Western Australian School of Mines

Department of Minerals Engineering and Extractive Metallurgy

Extraction and Separation of Cobalt From Acidic Nickel Laterite Leach Solutions Using Electrostatic Pseudo Liquid Membrane (ESPLIM)

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DECLARATION

'This thesis contains no material which has been accepted for the award of any other degree or diploma in any university. To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made'

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SUMMARY

Approximately 70% of the western world's known nickel reserves are contained in laterite ores, but only 30% of the world's nickel production comes from these ores. This is due to the lack of economically viable technology to extract the nickel from these ores. However, recent advances in pressure acid leaching technology have resulted in new commercial attempts to extract nickel and its valuable by-product, cobalt, from laterite ores. The commissioning of three nickel laterite projects in Western Australia in the late 1990s represents the first of these new generation nickel operations, with several other projects, in Australia and overseas, in various stages of development.

Unfortunately, several technical issues have hindered full production in these new refineries. Some of these problems are directly attributable to the mixer-settler contactors used in the solvent extraction process. This has highlighted a need to develop alternative contactors for industrial use.

Electrostatic Pseudo Liquid Membrane (ESPLIM) is an alternative, novel technique to conduct the solvent extraction process. It combines the basic principles of solvent extraction, liquid membrane and electrostatic dispersion into a simple, compact reactor that utilises many advantages of each technique. The aim of this study was to develop a method of extracting and separating cobalt from an acidic nickel laterite leach solution using ESPLIM.

Bench scale tests using synthetic and actual leach solutions have shown that:

- the design and construction materials of the baffle plate and electrodes have a significant effect on the performance of the reactor.
- an AC power supply provided better droplet dispersion than a DC power supply.
- an increase in the applied electric field strength above a critical value resulted in a decrease in the aqueous droplet size and an increase in residence time. These effects increased the extraction efficiency and the concentration of the loaded strip solution. However, further increases in applied electric field strength decreased efficiency due to excessive levels of swelling and leakage

- the known extraction isotherms for cobalt and nickel apply in the ESPLIM technique.
- salts of soluble organic acids influence extraction efficiency by changing the aqueous pH and interfacial tension.
- the use of ammonia was found to be effective as a replacement for salts of soluble organic acids.
- the ESPLIM reactor can cope with large changes in the flow rates of both feed and strip solutions. However, an increase in the feed flow rate should be accompanied by a relative increase in the strip flow rate to maintain high extraction efficiencies.
- the baffle design has a significant impact on the levels of swelling and leakage
- provided the electrostatic field strength is maintained and flow rates are increased proportionately to the size of the reactor, no significant scale-up issues were observed, indicating that the data generated in bench scale studies could be applied to plant scale contactors.

The optimum conditions, devised as a result of this investigation, to extract cobalt from an acidic nickel laterite leach solution using the ESPLIM technique are as follows: an applied electric field strength of 5.5 kV/cm, a raffinate pH of 5.5, a solvent containing 10% Cyanex 272 with 5% TBP in Solvent HF diluent, a feed to strip flow ratio of approximately 5 and a 1 M H_2SO_4 strip solution. At these conditions, almost complete cobalt extraction is achieved after only two extraction stages. A comparable extraction using conventional mixer-settlers could only be achieved after five stages.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Overview of the Nickel Laterite Industry

Approximately 70% of the world's nickel reserves are contained within nickel laterite ores, with the remaining nickel associated with sulphide deposits (Bacon, Dalvi and Parker, 2000). However, most of the world's nickel is produced from sulphide ores because the pyrometallurgy technology used to treat these ores is well established and relatively cheap.

A recent decrease in the nickel price placed considerable pressure on nickel sulphide operations and concerns over the quantity of sulphide reserves meant that attention was drawn to the relatively untouched but abundant nickel laterite deposits. New hydrometallurgy technology has become available to process nickel laterite ores at considerably lower cost than nickel sulphide operations. However, as widely reported, this attraction has been slightly diminished due to technical difficulties that continue to hinder these operations and thus, the expected increase in low cost nickel to the market.

Cobalt is commonly associated with nickel, either in sulphide or laterite deposits, because of their chemical similarities. Although often present in the ore at lower concentrations than nickel, cobalt demands a much higher price and therefore becomes a valuable by-product for the nickel refinery, if recovered.

One advantage of the new technology used to process nickel laterite ores is that cobalt can be recovered as a separate product. The credits gained from the recovery of this valuable by-product are essential for the supply of low cost nickel to the market. In addition, cobalt contamination of the final nickel product impacts on the price that the nickel refiners can obtain. Thus, the complete recovery and separation of cobalt from nickel is essential in any further development and advancement of this new technology.

1.1.1 The Importance of Nickel

The worldwide demand for nickel is dominated by the stainless steel industry, which accounts for approximately two thirds of the western world's nickel consumption

(Maurer, 2000). Nickel is used as an alloying element to produce a wide range of steels with different physical properties. Stainless steel is non-corrosive and is used extensively in the chemical, construction, automobile and shipbuilding industries.

Stainless steel has enjoyed strong growth of over 4% per annum since 1960 and is expected to continue at a projected rate of approximately 4-6% per annum (Bacon, Dalvi and Parker, 2000). Increased stainless steel consumption is partly due to an increase in demand for corrosion resistant materials and the rapid industrial development of Asian countries such as Japan, Chinese Taipei and South Korea (Maurer, 2000).

Nickel is also used in non-ferrous alloys, electroplating, alloy steels, batteries and the foundry industry (Clow, 1992). The demand for nickel-cadmium batteries for mobile phones, portable computers and other electronic equipment is expected to contribute to the world's increasing nickel consumption.

Because of increasing stainless steel production and an increase in demand for nickel-containing products, the future for nickel production is one of sustained growth, with nickel prices expected to be favourable, at least for low cost producers (Bacon, Dalvi and Parker, 2000).

1.1.2 Nickel Products

Nickel is saleable as one of two products: Class I or Class II. Class I nickel products have a purity of over 99% and are available as nickel cathodes, pellets, briquettes and rondelles. Superalloy and plating industries are the major consumers of Class I nickel products, as they require raw materials with a low impurity content (Clow, 1992).

Class II nickel products have a lower nickel content and are predominantly used in the stainless steel industry either as ferro-nickel alloys (16-35% nickel) or nickel oxide sinter (75-90% nickel). Ferro-nickel alloys are favoured in the steel-making industry as foundries receive 600-800 kg of 'free' iron for every 1 tonne of ferro-nickel bought. Nickel oxide sinter is favoured in some steel-making operations because of the 'free' oxygen in the oxide, which promotes the desired exothermic reaction (De Guingand, 1994).

1.1.3 Processing of Nickel Laterite Ores

Nickel products, either Class I or II, are the result of a metallurgical process that involves physical and chemical treatment of the ore. Nickel ores are classified as either sulphides or oxides (laterites), depending on the mineralogy of the ore. Nickel sulphide ores have been traditionally upgraded using the process of froth flotation. The concentrated solids from the flotation stage are then used as feed for smelting.

Most laterite ores are difficult to process because of their low grade and cannot be upgraded through physical means such as flotation (Canterford, 1994). Hence, it is not economically viable to use existing minerals processing and pyrometallurgical technology to produce a nickel product from laterite ores.

Since pyrometallurgy is not applicable to treat most nickel laterites, attention was drawn to the use of hydrometallurgy. There have been two hydrometallurgical routes developed to treat laterite ores: the reduction roast – ammonia-ammonium carbonate leach (Caron) process and the pressure acid leach (PAL) process.

Numerous plants utilising the Caron process have been built but most of them have performed poorly with the exception of the Yabulu plant in Queensland (Reid, 1996; O'Kane and Gormely, 2000). The new nickel laterite developers have disregarded the Caron process because of higher energy costs, low nickel and cobalt recoveries and higher capital costs (Motteram, Ryan and Weizenbach, 1997; Reid, 1996).

The pressure acid leach process was developed by the Freeport Sulphur Company of Louisiana and was first implemented on a plant scale at Moa Bay, Cuba in 1959 (Boldt Jr., 1967). In this process, the slurried ore is pumped into a series of high pressure/high temperature autoclaves, where it is leached with sulphuric acid. The leached slurry is then transferred through heat exchangers to a solid–liquid separation step where the solids are discarded. H_2S gas is bubbled through the pregnant liquor to precipitate a mixed nickel-cobalt sulphide that is then shipped to Port Nickel in Louisiana (Boldt Jr., 1967).

Despite the advantages of lower energy requirements, lower capital costs, and higher nickel and cobalt recoveries, there had been no other pressure acid leach plants built since Moa Bay until recently. Reid (1996) attributed this to the difficulty in obtaining a commercially viable method to remove impurities and increase the nickel and cobalt concentration. Other barriers to the use of pressure acid leaching are higher acid consumption with rising levels of magnesia content and effluent disposal problems.

The aggressive leaching conditions that are imposed on the ore during the PAL process (i.e. ~250 °C, ~40 atm) dissolve most of the metals that are contained within it. Therefore, not only do nickel and cobalt become soluble in the leach solution, but also iron, copper, zinc, chromium, magnesium, manganese and aluminium (Kyle, 1996). These metal impurities must be removed to comply with the specifications for nickel products and this adds considerable expense to the refining process.

The problem of impurity removal and increasing the nickel and cobalt concentration has been partly overcome with recent advances in solvent extraction-electrowinning (SX-EW) technology (Ritcey, 1996). Solvent extraction reagents are now available that can separate nickel and cobalt from an impure leach solution to produce final products on site.

Developments in both pressure acid leaching and solvent extraction have lead to the economic viability of processing nickel laterite ores. Now that the technology is available and there has been considerable research directed towards the hydrometallurgy of nickel, mining companies are beginning to gather the confidence to process laterite ores. This confidence can be characteristically seen in Western Australia.

1.1.4 Lateritic Nickel Deposits in Australia

The availability of new technology to treat nickel laterites has lead to the development of a number of projects in Western Australia such as the Cawse project (OMG), the Bulong project (Preston Resources) and the Murrin Murrin project (Anaconda Nickel). Other known laterite deposits in Australia include Marlborough (Queensland), Ravensthorpe (Western Australia), Mount Margaret (Western Australia) and Syerston (New South Wales). These projects are currently at various stages of feasibility studies.

A comparison between the mineralogical composition of the Western Australian laterites and that of Moa Bay is presented in Table 1. The mineralogy of each deposit largely determines what processing options are suitable to treat that ore type. The

Western Australian laterites are characterised by a low iron, high magnesium and high silica content, while the Moa Bay laterite has a high iron, low magnesium and low silica content. The high magnesium content of Bulong, Cawse and Murrin Murrin ores contributes to a higher acid consumption than their Moa Bay counterpart.

Table 1. Chemical composition of Western Australian and Moa Bay laterite ores (Kyle, 1996).

	Bulong (%)	Cawse (%)	Murrin Murrin (%)	Moa Bay (%)
Ni	1.11	1.0	1.24	1.35
Co	0.08	0.07	0.089	0.12
Fe	20.8	18.0	21.7	45
SiO_2	42.9	42.5	42.1	8.3
Al	2.75	1.71	2.51	4.8
Mg	4.62	1.58	4.02	0.55
Mn	0.36	0.17	0.40	-
Cr	0.6	0.92	0.88	2.0
Ca	0.03	0.03	0.09	-
Moisture	< 35	< 10	~ 30	> 20

1.1.5 *Nickel Laterite Processing*

Each of the three new Western Australian nickel laterite projects use the PAL process to dissolve the nickel and cobalt. However, the purification stages after pressure acid leaching vary significantly between the three projects, indicating that there is no standard method to treat these leach solutions (Taylor and Cairns, 1997; Kyle, 1996; Motteram, Ryan and Weizenbach, 1997). There are slight differences in the process flow sheets between each of the projects, but the basic steps in the PAL process may be classified as follows:

Ore Preparation. Run of mine ore is screened to reject oversize particles and then slurried. Ore slurry is then thickened to meet the requirements of the autoclaves.

Leaching. The slurry is preheated before being fed into the mechanically agitated autoclaves. Acid is injected into the autoclaves to dissolve the contained metals in the ore. After a residence time of 75-120 minutes at ~250 °C and 40 atm pressure, the leached slurry then passes through a series of flash tanks and heat exchangers to recover heat for preheating.

Clarification/Neutralisation. Cooled slurry is neutralised with limestone or calcrete to remove aluminium, iron and chromium prior to being fed to a series of counter-current decantation (CCD) thickeners. These thickeners separate the solids from the pregnant liquor so that a clear solution can be used for downstream processing.

It is after the CCD circuit that differences in the flow sheets between the three projects are more pronounced. However, the objective is the same for all projects, which is to eliminate the presence of the remaining impurity elements from the leach solution so nickel and cobalt can be separated by solvent extraction. The efficiency and effectiveness of the solvent extraction process can be seriously affected if certain impurities are present in sufficient quantities.

Murrin Murrin use H_2S gas to precipitate a mixed nickel-cobalt sulphide product. This process has excellent selectivity, with good rejection of all major impurities. However, re-dissolution of the sulphide precipitate requires oxidative pressure leaching at 165 °C and 11 atm before the nickel-cobalt leach solution can be processed by solvent extraction (Kyle, 1996).

The Cawse project precipitates a mixed nickel-cobalt hydroxide from its clarified liquor. This is done using caustic burned MgO. The hydroxide precipitate is not as selective as the H_2S process, with copper, zinc and manganese also precipitating. However, the ammonia re-dissolution process is selective for nickel and cobalt and has good rejection of manganese and magnesium. The releach solution passes through a partial ammonia strip stage where steam is injected to reduce the ammonia concentration and precipitate some minor impurities. The ammonia-stripped solution then proceeds to solvent extraction (Kyle and Furfaro, 1997). This method, however, has been changed since OMG took over Cawse in early 2002.

The Bulong operation has approached the problem of impurity removal slightly differently. After the CCD stage, solvent extraction is used immediately to remove cobalt and other dissolved impurities such as manganese, zinc, magnesium and copper, leaving a nickel-rich raffinate that also contains calcium and magnesium. The cobalt extract is stripped and treated with sodium sulphide to precipitate a cobalt sulphide product, which is subsequently releached in a pressurised, oxidising autoclave. Any remaining impurities are removed via an ion exchange column before the cobalt-rich solution enters electrowinning.

Regardless of how the impurities are removed, all three nickel laterite refineries use the solvent extraction process to separate the nickel from cobalt. The hydrometallurgical application of solvent extraction is critical to the success of these laterite operations in separating these two chemically-similar metals.

1.2 Overview of Hydrometallurgical Solvent Extraction

Solvent extraction is an equilibrium process that can be described by the following simplified equation:

$$M^{n+}_{(aq)} + nRH_{(org)} \quad \leftrightarrow \quad MR_{n\,(org)} + nH^{+}_{(aq)} \qquad (1)$$

where M^{n+} is the desired metal cation in the aqueous phase, RH is the extractant in the organic phase, MR_n is the organometallic complex in the organic phase and H^+ is the proton released from the extraction reaction.

