2	<0	22	15
t193		0.003	<0.01	0.044	4.58	0.04	6	<0	<12	34
t155		0.036	<0.01	0.105	11.88	0.07	5	<0	25	25

Table A20: (Contd.)

t153		0.061	<0.01	0.111	9.51	0.08	3	<0	15	38
bnano2		<0.01	<0.04	<0.01	0.01	<0.0	<2	<0	<85	<10
m32958t	washing HCl-4	0.012	<0.05	0.067	0.43	0.06	<3	5	<96	36100
m32957k	washing HCl-1	0.011	<0.05	0.062	1.64	0.51	<3	14	<95	36135
m32951j	1 g/L	<0.53	<4.10	<0.80	1.03	<0.1	<207	<33	2958	<944
m32951j dup		<0.60	<4.64	<0.91	0.38	<0.1	<235	<37	2157	<1068
m32952s	5 g/L	<0.66	<5.05	<0.99	0.81	<0.1	<256	46	6161	<1162
m32952s dup		<0.60	<4.60	<0.90	1.56	<0.1	<233	40	6229	<1060
m32953b	10 g/L	<0.57	<4.39	<0.86	0.63	<0.1	<222	48	11318	<1011
m32954k	50 g/L	4.355	<4.41	<0.87	2.79	<0.1	<224	<35	38608	<1017
m32955t	80 g/L	<0.50	<3.87	0.99	15.77	<0.1	<196	<31	53422	<892
m32956c	Co-w/o washing	<0.45	<3.45	69.54	8971.88	1.77	<175	<28	76367	<796

Table A21: ICP Result for Kinetic Study at Different Temperature.

file =		0								
run =		waters								
owner =		M.Azam(2262)								
date =		Sep 15 09 10:26 am								
calculated:		15-Sep-09	16:26:09							
waters (w), biol. (b):		w								
avg diln g/g:		0.041775								
conc given in:		ppb								
conc in:		wet								
interference correction?										
ppm intf.										
lld - intf.										
lld - ppb/ppm										
lld - blank		3.346	15.445	54.441	119300		5.877	12.544	455.262	80.009
bk average					450897	8943				
Sample		Li 7	Be	B	C	N	Mg	Al	Si	P
name		ppb	ppb	ppb	ppb	cps	ppb	Ppb	ppb	ppb
bnano-1		<2.62	<10.22	<103.17	0	10034	<6.9	<22.1	<1084	<443
t171		5.98	<2.73	<27.54	<41692	9314	2421	15.69	1172	<118
t143		16.68	7.2	<27.70	<41933	9159	9504	13.46	8952	<119
t145		25.09	8.45	36.14	<35979	9056	7803	47.37	4286	<102
t155		31.7	<2.47	86.96	<37786	8990	10786	52.73	4092	<107
t153		51.02	<2.92	84.81	47054	9254	8250	28.24	2263	<127
t191		4.41	<2.80	33.45	<42819	9142	3407	41.09	1751	<121
t193		2.74	3.6	31.74	<37769	9184	4117	29.55	5203	<107

Table A21: (Contd.)

blank-nano-2		<9.51	<43.88	<154.68		8744	<16.7	<35.6	<1294	<227
m32615v	C-50 10MIN	<9.10	<42.01	<148.07	352712	8701	58	<34.1	<1238	23665
m32616e	C-50 1 HR	<9.05	<41.78	<147.26		8376	66	<33.9	<1231	23613
m32617o	C-50 3 HR	215.75	<43.18	818.87	387061	8393	820	<35.1	<1273	51708
m32618x	C-50 22HR	<9.07	<41.85	<147.53	333530	8414	274	<34.0	<1234	27093
m32619g	D-50 10 MIN	<9.28	<42.84	<151.01		8490	124	<34.8	1838	159645
m32620w	D-50 1 HR	<9.67	<44.63	969.87		8337	155	<36.3	<1316	151754
m32621t	D-50 3HR	19.53	<41.67	<146.88	279200	8677	126	<33.8	2233	157034
m32622r	D-50 5HR	<9.53	<43.99	362.95	706821	8725	141	<35.7	9123	155193
m32623o	TC-30	<9.34	<43.12	<152.01	820100	8802	49	<35.0	2199	25236
m32624l	TC-40	<9.36	<43.20	298.65	1264420	9021	92	<35.1	3151	29440
m32625j	TC-50	<9.22	<42.58	206.53	1014305	8773	68	<34.6	2240	28914
m32626g	TD-30	<9.57	<44.19	<155.76	551633	8682	110	<35.9	2552	171813
m32627e	TD-40	<9.06	<41.81	320.35	768586	8927	165	<34.0	3834	170639
m32628b	TD-50	<9.55	<44.10	320.01	1003038	8778	116	<35.8	3568	173870
m32628b dup		<9.37	<43.28	310.92	860810	8775	119	<35.2	3196	174149