In hydrometallurgical applications of solvent extraction, three main stages are used to complete the process. The first is the extraction stage where the metal ion is transferred from the aqueous phase to the organic phase. The second step is scrubbing, where co-extracted impurity elements are washed from the organic phase under suitable conditions. The third step is a stripping stage where the desired metal ion is transferred from the organic phase to an aqueous phase and the extractant is regenerated for subsequent extraction stages.

The chemical similarity of nickel and cobalt makes the separation of these elements difficult. However, solvent extraction reagents have improved in terms of the selectivity of cobalt over nickel and has allowed high purity nickel and cobalt products to be produced (Ritcey, 1996).

1.2.1 Extractants Used for Nickel and Cobalt Solvent Extraction

The commercially available extractants for nickel-cobalt separation are presented in Table 2.

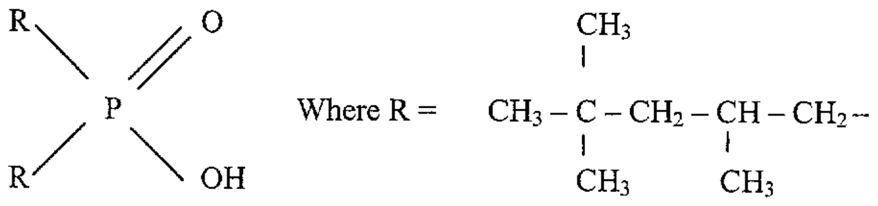
Table 2 General order of selectivity for nickel-cobalt extractants (Ritcey, 1996).

Co-Ni Extractant	Selectivity
D2EHPA	Fe > Cu > Zn > Ca > Mg > Co > Mn > Ni
PC 88A, P 507, Ionquest 801	Fe > Cu > Zn > Ca > Co,Mn > Mg > Ni
Cyanex 272	Fe > Cu > Zn > Co,Mn > Mg > Ca > Ni
Cyanex 301, 302	Fe > Cu > Co > Mn > Ni > Ca,Mg
Versatic 10	Fe > Cu > Zn > Ni > Co > Mn > Ca > Mg
Amines	Zn > Fe > Cu > Co > Mn > Ni
TBP	Fe > Zn > Cu > Co > Ni

From Table 2, it can be seen that iron, copper and zinc will all be preferentially extracted into the organic phase before nickel and cobalt. Therefore, it is essential that these metals should be either removed prior to the solvent extraction of nickel and cobalt or selectively extracted during the solvent extraction process (Ritcey, 1996).

After the removal of these, the next step in the purification process is the separation of nickel and cobalt. Of the above extractants, Cyanex 272 has been shown to separate nickel and cobalt most effectively (Sole and Hiskey, 1992; Tait, 1993b; Rickelton and Nucciarone, 1997; Rice and Gibson, 1996; Hubicki and Hubicka, 1996; Martínez et al., 1997).

Cyanex 272 is a phosphinic acid manufactured by Cytec. Its chemical structure is shown in Figure 1.1. This extractant has proven itself and been accepted by industry (Ritcey, 1995; Rickelton and Boyle, 1988) and is used commercially in the Murrin Murrin and Bulong nickel processing plants in Western Australia (Motteram, Ryan and Weizenbach, 1997; Ritcey, Hayward and Salinovich, 1996).



Where R = $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{CH}-CH_2-$

Cyanex 272

Figure 1.1 The chemical structure of Cyanex 272.

1.2.2 Solvent Extraction Equipment Used in Hydrometallurgy

Industrial solvent extraction equipment must be robust and be designed to carry out the operation on a continuous basis with minimal operator involvement. Solvent extraction in the mining industry has been generally carried out using mixer-settlers, but other contactors such as non-agitated differential, agitated differential and centrifugal types have also been used (Ritcey and Ashbrook, 1979). All of the Western Australian laterite projects have chosen to use mixer-settlers as the contactor to carry out their solvent extraction processes, so it is for this reason that focus has been directed towards these units in this section.

1.2.3 Mixer-settlers

Conventional mixer-settlers typically consist of a mixing tank that is attached to a large rectangular reservoir. The aqueous and organic phases are mixed in the tank and the overflow is directed into a settling tank. The settling tank is of sufficient surface area and length to provide enough residence time for the aqueous and organic phases to separate. After the two phases have separated, each solution is drawn off and sent for further processing. Various designs and configurations of mixer-settlers have been reported, each with their own advantages and disadvantages (Ritcey and Ashbrook, 1979; Nyman et al., 1992; Taylor, 1996).

1.2.4 Advantages of Mixer-Settlers

Mixer-settlers have been widely used in hydrometallurgy and consequently, a large amount of experience has been gained in their use (Godfrey, 1994; Taylor, 1996). Mixer-settlers are relatively simple in design, simple to operate and have a relatively low capital cost (Ritcey and Ashbrook, 1979). These units are reasonably flexible in terms of throughput and internal recycle streams may be used to maintain phase continuity (Taylor, 1996). Mixer-settlers are particularly useful when the kinetics of the extraction system are slow and the coalescing time is long (Ritcey and Ashbrook, 1979).

1.2.5 Disadvantages of Mixer-Settlers

A significant problem inherent with mixer-setters is that the intensity of agitation in the mixer must be adequately controlled. Insufficient mixing reduces mass transfer and stage efficiency. It can also cause the solutions in the organic and aqueous weirs to accumulate, upsetting the hydraulic balance in the settler (Spence and Soderstrom, 1999).

One of the roles of agitation is to decrease the average drop size, thereby increasing the interfacial area for chemical reactions to occur. However, Hanson (1971) states that the rate of increase in interfacial area decreases as the agitation rate increases. Furthermore, the mass transfer coefficient decreases as the drop size decreases because fluid circulation within the drops is suppressed and the droplets act as rigid spheres. Mass transfer can then only be achieved by the relatively slow process of molecular diffusion.

Excessive mixing increases the level of shear, entrainment and makes phase separation more difficult (Ritcey and Ashbrook, 1984; Spence and Soderstrom, 1999). When combined with even small amounts of solids, these effects can result in crud. Crud is a stable emulsion of aqueous and organic composition and often accumulates at the organic-aqueous interface in the settler (Ritcey and Ashbrook, 1984). Cruds represent a loss of valuable solvent and adds to operating costs of the plant.

In their study on cobalt and nickel extraction using Cyanex 272, Dreisinger and Cooper (1986) found that the rate of mass transfer for cobalt was ~28 times faster than nickel. It has also been shown that the kinetics of cobalt extraction is very rapid, with high extraction efficiencies obtained with contact times of 10 seconds or less (Lindell et al., 2000). Ritcey (2000) pointed out that if the agitation time was longer than that required for the kinetics of the reaction, then the extraction of impurity elements was likely to increase. Despite this, contact times in the order of 2 minutes or more are reported in the literature for cobalt-nickel separation using mixer-settlers (Feather and Cole, 1996; Rickelton, Flett and West, 1984).

The overall throughput of mixer-settlers is governed by the coalescing time of the emulsion in the settler (Ritcey and Ashbrook, 1984; Logsdail and Lowes, 1971). The settler area is considerably greater than the mixer and therefore makes a greater contribution to the overall cost of the unit (Hanson, 1971). Large volumes of organic solution are required to fill the settlers, which also add to the capital cost of the solvent inventory (Taylor, 1996). This cost begins to climb rapidly when multiple mixer-settler units are required.

The large area of plant floor space that is needed to house mixer-settlers also introduces other costs to the operation. Capital costs are increased due to extensive roofing requirements, piping and groundwork, and fire protection systems. The large surface area also increases the exposure of the organic solvent to air, which increases losses from evaporation and causes greater contamination from dust and insects (Taylor, 1996).

1.3 Introduction to Electrostatic Pseudo Liquid Membrane

A novel contactor for solvent extraction is Electrostatic Pseudo Liquid Membrane or ESPLIM. The ESPLIM technique combines the basic principles of electrostatic dispersion, solvent extraction and liquid membranes into a simple but effective unit operation that has been shown to operate at extraction efficiencies of greater than 99% in a single stage (Gu, 1990b; Williams, Bailey and Broan, 1997).

The first publication on the use of ESPLIM was in 1985 by Gu, the inventor of the technique (Gu, 1985). Since that time, Gu and other associates at the China Institute of Atomic Energy, where the technique was developed, have published the majority of ESPLIM literature. The only other research group to have investigated the

ESPLIM technique is a joint collaboration between Southampton University and British Nuclear Fuels Ltd (Williams, Bailey and Broan, 1997).

The extraction of rare earth metals using the ESPLIM technique has been the subject of a number of studies. Europium (Zhou and Gu, 1988), yttrium (Gu et al., 1994), scandium (Yang, Gu and Wang, 1995) and the selective separation of a mixture of rare earths (Yang, Gu and Fane, 1998; Yang, Gu and Fane, 1999) have been investigated. ESPLIM has been used to extract cobalt from synthetic solutions (Gu, 1990a; Gu, 1990b; Williams, Bailey and Broan, 1997) and nickel has been extracted from a synthetic solution and from an effluent in a nickel-plating process (Gu, Zhou and Jin, 1990). However, the separation of a combined nickel-cobalt solution, either synthetic or actual leach solution, has not been reported.

1.3.1 The Electrostatic Pseudo Liquid Membrane Reactor

A schematic diagram of an ESPLIM reactor can be seen in Figure 1.1. An ESPLIM reactor consists of a rectangular box that is separated into two compartments by a perforated baffle plate. The baffle plate also acts as an electrode for the electrostatic field. On either side of the baffle plate, near the wall of the unit, is an insulated electrode. Immediately below the baffle plate is a plastic blank separation plate. The reactor is made of a hydrophobic and chemically resistant material, typically polyethylene, Plexiglass® or acrylic plastics.

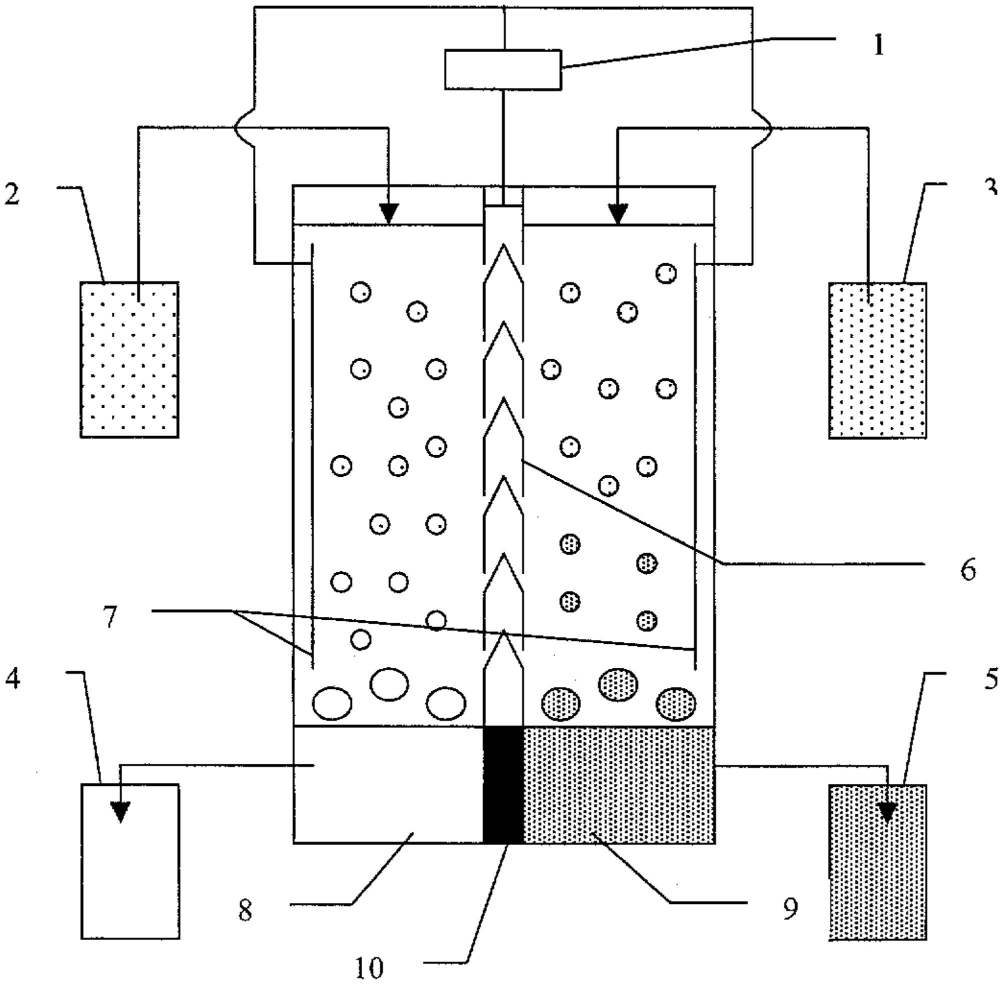


Figure 1.1 An Electrostatic Pseudo Liquid Membrane (ESPLIM)

(1) High voltage power supply (2) Feed solution (3) Stripping solution (4) Raffinate solution (5) Concentrate solution (6) Baffle plate/electrode (7) Insulated electrode (8) Extraction settler (9) Stripping settler (10) Blank separation plate

1.3.2 Basic Principles of the Electrostatic Pseudo Liquid Membrane

Feed solution is pumped to the top of the extraction compartment and acidic stripping solution pumped to the top of the stripping compartment. Drops of both solutions are finely dispersed into the organic phase by a high voltage electrostatic field between the baffle plate and the insulated electrodes. These small droplets have a large surface area-to-volume ratio, which allows mass transfer in the extraction and stripping processes to proceed very quickly.

The reaction that occurs in the extraction compartment is the same as equation (1), i.e.

$$M^{n+}{}_{(aq)} + nRH_{(org)} \leftrightarrow MR_{n(org)} + nH^{+}{}_{(aq)} \tag{2}$$

The desired metal ions in the feed solution, 'M^{n+}' are extracted into the organic phase by 'RH'. The extraction compartment now has an excess of the extracted species, 'MR_n' and a deficiency of the organic extractant, 'RH'. The concentration difference of 'MR_n' between the extraction compartment and the stripping compartment causes the extracted species to diffuse through the holes in the baffle plate into the stripping compartment.

The stripping process in the stripping compartment is the reverse of equation (2), i.e.

$$MR_{n\,(org)} + nH^{+}{}_{(aq)} \leftrightarrow M^{n+}{}_{(aq)} + nRH_{(org)} \tag{3}$$

The extracted species that has diffused into the stripping compartment reacts with the acidic stripping solution, which transfers the metal ion back into aqueous solution. The organic extractant is also simultaneously regenerated. The stripping compartment now has an excess of the organic extractant, 'RH' and a deficiency of the extracted species, 'MR_n'. By diffusion, the extractant 'RH' moves from the stripping compartment to the extraction compartment where the extractant can again react with feed solution and the cycle continues.

The overall effect of this situation is that there are two simultaneous concentration gradients of the two different organic carriers. These concentration gradients can be mutually satisfied by each carrier diffusing through the baffle plate into the other compartment. In this way, the desired metal ion is transferred from the impure feed solution to the pure stripping solution.

The extraction and stripping reactions occur while the feed and strip solutions are falling through the organic phase. By the time that the feed solution exits from the presence of the electric field, the desired metal ion has been extracted from the feed solution to the organic phase in the extraction compartment. Similarly, the stripping solution becomes loaded with the metal ion from the organometallic complex before it passes out of the electric field. Once out of the electric field, the barren feed solution (raffinate) and the loaded strip solution begin to coalesce again and separate from the organic phase in their own respective settler.

The use of a perforated baffle plate in ESPLIM means that it is possible that small, feed solution droplets can pass through the baffle plate and enter the stripping compartment. The ratio of the flow rate of entrained feed solution droplets to the flow rate of the stripping solution is termed swelling. Swelling is detrimental to the ESPLIM process because unextracted metal ions are transferred to the concentrated stripping solution and the concentrate also becomes diluted from the extra volume of aqueous solution. On the other hand, when small strip solution droplets pass through the baffle into the extraction compartment, this results in a loss of the valuable concentrate and decreases the efficiency of the process. The ratio of the flow rate of entrained strip solution droplets to the flow rate of the feed solution is termed leakage.

1.3.3 ESPLIM and Non-Equilibrium Mass Transfer

Gu (1992) states that the ESPLIM process is characterised by non-equilibrium mass transfer, a trait that is more related to liquid membranes than the process of solvent extraction. In support, Gu (1992) cites an example where a 1000 ppm cobalt feed solution is reduced to 10 ppm in the raffinate and the strip solution concentration was raised from 0 to 19,750 ppm in a single stage. The concentration of organometallic complex in the ESPLIM, however, was never greater than 300-400 ppm – much lower than the equilibrium concentration.

Non-equilibrium mass transfer is achieved in ESPLIM because the extractant is never fully loaded with the metal complex. There is a continual supply of regenerated extractant diffusing from the stripping compartment and therefore, there are always new reaction sites for metal ions to transfer to the organic phase. In comparison, each mixer-settler stage approaches a chemical equilibrium between the organic and aqueous phases, i.e. the rate of the forward reaction in equation 1 equals the rate of the backward reaction. In order to recover any further cations, another mixing stage is required under conditions that force the equilibrium apart.

1.3.4 Limitations of ESPLIM

Non-equilibrium mass transfer in ESPLIM may be useful to achieve maximum extraction of the desired metal ions, but with many free extraction sites available in the extraction compartment, the extraction of other impurities may present a problem. Co-extracted impurities will also diffuse into the stripping cell and be stripped with the desired metal, decreasing the purity of the concentrate solution.

In ESPLIM's present two-compartment form, no provision can be made for the organic phase to be scrubbed of impurities before being stripped. Scrubbing is usually carried out when the extractant is fully loaded with metal ions and impurity elements in the organic phase are swapped with the desired element in the aqueous phase. In ESPLIM, the organic phase is never fully loaded with metal ions. Therefore, the tendency for the desired element in the aqueous scrub phase to replace the impurity elements may be diminished even if a scrub stage could be incorporated into the ESPLIM process.

The use of an electric field to induce mixing means that certain criteria must be met before the process can be used. The organic phase must have a low electrical conductivity for the electrostatic dispersion effect to be observed. Fortunately, many of the organic systems used in industry have the required electrical properties (Bailes, 1981). Furthermore, the organic solution must always be the continuous phase and therefore, the aqueous solution has to be the dispersed phase (Gu, 1992). Also, the walls of the vessel must not be wetted by the aqueous phase in order to ensure proper dispersion (Stewart and Thornton, 1967). The range of applications that ESPLIM can be used for is limited by these restrictions.

1.4 Objectives of the Study

The main objective of this study was to develop a method of extracting and separating cobalt from a pressure acid leach solution of a nickel laterite ore using Electrostatic Pseudo Liquid Membrane. To achieve this objective, the following specific objectives were set:

- Design and construct a laboratory scale ESPLIM reactor.
- Investigate the variables and factors that control the efficiency of the ESPLIM process using synthetic solutions to optimise the reactor.
- Make improvements to the ESPLIM design as needed.

- Use the results to devise a method of extracting and separating cobalt from actual leach solutions obtained from a real nickel laterite operation.

- Design, construct and operate a larger ESPLIM reactor to determine scale up issues.

1.5 Scope and Limitations of the Investigation

Although there is some similarity between each of the three nickel laterite plants operating in Western Australia, the differences between them become quite marked at the nickel-cobalt separation step. Differences include nickel and cobalt concentration, the matrix of the leach solution, extractant/diluent characteristics, type and concentration of impurities and product specifications. Thus, an investigation that is applicable to all three operations would be a large project.

The Bulong Nickel Operation, which adopted a direct solvent extraction approach for separating nickel and cobalt immediately after counter-current decantation, is arguably the simplest processing route of the three operations. This approach minimises the number of solid-liquid phase separations and consequently, the associated losses from these separations are also minimised. This investigation attempted to separate cobalt directly from nickel laterite leach solutions using Electrostatic Pseudo Liquid Membrane, similar to the method practiced at Bulong.

As discussed in Section 1.2.1, there are many extractants that are commercially available for nickel-cobalt extraction. However, only Cyanex 272 was used in this investigation as it is used at Bulong, it has the best cobalt-nickel separation properties and is the most widely used extractant for cobalt-nickel extraction.

This study was conducted at a bench-scale level as the novelty of the ESPLIM technique is such that it does not yet warrant investigation at a larger scale.

1.6 Relevance of the Study

At present, three new nickel laterite projects have begun operations in Western Australia and there are numerous similar projects that are in various stages of development in Australia and around the world. The success of these projects is, in part, dependent on the successful separation of nickel and cobalt from each other and co-dissolved impurities. The process of solvent extraction, used to conduct these separations, must therefore be carried out in an optimal manner to ensure that maximum recoveries and minimal costs are obtained.

Mixer-settlers are currently the most favoured solvent extraction contactor. Although the design and operation of these units is relatively simple, mixer-settlers may not be completely suited to nickel-cobalt solvent extraction. There are many shortcomings inherent with mixer-settlers that not only impact on the process of solvent extraction itself, but also downstream operations such as electrowinning.

Alternative solvent extraction contactors should therefore be examined to determine their suitability for nickel-cobalt separation. If successful, such a contactor would be particularly useful to those nickel projects still undergoing feasibility studies, although existing operations could also benefit by incorporating such a contactor into any future plant expansions or upgrades. The contactor should overcome most, if not all, of the disadvantages that are inherent with current industrial solvent extraction equipment such as mixer-settlers. Ideally, the advantages of mixer-settlers such as simplicity in design and operation and high flexibility should also be retained.

Although ESPLIM appears to be suitable for cobalt-nickel separation, much of the published literature on the ESPLIM technique has been conducted using synthetic solutions. Questions exist on whether the electrostatic field will behave similarly on synthetic solutions of relatively low ionic strength and high ionic strength solutions with entrained particulates, as found in industry. This study attempted to answer some of these questions.

1.7 Summary

This chapter has outlined the importance of nickel for the production of stainless steel and other future technology applications. Nickel laterites are the largest known source of nickel, but due to their inherent characteristics, they have been relatively untouched because the technology to economically treat them has not been readily available. Now, with advances in pressure acid leaching and solvent extraction, lateritic nickel can be extracted cheaper than traditional smelting processes and has become an attractive proposition. The leaching of nickel laterites introduces many impurities into the leach solution and these impurities must be removed prior to the separation of nickel and cobalt by solvent extraction.

The hydrometallurgical application of solvent extraction has been used to separate and concentrate nickel and cobalt from leach solutions, but in practice, it is quite difficult due to the chemical similarities of these two metals. Mixer-settlers have been the preferred contactor to carry out nickel-cobalt solvent extraction in each of the three new nickel laterite plants recently commissioned in Western Australia. However, mixer-settlers have a number of disadvantages that contribute to both high capital and operating costs.

Electrostatic Pseudo Liquid Membrane (ESPLIM) is a novel solvent extraction technique and the basic principles of its use have been presented. This technique allows simultaneous extraction and concentration of metal ions from an impure feed solution in a single stage. It has many advantages over existing contacting equipment that may solve some of the problems that face the new nickel laterite operations in Western Australia.

CHAPTER 2

REVIEW OF STUDIES ON ELECTROSTATIC PSEUDO LIQUID MEMBRANE

2.1 Introduction

The performance of ESPLIM is influenced by a number of operating variables. These variables include: the applied voltage of the electrostatic field, the design of the baffle plate, the level of swelling and leakage, the flow rate of the feed and stripping solutions, the concentration of the feed and stripping solutions, the type and concentration of the organic extractant and the presence and concentration of any auxiliary ligands.

This chapter discusses how each of these variables affect the performance of the ESPLIM technique from information provided by previous investigators.

2.2 The Effects of the Electric Field

One of the most significant departures that ESPLIM makes from mixer-settler contactors is the use of an electrostatic field to induce a dispersion. A literature search on the use of electrostatic fields in liquid-liquid phase systems found that considerable research has focused on the ability of electric fields to coalesce a dispersed aqueous phase from a continuous organic phase, thus enabling enhanced phase separation.

Although electric field-induced coalescence does have a small role in the function of ESPLIM, the primary use of electric fields is to disperse the aqueous feed solution into the continuous organic phase. In the published literature, comparatively little attention has been given to the use of electric fields to induce a dispersion.

2.2.1 The Effect of the Electric Field on Drop Size

Garton and Krasucki (1964) showed that a droplet would undergo disintegration and subsequent dispersion when an applied electric field is strong enough. The droplet is elongated in the direction of the field and at the point just before disintegration, the major to minor axis ratio of the drop reaches 1.85. This is the maximum physical deformation that a droplet can withstand without breaking. Supporting evidence is given by Rosenkilde (1969) and Martin et al. (1983) who reported major to minor axis ratios of 1.8391 and 1.838 respectively.

Thornton (1968) proposed that in the presence of an electric field, a droplet with a surface charge has a mechanical force that is in an opposite direction to that of the inward-acting interfacial tension force. A reduction in the effective interfacial tension between the aqueous and organic phases can also promote oscillation of the aqueous droplets (Stewart and Thornton, 1967).

The field intensity at which maximum drop deformation and subsequent dispersion occurs has been described by Martin et al. (1983) in terms of the Weber electrostatic number. Accordingly, the Weber electrostatic number (W_{e_E}) is defined as the ratio of electrostatic drag force acting on the water drop to the interfacial tension force and can be represented by:

$$W_{e_E} = \frac{\varepsilon_r \, \varepsilon_0 \, E_0^2 \, d}{\gamma} \tag{4}$$

where d is the drop diameter (m), E_0 is the field intensity (Vm^{-1}), ε_0 is the vacuum permittivity, ε_r is the relative continuous phase permittivity and γ is the interfacial tension (Nm^{-1}). When the Weber electrostatic number reaches 0.409, the major to minor axis ratio becomes 1.838 and droplet disintegration occurs.

Gu (1990b) investigated the mean diameter of dispersed droplets as a function of the applied voltage using ESPLIM. An ESPLIM reactor 120 mm high, 80 mm wide and 15 mm thick was used. Each compartment was ~7 mm wide, with electrodes 100 mm high and a 20 mm settler at the bottom of each compartment. This experiment used water as the dispersed phase and an organic phase consisting of di-2-ethylhexyl phosphoric acid (D2EHPA) and kerosene.

Gu (1990b) found that there were three main regions of interest. Increasing the voltage from 0 to 1.3 kV increased the size of the droplets from 3 mm to ~5 mm, indicating that coalescence was favourable. Between 1.3 kV and 1.9 kV, the size of the droplets decreased from ~5mm back to 3 mm, indicating that both coalescence and disintegration were occurring simultaneously. At 1.9 kV, the mean size of droplets was equal to the value obtained under zero voltage (3 mm). Above 1.9 kV, water droplets became finely dispersed and had average diameters lower than 3 mm.

The results from Gu (1990b) are an indication of the type of behaviour expected with a dispersed water phase when the applied voltage is increased. However, no such similar information was given about the actual dispersed phase system used for extraction experiments, which contained 1000 ppm cobalt and 0.1 M sodium acetate. Therefore, no information can be obtained about what is the optimum drop size required to give maximum extraction for a given extraction system. Clearly, this information is useful in reactor design and process modelling.

Broan, Bailey and Williams (1996) investigated an in situ drop size distribution from an electrostatically induced dispersion by means of a laser scattering device. The authors found that there was a bimodal size distribution for all voltages tested (6-9 kV). Higher voltages increased the proportion of droplets in the 20-150 μm range and decreased the proportion of droplets >250 μm. For all voltages tested, very few droplets were observed to have drop diameters in the range of 150-250 μm.

In another ESPLIM study by Williams, Bailey and Broan (1997), the authors observed that at an applied voltage of 6 kV, the dispersion of a cobalt/acetate feed solution was much better than the 1 M H_2SO_4 strip solution. The authors did not attempt to explain this observation but instead, increased the voltage of the stripping compartment to 8 kV to give a similar dispersion for both solutions.

Similarly, Suyama et al. (1993) observed an unsatisfactory dispersion of 1 M HCl in a 10% D2EHPA/kerosene system, but overcame the problem by adding 0.5% surfactant (Span 80) to the organic phase. The authors measured the interfacial tension between a 1000 ppm Ni^{2+}/ 0.1 M sodium acetate solution and a 10% D2EHPA/kerosene system and found the interfacial tension to be 5.5 mN m^{-1}. The interfacial tension between a 1 M HCl solution and a 10% D2EHPA/kerosine solution was measured to be 17.3 mN m^{-1}. They concluded that the higher interfacial tension of the 1 M HCl acid solution limited the dispersion of that phase.

The observations from Garton and Krasucki (1964), Thornton (1968), Martin et al. (1983) and Gu (1990b) show that under appropriate conditions, electric fields may be used to increase the interfacial area of a two-phase liquid system by dispersion, or alternatively, reduce the interfacial area by coalescence. Electrically induced coalescence has been the subject of considerable research, particularly with respect to separating water-in-oil emulsions generated for emulsion liquid membranes (Hsu and Li, 1985; Bailes and Larkai, 1984; Bailes, 1992b; Yamaguchi and Ito, 1993).

Significant knowledge on the coalescing behaviour of water-in-oil dispersions in electric fields has been gained through research undertaken by Bailes (Bailes and Larkai, 1981; Bailes and Larkai, 1982; Bailes and Larkai, 1984; Bailes and Dowling, 1985; Bailes and Larkai, 1992; Bailes, 1992a; Bailes, 1992b). Some of the main conclusions that have arisen from these studies include (1) an optimum frequency of the electric field exists that maximises coalescence performance; (2) pulsed D.C. voltage is superior to constant D.C. voltage; (3) maximum coalescence is achieved when pulses are 'on' for the same time period as when they are 'off' and (4) thin electrode insulation coatings perform better than thicker coatings.