Table A22: ICP Result for High Temperature Study.

file =		0								
run =		waters								
owner =		MAliAzam (w2257)								
date =		Aug 24 09 11:16 am								
calculated:		25-Aug-09	9:57:16							
waters (w), biol. (b):		w								
avg diln g/g:		0.071277								
conc given in:		ppb								
conc in:		wet								
interferencecorrection?										
intf. factor										
ppm intf.										
lld - intf.										
lld - ppb/ppm										
lld - blank		0.213	7.427	6.98	2.002	2.07	1602.998	261.109	21586.42	2608.919
bk average										
Sample		Li 7	Be	B	Mg	Al	Si	P	S	Cl
name		ppb	ppb	ppb	ppb	ppb	ppb	Ppb	ppb	ppb
blanknano		<0.98	<34.03	<31.98	9.5	<9.5	<7344	<1196	<98898	<11953
t171		6.21	2.05	24.69	2875	32.3	1432	105	<14931	10689
t143		17.72	11.6	38.58	10720	52	11885	<182	<15017	23928
t145		26.41	8.73	48.22	8766	66.9	5362	<156	<12885	42391
t155		37.52	<4.66	109.7	12428	90.6	5394	<164	19688	25094
t153		54.26	<5.50	100.41	9086	43.5	2402	<193	2939	35412
t191		4.68	<5.29	48.4	3972	62	1990	<186	15921	14933

Table A22: (Contd.)

t193		2.44	5.51	45.16	4751	47	6821	<164	<13527	34874
m32557o	1 min	<1.01	<35.21	57.32	85	40.7	<7599	27943	71131	<12368
m32561v	10 min	1.44	<35.11	67.75	83	<9.8	<7577	26628	51030	<12332
m32558d	30 min	<1.01	<35.13	88.84	126	68.7	<7583	28903	88603	1773
m32559t	1 hr	<1.02	<35.59	122.76	184	66.8	<7681	28086	42157	47511
m32560h	5 hr	2.01	<35.84	79.32	262	25.5	<7737	27767	63321	<12592
m32562j	1 day	<1.03	<35.95	<33.79	256	24.8	<7760	32409	106602	<12629
m32557o dup	1 min *	<1.00	<35.01	71.83	93	37.6	<7557	28908	63020	<12300
dw		2.55	<35.29	<33.17	16	<9.8	<7617	<1241	13944	<12397

Table A23: ICP Result for Manganese Study.

file =		0								
run =		waters								
owner =		M.AliAzam w2296								
date =		Jan 26 10	9:56 am							
calculated:		26-Jan-10	13:52:10							
waters (w), biol. (b):		w								
avg diln g/g:		0.002883								
conc given in:		ppm								
conc in:		wet								
interference correction?										
intf. Factor										
ppm intf.										
lld - intf.										
lld - ppb/ppm										
lld – blank		0.054	0.098	0.404	289	0.274	0.158	20.32	1.742	54.63
bk average					66600					
Sample		Li 7	Be	B	C	Mg	Al	Si	P	S
Name		ppm	ppm	ppm	ppm	ppm	Ppm	ppm	ppm	ppm
bnano-1		<0.00	<0.00	<0.01	40	<0.0	<0.0	<0.6	<0.0	<2
t155		0.037	<0.00	0.095	43	12.43	0.07	5.19	<0.0	27.03
t153		0.055	<0.00	0.093	50	9.71	0.05	3.24	<0.1	22.77
t143		0.02	0.005	0.021	17	10.68	0.02	10.87	<0.0	7.32

Table A23: (Contd.)

t191		0.005	<0.00	0.029	<8	3.83	0.06	2.17	<0.0	20.23
t193		0.004	0.004	0.033	<8	5.15	0.05	7	<0.0	5.33
bnano-2		<0.00	<0.01	<0.02	46	<0.0	<0.0	<1.1	<0.1	3.58
m33581g	Mn-0.5-C	<0.01	<0.02	<0.08	870	0.1	<0.0	<4.1	29.44	511.99
m33581g dup		0.012	<0.02	<0.08	851	0.11	0.03	<3.9	26.57	466.72
m33582i	Mn-1-C	0.003	<0.02	<0.07	1000	0.21	<0.0	<3.6	28.36	721.63
m33582i dup		<0.01	<0.02	0.111	999	0.15	<0.0	<3.8	28.38	729.17
m33583k	Mn-5-C	0.006	<0.02	0.195	1053	0.21	<0.0	<4.0	28.75	3313.7
m33583k dup		0.003	<0.02	0.206	1025	0.21	<0.0	<3.9	28.31	3298.34