It is evident from the above literature that the size of the droplets, hence the size of the interfacial area for mass transfer, can be controlled by the strength of the electric field. At field strengths that yield a critical Weber electrostatic number of less than 0.409 droplet coalescence is favoured. When the field strength is sufficiently high such that the Weber electrostatic number is above 0.409, the aqueous phase forms a dispersion of small, oscillating droplets that have a large total interfacial surface area.

Although there have been a number of studies that have investigated electrostatic dispersion as a method of agitation, little work has been published on any differences in behaviour observed between various dispersed phases with the same organic phase. This has particular importance to industry, as the properties of both the pregnant liquor and the organic phase may change over the life of the operation. Thus, the behaviour of electrostatic dispersions of different aqueous phases under similar experimental conditions has yet to be reported and would prove useful in the further understanding of the technique.

2.2.2 The Effect of the Electric Field on Mass Transfer

The electrical forces imposed on a droplet will have an effect on the mass transfer coefficient because of the induced turbulence near the drop interface. This turbulence has been explained theoretically by Taylor (1966) and shown experimentally by McEwan and de Jong (1966).

Thornton (1968) showed that the molar rate of diffusion (N_A) in a mass transfer process could be increased by an increase in the eddy diffusivity (E_D) as represented by:

$$N_A = -(D + E_D)\frac{\partial C_A}{\partial y} \qquad (5)$$

where D is the molecular diffusivity, ∂C_A is the change in concentration and ∂y is the distance of diffusion. The author proposed that the eddy diffusivity could be increased via electrically induced droplet oscillations.

Wham and Byers (1987) investigated the mass transport of single droplets under an electric field using a tapered glass column. DC and pulsed DC electric fields were applied to a 2-ethylhexanol organic continuous phase and water was used as the dispersed phase. The authors found that oscillation frequencies of between 10-120 Hz did not significantly increase the surface area of droplets (less than 1%). However, an oscillation frequency of 50 Hz gave a 35% increase in mass transfer compared to the non-oscillating electric field.

When a droplet passes through a sufficiently intense electric field, the drop deforms in the direction of the field and as the field strength increases, it can disintegrate into numerous smaller drops (Yamaguchi, 1995). These deformations and ruptures contribute to the turbulence of the dispersed phase within the continuous oil phase and therefore increase the eddy diffusivity. The reported observation of increased mass transfer with increasing field strengths by many authors (Thornton, 1968; Bailes, 1981; Zhou and Gu, 1988) is, in part, due to the increased frequency of coalescence and redispersion of the drops (interfacial renewal) together with marked internal mixing in the drops (Yamaguchi, 1994).

However, there is contradictory evidence regarding the positive benefits of oscillating electric fields to mass transfer. He, Chang and Baird (1997) investigated the transfer of benzoic acid from water into a paraffin mineral oil using DC and pulsed DC electric fields. Using this system, pulsed DC electric fields yielded poorer mass transfer efficiencies than equivalent DC fields. Furthermore, similar drop sizes were observed at comparable field strengths for both DC and pulsed DC fields, indicating that the results were not due to interfacial surface area effects.

2.2.3 The Effect of Electric Field on Drop Velocity

Yamaguchi, Sugaya and Katayama (1988) examined the hydrodynamic behaviour of an aqueous dispersed phase under the presence of a horizontal electric field using a countercurrent column. They found that by increasing the electric field strength up to the point before drop breakage occurred, the velocity of the falling drops decreased. This effect was caused by an increase in the horizontal velocity component of the droplet, induced by the electric field. The falling velocity of the droplets could therefore be controlled by the strength of the horizontal electric field.

Similar results were obtained by Martin et al. (1983), who also used a countercurrent column. When the applied field strength was above the critical value for drop stability, they found that the dispersed phase hold-up, i.e. ratio of dispersed phase volume to total phase volume, was approximately twice that compared to a field strength below the critical value. Increasing the hold-up increases the contact time between the aqueous and organic phases, allowing mass transfer to occur for longer.

In an early ESPLIM study conducted by Zhou and Gu (1988), they found that increasing the voltage from 3.2 kV to 4.0 kV increased the degree of dispersion of the aqueous phase within the continuous oil phase. At 3.2 kV, large feed droplets sunk through the oil phase, resulting in a low Eu^{3+} extraction of 72%. As the voltage was increased from 3.2 kV to 4.0 kV, it was observed that the dispersion of the aqueous droplets in the organic phase increased with small, oscillating droplets being formed at higher voltages. At 4.0 kV, over 96% Eu^{3+} extraction was achieved with good aqueous phase dispersion and droplet oscillation.

2.2.4 The Effect of the Electrode Insulation

Gu (1990a) reported that the baffle and grounded electrodes used in an ESPLIM reactor were insulated to prevent sparking between the electrodes. In addition, if the insulation was not hydrophobic, phase dispersion was hindered because the aqueous droplets 'bridged' themselves between the two electrodes, but no reason was provided why this phenomenon occurred.

Hsu and Li (1985) suggested that when electric fields of high intensity were to be used, insulated electrodes were necessary to prevent sparking. Sparking of non insulted electrodes results from a chain of droplets extending from one electrode to the other forming a conductive pathway for current. Hsu and Li (1985) likened the layer of nonconductive, hydrophobic insulation to that of a capacitor. Because the surface conductivity of the insulation material is low and the surface is hydrophobic, the insulator acts as a "… parallel array of tiny independent capacitors. They are independent because when a water chain grows from the bottom electrode to touch the top electrode, this conducting chain only grounds one side of that tiny capacitor touched by the water droplet. The other part of the dielectric surface can still be at its original coalescing potential to continue coalescence action. Since the current passing through this conducting chain is limited by the reactance of this tiny capacitor (the smaller the capacitor, the lesser the current), sparking is suppressed. The maximum voltage can be determined by raising the applied voltage without causing sparking until the breakdown voltage of the insulation layer is reached."

It is important to note here that in order to compare electric field intensities, both the applied voltage and the distance over which that voltage is applied must be known. Some studies reported their results in kV/cm but others reported only the applied voltage. This makes a comparison between studies difficult because the intensity of the electrostatic field cannot solely be expressed as a function of voltage.

A further complication when comparing field intensities is the effect of the insulation material. Hsu and Li (1985) showed that the insulation acts as a capacitor and therefore consumes part of the applied voltage. Gu (1990a) reported that there was only a small drop in the applied voltage across the oil phase when a 0.1 mm Teflon® film was coated onto the electrodes. The significance of the insulation coating is perhaps best illustrated by Bailes and Larkai (1981). In their experiment, a 13 mm perspex insulation coating only provided an actual electrical field strength of approximately 0.6 kV/cm across the dispersed phase when an electrical field strength of approximately 4 kV/cm was applied. The difference between the two field strengths arises from the voltage-consuming nature of the insulation material.

These results indicate that comparisons of electrostatic fields between studies based on applied voltage alone are prone to error. Even comparisons of electric field strength in applied kV/cm are not always reliable because the insulation material consumes much of the applied voltage and therefore this value is not indicative of the true electric field strength. Different insulation coatings and thicknesses behave in different ways. The only true measurement that can be made of the electric field strength that a dispersed phase is subjected to is by measuring the potential difference within the field over a given distance.

However, certain trends and information can be obtained using applied voltage or applied voltage per centimetre as it is often only a trend and not absolute values that provide useful data. Care must be taken though in assuming these values are the actual forces being imposed on the solvent extraction system.

2.2.5 The Effect of the Electric Field on Swelling and Leakage

Enhancing mass transfer by applying a very high electric field strength to produce extremely small droplets is limited by two factors. The first is that if intense agitation is used, an extremely fine dispersion is created, which causes emulsification of the oil phase and phase separation then becomes difficult (Gu, 1990a). The second problem occurs in the form of an increase in the level of swelling and leakage. Swelling is defined as the ratio of the flow rate of feed droplets that enter the stripping compartment to the flow rate of the strip solution. Leakage is defined as the ratio of the flow rate of stripping droplets entering the extraction compartment to the flow rate of the feed solution.

Gu (1990a) reported that increasing the applied voltage increased the amount of leakage from 0% at 1.0 kV to 0.06% at 4.0 kV. Higher voltages produced a more finely dispersed stripping solution, so smaller droplets can easily move through the baffle channels and into the extraction compartment.

Increasing the voltage from 2.0 kV to 4.0 kV also increased the level of swelling from 0.25% to 0.78%. In this case, finely dispersed feed droplets at higher field intensities escaped from the extraction compartment to the stripping compartment through the baffle plate.

Williams, Bailey and Broan (1997) performed an ESPLIM experiment to determine the effect of an increase in the voltage applied to the extraction compartment. Initially the applied voltage in both compartments was 6 kV and this was maintained until a steady state was reached. The voltage applied to the extraction side was then increased to 8 kV. The level of swelling was observed to rapidly increase from approximately 1% to approximately 2%. It was also observed that the level of leakage remained relatively steady at ~0.2% before and after the increase in voltage. This was to be expected, as there was no change in conditions on the stripping side of the vessel.

Gu (1990a) determined the swelling rates of the ESPLIM vessel using an acidic feed solution containing 1000 ppm cobalt in 2.4 M HCl and deionised water as the 'strip' solution. This feed solution is very different to the feed solution that contained 1000 ppm cobalt and 0.1 M sodium acetate at pH 5.0 that he used to conduct extraction experiments. The author assumed that the dispersion behaviour of a very acidic cobalt solution is similar to a slightly acidic cobalt solution containing sodium acetate. If these solutions do not behave in a similar manner under the influence of an electric field, the values that Gu (1990a) reported as swelling rates for the ESPLIM reactor may not necessarily be a true indication of the swelling rates that are observed under normal extraction conditions.

Williams Bailey and Broan (1997), however, attempted to minimise the differences between the solutions used for extraction experiments and those used for swelling and leakage determinations. They maintained a similar feed solution, containing 1000 ppm cobalt and 0.1 M sodium acetate, except it required acidification to prevent the extraction of trace chemicals into the organic phase. The usual 1 M sulphuric acid stripping solution had 0.1 M lithium sulphate added to act as a tracer.

The studies of Gu (1990a) and Williams, Bailey and Broan (1997) showed that a compromise is needed between increasing the electric field strength to give better dispersion and thus greater mass transfer, and minimising the extent of swelling and leakage.

2.2.6 Power Consumption Using Electric Fields

Power consumption using electrostatic dispersion is negligible. Thornton (1968) reported that a continuous electrostatic extraction unit with a combined throughput of 136 L/hr only consumed 2 watts. A similar power consumption was reported by Gu, Zhou and Jin (1990) who used ESPLIM at a feed throughput of 0.112 L/hr. Gu

(1990b) found power consumption of only 3.1 watts at a feed throughput of approximately 0.7 L/hr using ESPLIM.

When compared to mechanical agitation, electrostatic mixing is extremely energy efficient. Scott and Wham (1989) reported that electric field dispersion energy requirements were less than 1% of a baffled agitated tank mixer that produced a similar average drop size distribution Yamaguchi (1995) attributes this to the electrical force only acting at the interface between the conducting aqueous phase and the non-conducting continuous phase, instead of distributing the energy throughout the entire liquid-liquid system.

2.2.7 Practicalities for Using Electric Fields

It is paramount for the effective operation of an ESPLIM reactor that the electric field is optimised. It is advantageous to apply an electric field of sufficient strength to break up and disperse incoming feed and stripping solutions, allowing mass transfer to take place as quickly as possible. However, the field strength must be controlled to prevent an extremely fine dispersion, as this will increase the level of swelling and leakage.

The use of an electric field to control the degree of aqueous phase dispersion in ESPLIM has a number of practical advantages. Adjusting the intensity of the electric field can control the size of the aqueous drops and droplet residence time. Therefore, any change in operating conditions such as feed viscosity or feed concentration may be allowed for by changing the electric field strength and hence mixing conditions within the unit. Any changes made to the electric field can be done with immediate results. This gives the operator a large degree of control over the process and makes it easy to optimise the unit for a given set of conditions.

Electrically induced mixing also eliminates a large amount of maintenance for the unit. Grease and oil changes that are required with mechanical agitation and impeller wear and corrosion are eliminated with the ESPLIM technique. Unlike mechanical agitation in mixer-settlers, the use of electrostatic dispersion in ESPLIM eliminates the problem of air entrainment. Air containing dust is a significant factor for the formation of cruds in solvent extraction systems (Ritcey and Ashbrook, 1984).

The use of electrostatic fields in solvent extraction, however, has its limitations. Electrically induced dispersions can only be made when the dispersed phase is a conductive aqueous solution and the continuous phase is an organic solution of low polarity (Gu, 1992; Scott, 1989). Thus, the electrical properties of the solutions to be mixed must meet certain criteria. Scott (1989), however, pointed out that many of the liquid-liquid systems that are presently used in industry meet these requirements.

There are also safety aspects that are inherent with the use of electric fields. Although only a very small current is drawn from the power supply, high voltages still pose a safety risk and therefore adequate security measures need to be taken to ensure operator safety.

2.3 The Effect of Extractant Concentration on Extraction Efficiency

Zhou and Gu (1988) increased the P5709 (hexylphosphonic acid –1-methylheptyl ester) extractant concentration from 4% to 10% and observed an increase in Eu^{3+} extraction efficiency from ~83% to ~96%. An extraction efficiency of 94% was achieved at a 6% extractant concentration, indicating that the process can operate at high efficiencies with low reagent concentrations.

Similarly, Gu et al. (1994) used the P5709 extractant to recover yttrium and found that increasing the extractant concentration from 5% to 10% increased the extraction efficiency from ~73% to ~93%. However, a further increase in the extractant concentration to 20% only increased the extraction efficiency by another 4.6%.

Gu (1990b) found that increasing the di-2-ethylhexyl phosphoric acid (D2EHPA) extractant concentration from 0.03 mol/L to 0.3 mol/L increased the cobalt extraction efficiency from ~89% to ~99%. Therefore, a tenfold increase in extraction concentration had a relatively small effect on extraction efficiency. Gu (1990b) observed that changing the extractant concentration did not significantly change the organometallic complex concentration in the oil phase. Furthermore, the organometallic complex concentration was always lower than the equilibrium concentration, indicating that the organic phase was never completely loaded because of the shuttling movement between the extraction and stripping compartments.

These studies indicate that there is an optimal extractant concentration required for the ESPLIM technique. However, this concentration is often lower than that required for other commercial solvent extraction operations because of the non-equilibrium nature of the ESPLIM technique. The extractant is continually loaded and unloaded in the extraction and stripping compartments respectively and therefore, there is always a constant supply of extractant ready to extract metal ions from the feed solution.

2.4 The Effect of Feed Concentration on Extraction Efficiency

Zhou and Gu (1988) found that an increase in Eu^{3+} concentration from 135 ppm to 1050 ppm decreased the extraction efficiency from ~97% to ~92% respectively. Yang, Gu and Wang (1995) increased the scandium concentration in the feed from 10 to 100 ppm and observed an increase in extraction efficiency from ~97% to ~99%. However, when the scandium concentration in the feed was raised to 250 ppm the extraction efficiency dropped dramatically to ~46%.

The drop in efficiency when high feed concentrations were used is likely due to the large increase in H^+ ions released into the aqueous phase from the extraction reaction. The ion exchange between metal ions in the aqueous droplets and H^+ ions in the organic phase results in a decrease in pH of the aqueous phase to such an extent that the extraction reaction becomes unfavourable. Feed droplets containing the desired metal ions then pass through the oil phase without being extracted.

The decrease in extraction efficiency can also be attributed to a decrease in the free extractant concentration. As the extraction cell became 'flooded' with metal ions, there is insufficient extractant available for efficient extraction to take place (Yang, Gu and Wang, 1995).

All of the ESPLIM studies that have investigated the effect of feed concentration have been carried out using rare earth elements. These elements are generally extracted at low pH values (i.e. < pH 3.0). This means that when H^+ ions in the organic phase are exchanged with metal ions in the aqueous phase, the pH of the aqueous solution only decreases slightly and extraction still remains favourable. Thus, pH control is relatively easy.

Transition metals such as cobalt and nickel are generally extracted at higher pH values, i.e. $4<pH<6$. When mass transfer takes place at higher pH, H^+ ions that are transferred to the aqueous phase result in a significant decrease in pH. Therefore, pH control is usually achieved by the addition of sodium hydroxide or ammonia solution to keep the aqueous pH at the required level and maintain high extraction. Feed solutions that contain high concentrations of transition metal ions should still be able to be treated by ESPLIM with high extraction efficiency as long as the pH of the aqueous phase remains favourable for extraction. Previous ESPLIM studies conducted on cobalt solutions (Gu 1990b; Williams, Bailey and Broan 1997) used sodium acetate for pH control. The use of sodium acetate is described in Section 2.9.

2.5 The Effect of Feed Flow Rate on Extraction Efficiency and Swelling

Zhou and Gu (1988) increased the Eu^{3+} feed flow rate from 90 mL/hr to 400 mL/hr and observed a small decrease in extraction efficiency of 96.9% to 94.2% respectively. The organometallic complex in the extraction compartment increased from 260 ppm at 90 mL/hr to 530 ppm at 400 mL/hr. Similarly, the organometallic complex in the stripping compartment increased from 230 ppm at 90 mL/hr to 470 ppm at 400 mL/hr. Although no explanation for these results were given, it appears that under the experimental conditions, the stripping flow rate (6 mL/hr) was adequate to produce enough free extractant for the extraction compartment to sufficiently cope with the increase in feed flow rate. The authors also found that increasing the feed flow rate up to 630 mL/hr caused the raffinate to become emulsified and the ESPLIM reactor became 'flooded'.

Yang, Gu and Wang (1995) increased the feed flow rate from 240 mL/hr to 840 mL/hr and experienced no significant effect on scandium extraction efficiency. However, at 960 mL/hr, the extraction efficiency showed a declining trend.

The same authors measured the influence of feed flow rate on the level of swelling and leakage in ESPLIM. They found that the level of swelling increased from 0% at 240 mL/hr to 0.38% at 1680 mL/hr. The leakage level was low for all feed rates at <0.002%.

Gu et al. (1994) found that a high extraction efficiency of yttrium could be maintained at high feed rates as long as the feed concentration was kept low. Even at low feed rates, highly concentrated feed solutions gave poor extraction efficiencies. The authors explained these results by using the mass flow rate of metal ions into the reactor i.e.

$$\text{Mass Flow Rate (g/hr)} = \text{Volume Flow Rate (L/hr)} \times \text{Metal Concentration (g/L)}$$

Gu et al. (1994) used an example whereby a high flow rate (1.5 L/hr)-low feed concentration (0.507 g/L) had a mass flow rate of 0.76 g/hr and yielded an extraction efficiency of ~98%. When compared to a low flow rate (0.75 l/hr)-high feed concentration (1.399 g/L), this had a mass flow rate of 1.049 g/hr and yielded an extraction efficiency of ~84%. Therefore, high mass flow rates led to a decrease in extraction efficiency.

This explanation, however, does not necessarily hold true. On closer examination of the results presented (Gu et al., 1994 Fig. 8), there are several data points that have similar mass flow rates, but large differences in extraction efficiency. If the authors' explanation of the dependency of extraction efficiency on feed concentration and feed flow rate, i.e. mass flow rate was correct, then similar mass flow rates should give similar extraction efficiency. This is not the case, so it appears that there is another relationship between extraction efficiency, feed concentration and feed flow rate.

An alternative explanation of the data produced by Gu et al. (1994) is proposed. For a given mass flow rate, greater extraction efficiency will occur if that same mass is spread throughout a larger volume because there is a corresponding increase in the surface area for extraction to take place. ESPLIM generates a larger surface area by using an electric field to break up and disperse feed solution. However, a greater surface area can also be generated by feeding in more solution. As an example, if one droplet contains 3 g/L of metal ions, it is less likely to achieve complete extraction than three droplets that each contain 1 g/L. Although the mass flow rate is the same in each case, there is three times as much surface area for extraction to take place in the second instance. A relationship between the mass flow rate and total surface area could possibly describe the results of Gu et al. (1994) more accurately than mass flow rate alone.

Nevertheless, it has been shown that the ESPLIM technique can work efficiently over a wide range of feed flow rates with only small decreases in extraction efficiency. The relative flexibility of ESPLIM with respect to feed flow rate is an advantage, as fluctuations in volumetric throughput can be common in solvent extraction plants.

2.6 The Effect of Strip Flow Rate on Extraction Efficiency and Leakage

Gu (1990b) increased the strip flow rate from 11 mL/hr to 24 mL/hr at a constant feed flow rate of 144 mL/hr and the cobalt extraction efficiency increased slightly from 99.3% to 99.5%. It is clear from these results that a strip flow rate of 11 mL/hr was more than adequate to provide enough free extractant in the extraction compartment to complex with the feed solution.

Yang, Gu and Wang (1995) found that a stripping solution flow rate of 300 mL/hr kept the metal complex concentration in the stripping compartment to less than 5 ppm, but suggested that the strip flow rate should be increased to 480-600 mL/hr to maintain an adequate concentration gradient between the extraction and stripping compartments.

They also investigated the effect of strip flow rate on the leakage level. An increase in strip flow rate from 480 mL/hr to 1440 mL/hr did not change the leakage rate of <0.002%. A strip flow rate of 2160 mL/hr increased the leakage level slightly to 0.0034%. The low level of leakage reported by Yang, Gu and Wang (1995) suggests that leakage is relatively unaffected by the strip flow rate. This is contradictory to other results from Yang, Gu and Wang (1995) and Gu (1990a) who suggest that swelling has a dependency on feed flow rate. It may be possible that the acidic strip solutions used in all ESPLIM studies have a lower degree of dispersion than the feed solutions. Thus, under similar electric field conditions, acidic strip solutions may have larger drop sizes that are not as amenable to crossing through the baffles compared to the feed solution. This may explain the apparent lack of leakage dependency on flow rate.

It has been shown that the stripping flow rate affects the amount of regenerated extractant that is potentially available to the extraction compartment and therefore, indirectly affects the extraction efficiency. It also determines the concentration of the loaded strip solution for a given feed flow rate, as described below.

2.7 The Effect of Flow Ratio on Extraction Efficiency and the Loaded Strip Solution Concentration

The flow ratio, i.e. feed flow rate/ strip flow rate, is an important parameter that can measure the performance of the extraction system (Gu, 1990b). Assuming high extraction efficiency, when the flow ratio is multiplied by the feed concentration, it indicates the theoretical concentration of the loaded strip solution. High flow ratios increase the concentration of metal ions in the loaded strip solution. However, the flow ratio should not be increased to such an extent that insufficient stripping of the organic phase occurs. This will lead to a decrease in the free extractant concentration in the extraction compartment and result in a decrease in extraction efficiency (Gu, 1990b).

Gu (1990b) showed that ESPLIM was able to operate at high extraction efficiency under a wide range of flow ratios. In the extraction of cobalt, it was shown that 99.5% extraction efficiency was obtained with a flow ratio of 6.0 and 95.6% extraction efficiency was obtained at a flow ratio of 50.4. At a flow ratio of 50.4, the concentration of the loaded strip solution was 47.8 g/L, a considerable increase from the 1 g/L feed solution. As mentioned by the author, a 47.8 g/L cobalt strip solution meets the requirements of an electrowinning process.

When a further increase in the concentration of the loaded strip solution is required, recycling of the loaded strip solution is possible. The loaded strip solution can be recycled as long as it is partially supplemented with fresh acidic solution, otherwise the acidity of the strip solution will decrease over time (Yang, Gu and Fane, 1999). Gu et al. (1994) increased a 1 g/L Y^{3+} feed concentration to 167 g/L in the concentrate by recycling the loaded strip solution.

If recycling of the loaded strip solution is used, Gu et al. (1994) suggests the use of two modified flow ratios. The apparent flow ratio and the effective flow ratio are defined as:

$$Apparent\ Flow\ Ratio\ (AFR) = \frac{feed\ \ flow\ rate}{recycled\ conc.\ flow\ rate + fresh\ acid\ \ flow\ rate} \quad (6)$$

$$Effective\ Flow\ Ratio\ (EFR) = \frac{feed\ \ flow\ rate}{fresh\ acid\ \ flow\ rate} \quad (7)$$

The authors suggest that by using a recycle stream, a sufficiently large interfacial area can be maintained to improve the efficiency of the stripping process, while the fresh acid stream provides the chemical driving force for the process.

2.8 The Effect of Baffle Design on Swelling and Leakage

Illustrations and descriptions of the ESPLIM baffle in early publications by Zhou and Gu (1988), Gu (1990b) and Gu, Zhou and Jin (1990) do not describe the Λ-shaped baffle that is reported by Gu (1990a). Instead, the baffle plates appear to merely consist of two insulated, perforated metal plates.

There have only been two major variations on the structure of the baffle. Gu (1990a) used two perforated stainless steel plates with Teflon® insulation as the baffle electrode and thin, angled baffle barriers were attached to the inside surface of the plates.

More recently, an alternative design has been used (Gu et al., 1994; Yang, Gu and Wang, 1995; Yang, Gu and Fane, 1998; Yang, Gu and Fane, 1999). Plastic Λ-shaped baffle elements were used as the supporting structure and insulated wires were wound around the baffle structure to act as the electrode.

Wu, Gu and Jin, (1991) compared two different baffle designs using the plastic baffle structure described above. Two plastic baffle structures were moulded, one with a baffle angle of 45° and a gap width of 1.5 mm (4515), and the other with a baffle angle of 60° and a gap width of 2 mm (6020). It was found that the 4515 baffle gave very low values of swelling (0.21% to 0.73%) and leakage (0% to 0.03%). The 6020 baffle produced undesirable results with more swelling (13.6% to 47%) and leakage (0.012% to 2.9%).

Baffles that have large gap widths and squat angles are inadequate in preventing entrained water droplets from flowing between compartments. Large gaps increase the probability of droplets entering the baffle channel, while shallow angles provide an easy passage. Recent ESPLIM papers (Yang, Gu and Wang, 1995; Yang, Gu and Fane, 1998; Yang, Gu and Fane, 1999) use a baffle with a 35° angle and a 2 mm gap width.

The wound wire and perforated plate baffle designs have each been used to obtain >99% extraction efficiency, albeit for different extraction systems, so there is little difference in performance. In terms of industrial use, the baffle with insulated wires wrapped around it has some advantages. This baffle design is made up of individual baffle elements that can be stacked upon one another to any desired height. These baffles can also be easily mass-produced by plastic injection technology. However, wound wire electrodes do not provide a uniform electric field, which may be a disadvantage in producing droplets with a narrow size distribution.

Wound wire electrodes may also suffer from a loss of tension over time, especially in the presence of organic solutions. The wires could sag and decrease the electrode-electrode distance and as they are only 8-10 mm apart to begin with, small changes will have a large effect on the electric field strength. The baffled perforated plates do not suffer from this behaviour. However, any damage that a baffled plate incurs would most likely require the construction of a new baffle, while the wound wire electrodes can have individual elements replaced.

2.9 The Effect of Salts of Soluble Organic Acids

There appears to be conflicting views and experimental evidence as to the role and mechanism that salts of soluble organic acids, such as acetate, have on mass transfer in solvent extraction systems.

Wasan, Gu and Li (1984), Gu, Wasan and Li (1985) and Gu, Wasan and Li (1986) used a Lewis cell to investigate the kinetics of cobalt extraction in the presence of various ligands such as acetate. They reported that without the addition of acetate, cobalt extraction only reached 80% after 15 minutes. With 0.1 M acetate, a cobalt extraction of 98% was obtained within 2 minutes. The authors proposed that acetate replaces some of the coordinated water molecules surrounding the metal ion, thereby providing a thermodynamically less stable but a kinetically more labile complex with the metal ions (Wasan, Gu and Li, 1984). Thus, they suggested that the acetate ions act as accelerating ligands. The metal-ligand complex consists of a hydrophilic end and a hydrophobic end with the latter orientating itself towards the oil-water interface. This allows the ligand-metal complex to populate at the oil-water interface, making extraction more favourable (Gu, Wasan and Li, 1986).

The ESPLIM studies that have been conducted previously on cobalt or nickel have used the 'accelerating' acetate ligand. Only one experiment has been performed with ESPLIM that did not use acetate as a ligand and the results were poor. Gu, Zhou and Jin (1990) found that approximately 16% of nickel was extracted by di-2-ethylhexyl phosphoric acid (D2EHPA) when no acetate was added, while approximately 98% of nickel was extracted when 0.1 M acetate was present. However, the authors presented no evidence on the pH of either raffinate solution from these tests. One suspects that the pH of the raffinate solution from the acetate test had a higher pH because of the buffering action of sodium acetate. With extraction occurring at higher pH values in the acetate test, this may account for the large discrepancy in extraction efficiencies.

Furthermore, no data has been presented on the effect that ligands, such as acetate, has on the dispersion process. It may be possible that the good results observed with acetate by Gu, Zhou and Jin (1990) could be partly due to smaller drop sizes when the acetate ligand is present.

Gu, Wasan and Li (1986) presented evidence that the thermodynamic equilibrium of extraction did not change with addition of an acetate ligand. Using the extraction of cobalt with D2EHPA as an example, a plot of distribution coefficient versus pH showed that the distribution of cobalt in the organic phase was the same, whether acetate was present or not. The authors argued that if the thermodynamic equilibrium was changed by the addition of acetate, the equilibrium curve should be changed also. Nuclear magnetic resonance measurements showed that similar spectra were obtained from the organic phase, with and without the use acetate. Gu, Wasan and Li (1986) concluded that the acetate did not enter the organic phase as a Co-D2EHPA-acetate complex.

These results appear to contradict those of Inoue, Ohto and Mori (1998) and Danesi et al. (1984). Inoue, Ohto and Mori (1998) found that at low acetate/acetic acid buffer concentrations (0.01 M), the charge of calcium ions is completely neutralised by the deprotonated extractant (PC-88A, i.e. 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and the acetate was not extracted in the metal complex. However, with increasing acetate / acetic acid buffer concentration (0.06-0.3 M), the charge of the calcium ions became increasingly neutralised by the acetate anion and the acetate ions were extracted with the metal complex.

Similar findings were presented by Danesi et al. (1984). Using a cobalt-D2EHPA extraction system, the authors found that increasing the acetate concentration also increased the fraction of acetate ions in the extracted metal complex. Using a cobalt-Cyanex 272 extraction system, Danesi et al. (1984) also found that the fraction of acetate ions in the metal complex could be lowered by decreasing the pH of the system from 6.2 to 5.1.

An alternative theory on the effect that acetate has on mass transfer is given by Dreisinger, Cooper and Distin (1989). The authors opposed the idea that acetate acted as an accelerating ligand by citing an argument from Cotton and Wilkinson (1980) that for a given metal ion, all ligand exchange rates are similar, irrespective of the anion. They proposed that when acetate was present, the increase in mass transfer was due to an interfacial pH buffering effect. They argued that the extent of the buffering action was dependent on the pK_a of the weak acid. In support, they showed that the mass transfer rate of cobalt to the organic phase increased with increasing pK_a of different ligands. Succinic acid (pK_{a2} of 5.64) proved to be even superior to acetic acid (pK_a of 4.76) in terms of the mass transfer rate. This is in conflict with the results of Wasan, Gu and Li (1984) who found that succinate was inferior to acetate.

Ligands such as acetate certainly act as a proton sink that resist large changes in pH. Their addition to the feed solution simplifies the ESPLIM process because there is no need for other forms of pH control such as organic pre-neutralisation or continuous base addition.

Pre-neutralisation of the organic phase would only be effective in ESPLIM for a short time period because the organic phase would eventually revert back to its acid form through the continual stripping process. Therefore, the only other alternative for pH control is the constant addition of base to the extraction compartment. The complications that are inherent with this include (1) a probable increase in swelling due to the extra volume of aqueous solution added to the extraction compartment; (2) dilution of the raffinate, and (3) a reduction in feed capacity.

Thus, pH control for cobalt-nickel extraction using ESPLIM is a challenge, which is perhaps the reason why sodium acetate addition to the feed solution has been the preferred method.

2.10 Summary

The application of a high voltage electrostatic field in ESPLIM to induce a water-in-oil dispersion is a significant departure from conventional solvent extraction contactors. Increasing the applied electric field strength decreases the drop size and therefore increases the total surface area for extraction to occur. The application of an electric field enhances mass transfer by promoting internal circulation within the drop and increasing the interfacial turbulence. The intensity of the electric field should be a compromise between creating small drop sizes to assist mass transfer whilst minimising swelling and leakage.

ESPLIM can obtain high extraction efficiencies when using lower extractant concentrations than conventional solvent extraction methods. Increasing the feed concentration generally decreases the extraction efficiency because of the increased concentration of protons that transfer to aqueous phase.

ESPLIM is able to cope with wide variations in feed flow rate whilst maintaining high extraction efficiency, providing that there is enough supply of regenerated extractant diffusing from the stripping compartment. An increase in the strip flow rate increases the extraction efficiency but decreases the loaded strip solution concentration. However, recycling the loaded strip solution with a small flow of fresh acid can produce a highly concentrated strip solution.

Swelling and leakage can be minimised by proper design of the baffle plate. Baffles that have a low angles and large gap widths are more conducive to swelling and leakage. Perforated plate and wound wire baffles have both been used to produce highly efficient extraction results.

According to previous researchers, the addition of salts of soluble organic acids to the feed solution have different effects. Some suggest that these additives act as an intermediate ligand and accelerate the extraction reaction. Others suggest that they buffer the pH of the aqueous phase, favouring extraction.

CHAPTER 3

METHODS AND MATERIALS

3.1 Preparation of Standard Solutions

A standard NaOH solution (1 M) used for pH adjustment and other titrations was prepared by dissolving 40.06 g of AR grade NaOH pellets (BDH Chemicals) into 1 L of deionised water. All deionised water used had a conductivity of $< 12.5\ \mu S\ m^{-1}$. A sample of potassium hydrogen phthalate (KHP)(BDH Chemicals) was dried in an oven at 110 °C for 2 hours and allowed to cool in a desiccator. Four sub-samples of KHP (~0.67 g) were each dissolved in ~75 mL of deionised water and two drops of phenolphthalein indicator were added. The NaOH solution was titrated against the KHP solution to a permanent pale pink colour.

An approximately 1 M HCl solution was prepared by diluting 90 mL of 32% HCl solution (Ajax Chemicals) in 1 L of deionised water. Three 10 mL aliquots were titrated with standard NaOH solution using bromothymol blue indicator.

A sulphuric acid solution (~2 M) was prepared by diluting 225 mL of AR grade 36 N H_2SO_4 (BDH Chemicals) into 2 L of deionised water. Three 10 mL aliquots of H_2SO_4 were each placed in a 100 mL conical flask and 2 drops of bromothymol blue indicator were added to each flask and then titrated with standard sodium hydroxide solution to a permanent blue colour. This solution was then diluted to make up 1 M sulphuric acid solutions for use as strip solution.

An ammonia solution (~1 M) was prepared by diluting 72 mL of 28-30% NH_3 solution (Sigma Chemicals) in 1 L. This solution was titrated against three 10 mL aliquots of standard HCl solution using a phenolphthalein indicator. This solution was used primarily for pH control during testing of actual leach solutions.

3.2 Preparation of Synthetic Leach Solutions

Cobalt and nickel stock solutions (~10 g/L) were prepared by dissolving the required quantity of AR grade $NiSO_4.6H_2O$ or $CoSO_4.7H_2O$ (both Ajax Chemicals) in 1 L of deionised water. An aliquot of each solution was diluted and analysed for the metal concentration by Atomic Absorption Spectroscopy (AAS) (Varian SpectrAA 50 model).

A 1 M sodium acetate stock solution was prepared by dissolving 82.03 g of the AR grade salt (Ajax Chemicals) into 1 L of deionised water.

ESPLIM feed solutions were prepared by adding an aliquot of the cobalt or nickel stock solutions to an aliquot of the sodium acetate solution as required and then diluting this solution to the desired volume. The pH of the solution was adjusted by adding either standard NaOH or H_2SO_4. A sample of feed solution was diluted and analysed by AAS to determine the metal concentration.

3.3 Preparation of Organic Solutions

Organic solutions were prepared by dissolving 200 mL of Cyanex 272 (Cytec) in 1800 mL of Solvent HF diluent (Mobil) to make 2 L of 10% extractant solution. When tributylphosphate (TBP) was used as a modifier, 200 mL of Cyanex 272 and 100 mL of TBP (Rowe Scientific) was dissolved in 1700 mL of diluent to produce 2 L of 10% extractant, 5% modifier organic solution. All organic solutions were used as received.

3.4 Extraction Test Procedures

Flexible tubing that was attached to the bottom of each settler was clamped with Hoffman clips and the other end of the tubing was attached to a siphon breaker/sample container that was mounted onto a height adjustable jack. The baffle plate was inserted into the reactor and organic solution was added to the reactor to a height just below the top of the wall-mounted electrodes (approximately 150 mL).

The leads connecting the AC power supply to the reactor were then attached to the electrodes. Tubes supplying feed and strip solutions were positioned above their respective compartments. The voltage was then applied at the desired strength before aqueous solutions were fed into the vessel. Once the aqueous solutions were added, the timer was started. Once sufficient aqueous raffinate had collected at the bottom of the extraction settler, the Hoffman clip was removed to allow the aqueous solution to flow out of the cell. A similar procedure was carried out for the stripping solution.

The organic/aqueous interface level in each settler was adjusted by changing the height of the sampling container via a height adjustable jack.

Aqueous samples (5 mL) were taken for metal assay from the sample containers at regular intervals. Once the level of aqueous solution in the raffinate sample container was high enough, the pH of the solution was recorded periodically using a TPS 900-P pH meter. Overflow from the sample containers drained into a reservoir.

Experiments that required organic samples to be taken were performed in a similar manner as described above, except for the following. Once the experiment was completed, the electrostatic field was turned off and the feed and stripping solution tubes were removed from the top of the reactor. Two 2.5 mL needleless syringes (Terumo) were placed above either compartment and a sample of the organic from each compartment was withdrawn at the same time. The syringes had a 45 mm length of 0.34 mm ID tubing attached to the inlet of each syringe. A 1 mL aliquot from each organic sample was taken and stripped with 10 mL of 1 M H_2SO_4 solution in a 25 mL beaker for 10 minutes. The strip solution was then analysed for the metal ion concentration by AAS.

Experiments that involved ammonia addition were performed in a similar manner as the original method, except for the following. An autotitration system (model ETS822 from Radiometer Copenhagen) was used to deliver ammonia solution (1 M) to the feed compartment to maintain the desired pH of the raffinate solution. The volume of ammonia delivered was displayed on an LED panel, so an accurate record of the volume added each hour was available. Dilution of the raffinate by the added ammonia solution was accounted for when calculating the true metal concentration in the raffinate.

All ESPLIM experiments were conducted at room temperature (22° C ± 2° C).

3.5 Interfacial Tension Measurements

The interfacial tension between aqueous and organic phases was measured using an Analite surface tension meter (model 2141). This instrument used the Wilhemy plate method for measuring interfacial tension.

Glass plates were cleaned with 4 M NaOH solution, washed with deionised water, washed with acetone and then allowed to dry. A glass plate was then attached to the plate carrier.

A clean, tall petri dish was partly filled with aqueous solution to a depth of approximately 10 mm. Organic solution was carefully added to the petri dish to a depth of approximately 20 mm. The glass plate was lowered into the organic solution and the instrument was zeroed.

The glass plate was lowered further, until an aqueous meniscus just formed at the bottom of the plate. The plate was raised until the meniscus was broken and the surface tension value was recorded. This process was repeated twelve times for each aqueous/organic system and an average value was calculated.

3.6 Determination of Total Dissolved Solids of a PLS Solution

The method used to determine the total dissolved solids (TDS) of a pregnant liquor stream (PLS) solution was similar to that described by Lenahan and Murray-Smith (1986).

A 150 cm^3 porcelain evaporating dish was placed in a furnace at 500 °C for 1 hour and then cooled in a desiccator. Approximately 150 mL of PLS was vacuum filtered using a glass fibre microfilter. A 100 mL aliquot of filtered solution was transferred to the evaporating dish and dried overnight at 110 °C.

The oven temperature was increased to 180 °C and the solids were dried for a further two hours. The evaporating dish was removed from the oven and placed in a desiccator to cool. Once cooled, the dish was weighed and the weight recorded.

The evaporating dish was returned to the oven and dried for a further two hours. After cooling in a desiccator, the dish was weighed again to check if further weight loss had occurred. The same weight was recorded the second time so it was assumed that total dryness was achieved. The following calculation was used to determine total dissolved solids:

$$\begin{aligned}\text{Total Dissolved Solids (mg/dm}^3) &= \frac{m_1 - m_2}{v} \times 1000 \\ &= \frac{84621 - 64649.2}{100} \times 1000 \\ &= 199718\end{aligned}$$

where m_1 is the mass of dried residue and dish (mg)

m_2 is the mass of the prepared dish (mg)

and v is the volume of the filtered sample used (cm^3)

3.7 Determination of Drop Sizes

The ESPLIM reactor was set up as described in Section 3.4. The reactor was filled with 10% Cyanex 272 in Solvent HF organic solution. A number of aqueous solutions were tested; 0.1 M sodium acetate, 0.1 M sodium formate, 0.1 M sodium propionate, 1 M H_2SO_4 and PLS.

A Pentax Spotmatic single lens reflex camera with an electronic flash was used to take the pictures. Four sheets of white A4 paper were positioned directly behind the reactor to reflect light back from the flash of the camera.

The desired applied voltage was set before aqueous solution was fed into the reactor. Once the pictures were taken, the voltage was turned off to allow all of the dispersed droplets to settle to the bottom of the reactor. After all of the droplets had settled, the next experiment was conducted.

A ball bearing of known diameter (2.48 mm) was attached to a length of plastic wire and was suspended inside the reactor. This served two purposes. The first was to allow the camera to accurately focus on one part of the reactor. The second purpose was to be able to determine the magnification factor of the camera. After the photos were developed, an electronic vernier calliper was used to measure the diameter of the ball bearing from the photo. This measurement was compared to the known diameter of the ball bearing and a magnification factor was determined. This method also allowed for any errors that may have been caused by the distortion of light through the plastic walls of the reactor and the organic phase. The major axis and minor axis of each drop was measured with the vernier callipers and only those drops that were sharply defined were considered for measurement. The drop diameter was calculated from the method used by Lewis, Jones and Pratt (1951) i.e.

$$\varphi = \sqrt[3]{d_1^2 d_2} \tag{7}$$

where ϕ is the drop diameter, d_1 is the major axis diameter and d_2 is the minor axis diameter.

3.8 Dielectric Constant Measurements

The apparatus and experimental method used to conduct the dielectric constant measurements was a variable-capacitance dielectric cell, similar to that described by Shoemaker, Garland and Steinfeld (1974).

Six organic solutions were tested. A 10% Cyanex 272 in Solvent HF diluent solution was used in all cases but with different cobalt concentrations in the organic phase. The cobalt concentrations used were 0 g/L, 0.28 g/L, 0.54 g/L, 1.06 g/L, 2.05 g/L and 4.34 g/L. The respective dielectric constants were calculated to be 2.26, 2.23, 2.21, 2.22, 2.23 and 2.22.

3.9 Determination of the Effects of Salts of Carboxylic Acids on the Kinetics of Extraction

Three salts of carboxylic acids were chosen to investigate their effect on the kinetics of cobalt extraction: formate, acetate and propionate. To conduct experiments at constant pH, buffer solutions of each ligand were prepared from the sodium salt and the respective acid. Approximately 300 ppm of cobalt was added to each solution as well as 0.5 M sodium chloride. The natural pH of a 0.085 M sodium propionate/ 0.2 M propionic acid solution was 4.27; the natural pH of a 0.115 M sodium acetate/ 0.2 M acetic acid solution was 4.27 and the natural pH of a 1.15 M sodium formate/ 0.2 M formic acid solution was 4.31.

A 50 mL aliquot of aqueous solution was transferred to a 250 mL glass beaker and was agitated by an overhead stirrer (Heidolph model RZR 1) at 518 rpm with a 3-bladed impeller. A 50 mL aliquot of 10% Cyanex 272 in Solvent HF solution was then transferred to the mixing vessel and a timer was started simultaneously. Once the desired mixing time had elapsed, mixing was stopped and the dispersion was quickly transferred to a 250 mL separatory funnel. A sample of the settled aqueous phase was taken, its pH recorded and its cobalt concentration was measured by AAS.

3.10 Analytical Techniques

The majority of metal ion analyses were carried out by AAS. The matrix of the standard solutions was prepared to match those of the sample solutions.

Samples of actual leach solutions from Bulong were analysed by Inductively Coupled Plasma Optical Emission Spectrometry (Varian Liberty 200 model). For independent confirmation, some of the solutions were also sent to Bulong's on-site laboratory.

CHAPTER 4

DEVELOPMENT OF THE ESPLIM REACTOR

4.1 The Original ESPLIM Reactor Configuration

As the first step of this investigation, construction of an ESPLIM reactor similar to that of Gu (1990a) was attempted. A schematic diagram of the ESPLIM reactor can be seen in Appendix A. The ESPLIM reactor was constructed from 9 mm thick Plexiglass® of inside dimensions 40 × 50 × 140 mm. An acrylic separator plate (40 × 8 × 20 mm) was positioned at the centre of the base of the reactor. Two sets of two guide rails (3 × 3 × 140 mm each) were placed near the centre of opposing walls, alongside the separator plate. This ensured that the baffle plate would remain in an upright position and prevented droplets leaking around the edges of the baffle plate.

A lid had another separator plate (40 × 8 × 40 mm) centred on the bottom of it. On either side of this separator plate, a hole (6 mm diameter) was drilled so that tubing could be fed into the reactor. The separator plate also slid between the guide rails and sat on the top of the baffle plate.

An 8 mm diameter hole was bored into the base of each compartment and a piece of acrylic tube was glued into the hole so that provision for the attachment of flexible tubing could be made. A flexible tube (6 mm internal diameter) was attached from the bottom of each compartment to a sampling container that was mounted onto a height-adjustable jack. An overflow tube was connected from the sampling container to a 5 L collection reservoir.

Two diaphragm pumps (model CONB1601PP1000C001 and model E 0803, both from ProMinent) were used to pump feed solution and stripping solution respectively into the top of the reactor through flexible tubing. A high voltage DC power supply (0-15,000 V) was connected to the reactor via high voltage cabling. The voltage could be adjusted through an external potentiometer and the applied voltage was observed from an LED display. This power supply had an arc protection safety feature that restricted the voltage in the event that an arc occurred.

4.2 Investigation on the Use of Wound Wire Electrodes

The wound wire baffle design of Gu et al. (1994) and Yang, Gu and Wang (1995) was initially investigated with first consideration given to the electric wires used to establish the electric field. Yang, Gu and Wang (1995) and Yang, Gu and Fane (1998) used a 0.5 mm diameter wire coated with 0.25 mm of polyethylene film. A 0.64 mm internal diameter wire with 0.25 mm thick polyethylene insulation (OLEX Cables) was tightly wrapped around a plastic plate (70 × 36 × 3 mm) to a height of 45 mm. Two of these electrodes were made and they were placed 8 mm apart into a 10% Cyanex 302/ 90% Solvent HF solution. Cyanex 302 extractant was used in preliminary experiments, as Cyanex 272 was unavailable at the time. When a 1 M sulphuric acid solution was fed between the two plates, no dispersion was observed, even at 9 kV of applied voltage.

A 0.4 mm core diameter copper wire with a 0.24 mm thick polyethylene sheath was then wrapped around two plastic plates in a manner described previously. These electrodes were placed 8 mm apart in a 10% Cyanex 302 / 90% Solvent HF solution and a 1000 ppm cobalt solution was used as the dispersed phase. The applied voltage was increased to 9 kV but no dispersion was observed.

Another experiment was performed with magnet wire. Magnet wire is used in high voltage applications such as transformers, motors and coils. Magnet wire has an enamelled coating that is chemically and thermally resistant (ATCO Magnet Wire Product Information). The wire used in this experiment was 0.5 mm in diameter with a 0.03 mm thick coating of enamel, giving a total wire diameter of 0.56 mm. The magnet wire was wound around two plastic plates to a height of 45 mm and both plates were submerged 8 mm apart in a 10% Cyanex 302/ 90% Solvent HF solution. A syringe needle (0.45 mm diameter) was connected to the flexible tubing so that smaller feed droplets were formed, instead of the larger ones formed by using the flexible tube itself. When H_2SO_4 acid solution (1 M) was used as the aqueous phase, a poor dispersion was formed at 4.5 kV but arcing between the electrodes occurred.

There was also evidence of 'bridging', that is, water droplets attached themselves to both electrodes and any subsequent droplets that fell between them merged and connected the electrodes forming an aqueous 'bridge'. This effect was put down to the hydrophilic nature of the enamel coating. Also, the wound wire surface was not entirely flat, so droplets were able to sit on exposed horizontal edges and thus not continue their fall through the organic solution.

Achieving an adequate dispersion with the wound wire electrodes proved difficult, so attention was directed towards the baffle plate electrode design that was used in early ESPLIM investigations (Gu and Zhou, 1988, Gu 1990a, Gu 1990b)

4.3 Investigation on Baffle Plate Electrodes

The baffle plate electrodes consisted of two 0.92 mm thick stainless steel plates (40 × 80 mm) with seven rectangular slots (2 × 34 mm) laser cut into them at 8 mm intervals. Seven acrylic Λ-shaped baffle elements were constructed. Each baffle element resembled an isosceles triangle (6 mm base with 35° apex angle) mounted upon a rectangular base (6mm wide and 2 mm high). Each baffle element was 40 mm long and was glued in between the two stainless steel plates. The top of each rectangular section of the baffle element was aligned to the bottom of each of the rectangular slots on the plates.

Two 1 mm thick copper plates (40 × 65 mm) had a brass screw silver-soldered to the centre of each of them and the plates were coated with approximately 0.08 mm of polytetrafluoroethylene (PTFE) insulation. The insulation process consisted of coating the plates with PTFE powder and then baking the plates in an oven to around 400 °C. The powder liquefies and when cooled, hardens to form a protective layer. These PTFE coated plates were mounted to opposite sides of the reactor and were 20 mm apart from the centre baffle. The reactor maintained its seal through an O-ring that was embedded into the wall around each hole where the brass screw was inserted.

Two L-shaped steel bars were screwed to the top of the baffle plate to act as connectors to the high voltage power supply. A threaded brass bolt was screwed onto each of the screws attached to the PTFE covered plates and the bolts were also connected to the high voltage power supply.

Initial experiments conducted using the above apparatus showed sparking occurring between the stainless steel baffle plate and the PTFE covered electrodes at voltages above 4 kV. Below 4 kV, no dispersion of the feed droplets was observed. Sparking caused a drop in the applied voltage from the power supply due to an arc protection feature built into the power supply. Thus, whenever a spark occurred between the two electrodes, the voltage would drop and the residual field strength was insufficient to maintain an adequate dispersion of the aqueous phase.

An experiment was conducted with two copper plates that were both coated with PTFE; one with a thickness of 0.08 mm, the other with a thickness of 0.12 mm. The electrodes were placed 8 mm apart in a 10% Cyanex 302 / 90% Solvent HF solvent system and a 1000 ppm cobalt solution was used as the aqueous phase. No dispersion or arcing was observed until 2.5 kV was applied. At this voltage, sparking was observed at intermittent intervals. As the applied voltage was gradually increased to 5 kV, sparking became more intense and more frequent and no dispersion was observed. At 5 kV, the electrical leakage from constant sparking caused the arc protection feature built into the power supply to restrict the voltage to ~2.0 kV. This voltage was insufficient for any dispersion to occur.

4.4 ESPLIM Reactor Modifications

Sparking was not only evident between electrodes, but also between the wall-mounted electrodes and the L-shaped steel bars that connected the baffle to the high voltage power supply. It became apparent that this was due to the close distance between the wall-mounted electrodes and the bars. The L-shaped bars were replaced by a metal connector that was inserted through the lid, directly above the baffle. This ensured that the greatest distance possible separated the oppositely charged electrodes and consequently, this type of sparking was completely suppressed.

Another modification was the insertion of a spacer plate between the back of the PTFE coated electrode and the reactor wall to decrease the distance between the electrodes. It was considered that a lower applied voltage might suppress the sparking, whilst still maintaining the required electric field strength to induce a dispersion. A 7 mm thick spacer plate was inserted to reduce the electrode distance from 20 mm to 13 mm. Sparking still inhibited dispersion, even when the 7 mm spacer plate was replaced by a 11 mm thick plate.

The thickness of the PTFE insulation coating was also modified. It was considered that the insulation thickness was inadequate to prevent electricity from passing through it to the baffle electrode. A 0.17 mm thick PTFE coated electrode was used with both the 7 mm and 11 mm spacer plates, but sparking still persisted and consequently, the degree of dispersion was limited.

4.5 Investigation of Electrode Insulation

It became apparent that the PTFE insulation used to coat the wall-mounted electrodes was insufficient to prevent sparking. To overcome sparking and achieve a good dispersion, several other insulating materials were investigated: (1) plastic tape, (2) heat shrink plastic and (3) polycarbonate insulation.

4.5.1 Plastic Tape Insulation

A length of plastic packaging tape, an emulsion based polyethylene tape manufactured by Cling Adhesive Products, product code RB9, was wrapped around two PTFE coated electrodes and these electrodes were placed 8 mm apart in a container containing a 10% Cyanex 302/ 90% Solvent HF solution. When 6.5 kV was applied, a 1000 ppm cobalt solution was dispersed into numerous droplets and no sparking occurred. The drops fell through the oil in a zigzag motion as they moved from one electrode to the other. This experiment was a success in that it was the first time a dispersion was observed without the presence of sparking.

Another experiment was performed with only one of the electrodes covered in the plastic tape. In order to obtain an adequate dispersion, 8 kV was required, which was higher than with the previous experiment but sparking was still absent. The success of this test meant that the wall-mounted electrodes could be insulated without having to insulate the perforated baffle plate.

A number of experiments were conducted using the plastic tape insulation and the results are presented in Appendix B. The plastic tape insulation was, however, not ideal. The tape required replacing after several experiments because it gradually became degraded due to chemical attack from the organic solvent. Occasional sparking did occur throughout the course of the experiments and these electrical discharges punctured holes in the tape, allowing further discharges to occur.

4.5.2 Heat Shrink Insulation

The next insulation material investigated was a heat shrink plastic manufactured by Wattmaster. The electrode was sheathed by the heat shrink plastic and then subjected to a blast of hot air from a heat gun. Once the plastic had shrunk around the electrode, the ends were sealed with an epoxy resin and clamped together until dry.

The heat shrink insulation performed better than the plastic tape in that a good dispersion was achieved with complete suppression of sparking at all voltages used. This was likely due to the increase in insulation thickness (0.92 mm) compared to the plastic tape (0.18 mm). These insulated electrodes performed well for a couple of experiments, but prolonged exposure to the organic solution caused the heat shrink material to 'bubble'. Rather than being parallel to the surface of the electrode, parts of the insulation became curved and detached from the electrode. It was believed that the plastic had absorbed some organic solvent and this increase in the volume of the plastic caused it to 'bubble'. Continued experiments with the heat shrink insulation were abandoned. The results from these experiments are also presented in Appendix B.

4.5.3 Polycarbonate Insulation

Lexan® plastic (a polycarbonate) was investigated to determine whether the chemical attack by the solvent could be overcome. This electrode insulation proved to be successful in providing resistance to both sparking and organic solvent attack as well as having a hydrophobic surface to prevent bridging.

Lexan® covered electrodes were prepared by milling out a 2 mm cavity from a 3 mm wide Lexan® sheet. The cavity was of similar size of the metal electrodes (35 × 100 × 1 mm) and the metal electrodes were then inserted into the cavity. Another sheet of Lexan® plastic was milled down to 1 mm in thickness and then placed on top of the electrodes. Any gaps were then sealed using a plastic weld. The Lexan® material proved to be a good insulator and sparking between electrodes was eliminated, hence this insulation material was used for all subsequent experiments.

4.6 ESPLIM Baffle Modifications

Throughout the testing of various wall-mounted electrode configurations in the ESPLIM reactor, it was observed that some corrosion had occurred on the stainless steel baffle plate. This corrosion created sites where aqueous droplets attached themselves to the plates, rather than falling through the organic phase.

Another baffle plate was constructed and coated in 0.08 mm of PTFE to prevent any corrosion. The new baffle was of a similar design, except that it was 30 mm taller and had two more baffles. The extra height could be accommodated by the removal of the separator plate attached to the lid.

This baffle plate, and the previous one, had the problem of air being trapped between the top of one baffle element and the bottom of the element above it. These air bubbles extended from one end of the baffle to the other and restricted the movement of the oil phase between compartments. This problem was overcome by drilling small holes into one end of the plastic baffles that extended all the way to the cavity between successive baffles. When the vessel was filled with organic solution, air was expelled through the holes as the level of organic solution increased. A schematic diagram of this baffle is shown in Appendix G.

4.7 Auxiliary Equipment Modifications

A major equipment modification was made when a 0-15,000 V AC power supply was used instead of the DC power supply that was used for all previous experiments. Many authors (Yamaguchi, Sugaya and Katayama, 1988; Scott, 1989; Scott and Wham, 1989) have shown that either AC or DC electric fields can induce a dispersion. Previous ESPLIM studies (Gu and Zhou 1988, Gu 1990a, Gu 1990b, Gu et al. 1994, Yang, Gu and Wang 1995) did not indicate the type of power supply used to generate the electric fields. Only Williams, Bailey and Broan (1997), from a different research group, indicated that an AC power supply was used in their ESPLIM investigation. Therefore, a new AC power supply was constructed and used for all future experiments. The AC electric field gave a more even size distribution of dispersed droplets and the zigzag motion of the drops was much less pronounced. The reduction in sideways movement was considered to be beneficial to the process, as it was less likely for droplets to pass through the perforations in the baffle plate and contribute to swelling and leakage.

The diaphragm pumps that were originally used to pump feed and stripping solutions to the reactor worked well at high flow rates (ie. >100 mL/hr) but at lower flow rates, accuracy varied by up to 20%. To solve this problem, custom-made syringe pumps were built for the feed and strip solutions. Both syringe pumps worked very well and dosage rates were accurate to within 2 to 5%. At the designed flow rate for each pump (60 mL/hr for feed, 14 mL/hr for strip), the syringes had a capacity for 4 hours running time.

The syringe pump used for the feed solution had provision for three syringes to be used at the same time so flow rates up to 180 mL/hr could be used. Each feed solution syringe tube had an internal diameter (ID) of 26 mm, was 520 mm in length and made from polyvinylchloride (PVC). Each syringe had a plunger that consisted of a metal tube with a plastic end-piece. The end-piece had a groove cut into it and two O-rings sat in the groove to provide a seal between the plunger and syringe. All three plungers were connected by a crossbar. A length of threaded rod was threaded into the middle plunger and this rod was connected to a gear system via a magnetic clutch. The gear system was driven by variable speed DC motor that was controlled by a variable DC power supply.

The stripping pump was similar to the feed pump except that there were only two syringes and each syringe was made from clear acrylic tubing 12 mm ID and 527 mm long. Instead of a magnetic clutch, the threaded rod was connected straight to the gear system, which in turn was connected to a fixed speed AC motor.

4.8 Summary

The original ESPLIM reactor has undergone many modifications before being suitable for experimentation. The conclusions drawn from these modifications are that:

- wound insulated wires gave poor droplet dispersion and could not be used as baffle electrodes.
- baffle plates made from perforated stainless steel and insulated with PTFE gave good drop dispersion and resisted chemical attack.
- wall electrodes with polycarbonate insulation were long lasting and prevented sparking.

- an air outlet between each baffle element is required to expel air that is trapped when filling the reactor with organic solution.
- an AC power supply gave better drop dispersion with less horizontal drop movement than a DC power supply.
- custom-made syringe pumps were found to have much better accuracy and repeatability than the original diaphragm pumps.

CHAPTER 5

EXTRACTION OF COBALT FROM SYNTHETIC LEACH SOLUTIONS

5.1 Introduction

Before investigating the separation of cobalt from nickel using actual leach solutions, many of the variables that affect the operation of the ESPLIM reactor required investigation and optimisation. The use of synthetic leach solutions simplified this optimisation process.

5.2 The Effect of Applied Voltage on Drop Diameter

To determine the effect of the applied voltage on the diameter of aqueous droplets dispersed in the organic phase, a number of tests were conducted under identical conditions except that different applied voltages were used. Different types of solutions were investigated to observe any changes in behaviour between solutions. The distance between the electrodes for this experiment and all other experiments that follow was 1 cm. The results are shown below in Table 3.

It can be seen from Table 3 that an increase in applied voltage from 0 kV to 1.5 kV slightly increased the drop diameter of all solutions. Further increases in applied voltage decreased the drop diameter, indicating the onset of dispersion. At 3 kV, there is a large difference in the dispersion behaviour of solutions containing salts of soluble carboxylic acids i.e. sodium acetate, sodium propionate and sodium formate compared to those solutions without them (1 M H_2SO_4 and PLS). This observation suggests that the composition of the aqueous phase has a significant influence on the degree of dispersion, particularly at low applied voltages (3-4 kV). However, at applied voltages where significant dispersion occurs (5.5 kV), the difference in drop size is relatively small between all solutions.

Table 3 The effect of applied voltage on average drop diameter (mm)

Applied Voltage	Avg. Drop Diameter (mm) 0 kV	1.5 kV	3.0 kV	4.0 kV	5.5 kV
1 M H_2SO_4	3.40	3.50	3.00	1.41	0.56
PLS	3.21	3.30	3.07	0.88	0.47
0.1 M Acetate	3.06	3.36	0.97	0.65	0.30
0.1 M Propionate	3.07	3.42	0.65	0.34	*[1]
0.1 M Formate	3.09	3.11	1.05	0.73	0.35

To illustrate the difference in dispersion behaviour between solutions, the results from the 0.1 M sodium acetate (NaOAc) and the 1 M H_2SO_4 experiments in Table 3 have been represented graphically in Figure 5.1.

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[1] *The average drop diameter for the propionate solution at 5.5 kV could not be accurately measured due to the very fine size of the droplets produced.

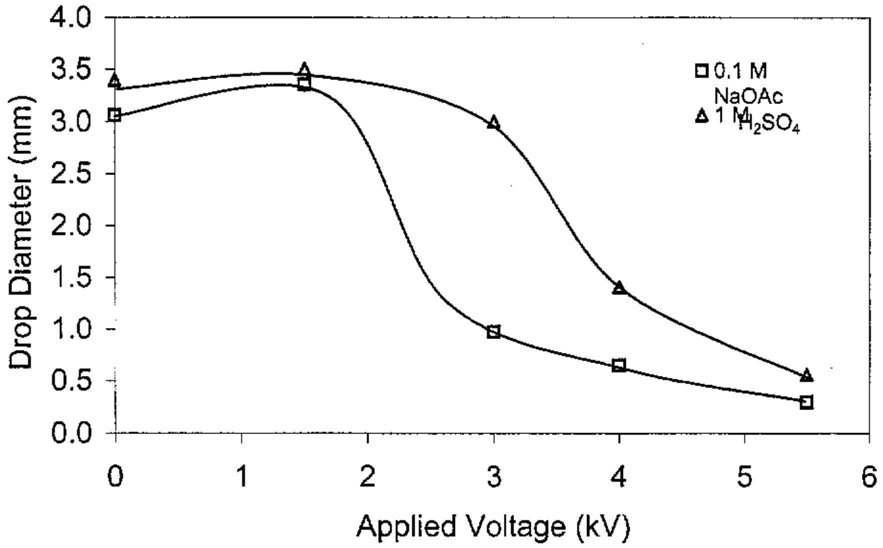

Figure 5.1 The effect of applied voltage on average drop diameter.

The apparent slight increase in drop diameter observed at 1.5 kV, compared to 0 kV, is due to elongation of the droplets caused by the electric field. The imposed electrical stresses deform the droplet in the direction of the electric field, but the stresses are not high enough to cause drop disintegration. The drop diameter was estimated using an equation given by Lewis, Jones and Pratt, (1951). Using this method, greater emphasis is placed on the major axis length than the minor axis length i.e.

$$\varphi = \sqrt[3]{d_1^2 d_2} \qquad (8)$$

where ϕ is the drop diameter (mm) , d_1 is the major axis diameter and d_2 is the minor axis diameter. Thus, increases in the length of the major axis, even when accompanied by a decrease in the minor axis is likely to give an increase in the average drop diameter. The drops formed at 0 kV and 1.5 kV were large, single drops, so the increase in drop diameter was not a result of any coalescence between drops.

At 3 kV, dispersion of the sodium acetate solution occurred, but the size distribution was large as indicated by a mean of 0.97mm with a standard deviation of 0.32mm. This suggests that dispersion and coalescence was occurring simultaneously. The acid solution, however, essentially remained as large discrete droplets with a few small daughter droplets also present. At 4 kV the sodium acetate solution was dispersed into large numbers of small, similarly sized drops. At a similar voltage, the acid solution had only broken up into two or three smaller droplets along with a number of very small daughter droplets.

At 5.5 kV an extremely fine dispersion of sodium acetate solution was observed. The size distribution of these droplets was also very narrow as indicated by a mean of 0.3 mm and a standard deviation of 0.03 mm. At the same voltage, the acid solution had dispersed into numerous droplets, but the droplets were significantly larger (0.56 mm) and the size distribution was slightly higher with a standard deviation of 0.11 mm.

The size distribution of all solutions tested, except PLS, appeared to have a similar trend. With no dispersion occurring at low applied voltages (0 - 1.5 kV) the size distribution of drops was narrow as drop size was dependent on nozzle diameter and flow rate, both of which were constant. At 3 - 4 kV, the size distribution was large due to considerable coalescence and dispersion occurring simultaneously. At higher voltages (4 - 5.5 kV), the size distribution became narrow again and many solutions had drop size standard deviations of less than 0.1 mm. It is unknown why the behaviour of the PLS did not exhibit these same characteristics.

The creation of small, similarly sized droplets is a very important advantage that electrostatic dispersion has over the mechanical agitation used in mixer-settlers and pulse columns. A narrow size distribution of droplets prevents excessive short-circuiting and helps to maintain a consistent rate of mass transfer.

The results from Figure 5.1 also show that the sodium acetate drops were always smaller than the acid drops under all voltage conditions tested. To further understand the differences in dispersion behaviour, the interfacial tension between a number of different aqueous phases and a 10% Cyanex 272/Solvent HF organic phase was measured. The results in Table 4 show similar interfacial tension values of ~18-19 mN m^{-1} for a variety of aqueous solutions. However, with the addition of certain ligands, the interfacial tension dropped significantly. Statistical analysis indicated that the interfacial tension values of propionate and acetate are not significantly different. The decrease in interfacial tension appears to be dependent on the length of carbon chain, with shorter chains i.e. formate, having less effect than longer chains.

Table 4 Interfacial tension of different aqueous phases with a 10% Cyanex 272 in Solvent HF diluent organic phase

Aqueous Phase	Interfacial Tension ($mN\ m^{-1}$)	95% Confidence Limit ($mN\ m^{-1}$)
Deionised H_2O	19.3	± 0.27
1 M H_2SO_4	18.2	± 0.39
PLS	18.2	± 0.31
0.1 M NaCl	18.2	± 0.24
0.1 M Propionate	8.4	± 0.09
0.1 M Acetate	8.5	± 0.49
0.1 M Formate	12.1	± 0.36

The results from Table 3 and Figure 5.1 shows that increasing the electric field strength above a critical value will reduce a droplet's size. The application of an electric field serves to reduce the interfacial tension due to an electrostatic repulsive force at the surface (Thornton, 1968). The addition of salts of carboxylic acids, such as sodium acetate, to the aqueous phase also reduces the interfacial tension so droplets require less electrostatic force to cause drop deformation and instability. The interfacial tension also decreases with increases in the carbon chain length of the carboxylic acid. Thus, the strength of the electric field required to reduce a droplet to a given size will be partly dependent on the nature of the aqueous phase.

5.3 The Effect of Applied Voltage on Residence Time

The effect of applied voltage on the residence time of droplets in the ESPLIM reactor was investigated using deionised water as the aqueous phase. Two measurements of residence time were made. The first measurement was the time interval from when the feed drop entered the organic solution to when the first dispersed drop had coalesced in the settler. The second measurement was the time interval from when the feed drop entered the organic solution to when the last dispersed drop had coalesced in the settler. The drops travelled through a 10 cm high electric field and an additional 1.5 cm between the bottom of the electrodes and the aqueous/organic interface in the settler. The results in Figure 5.1 show that as the applied voltage is increased, the residence time also increases.

The residence time of the aqueous phase, however, was not an even distribution from the moment the first drop had coalesced to the moment the last drop had coalesced. The majority of the drops passed out of the electric field shortly after the first drop had coalesced. For example, at 5.5 kV, most of the water droplets had coalesced into the settler between approximately 10 and 20 seconds. The smallest of drops took the longest time to coalesce into the settler, i.e. > 20 seconds, because as they reached the bottom of the electric field, they encountered a region of non-uniform field strength near the bottom edges of the metal electrodes. The non-uniformity of the field caused erratic movement of the small drops to such an extent that some drops were thrust upwards into the reactor, thus causing residence times to increase. As the travelling distance was quite small (~100 mm) and the residence times were quite short (10-20 secs), a small amount of backmixing had a relatively large effect in this reactor.

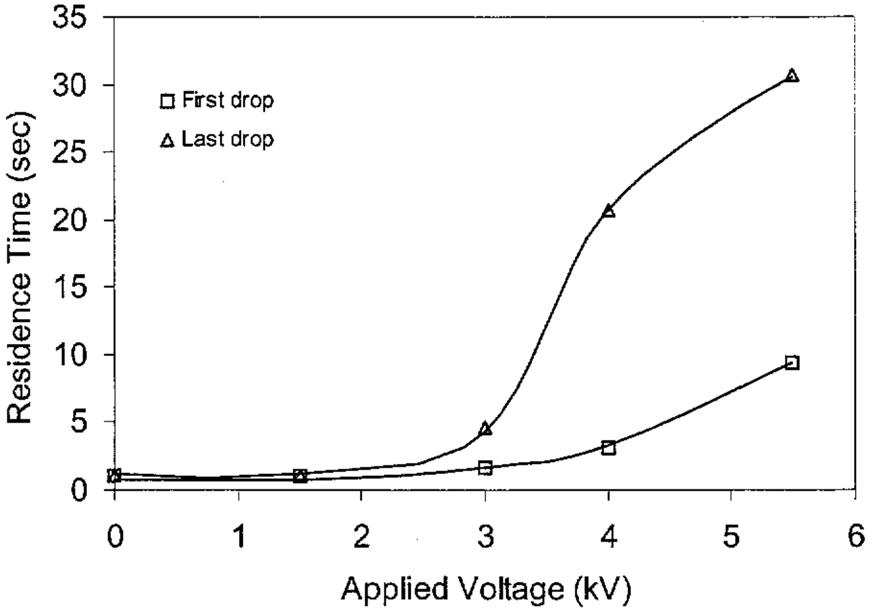

Figure 5.1 The effect of applied voltage on residence time. (Feed: Deionised H_2O; Organic: 10% Cyanex 272 in Solvent HF)

Gu (1990a) reported a mean residence time of 4 seconds at field intensities of 3.8-4.3 kV/cm. However, Suyama et al. (1993) reported residence times of 10-20 seconds when only 2.5 kV/cm was applied. Both of these studies and the present investigation all had electric fields 10 cm in height. The differences between the three studies result from marked differences in chemical and physical properties of the systems used.

5.4 The Effect of Applied Voltage on Extraction Efficiency

To determine the effect of the applied voltage on the extraction efficiency of ESPLIM, a number of extraction tests were conducted using a synthetic cobalt solution. The results of this experiment are shown in Figure 5.1.

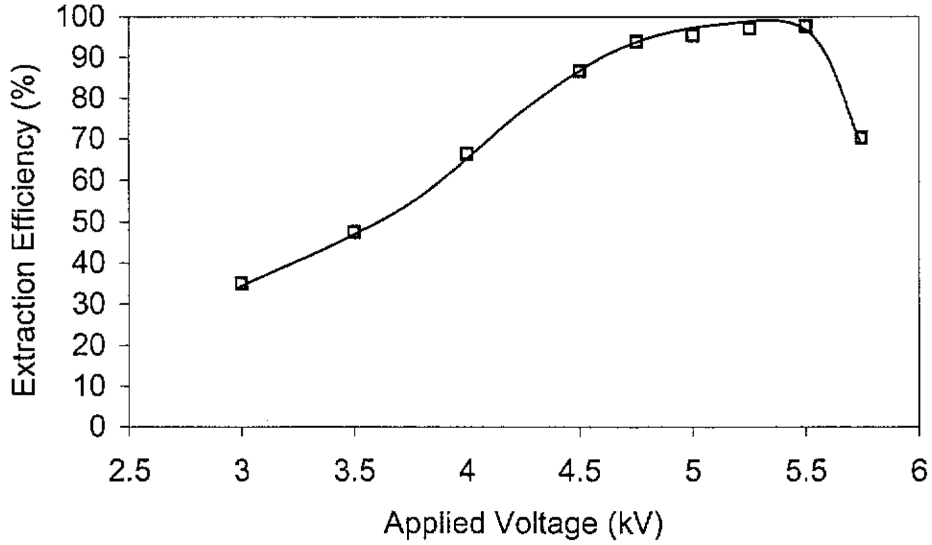

Figure 5.1 The effect of applied voltage on extraction efficiency. (Feed: 1014 ppm Co^{2+}, 0.1 M $NaCH_3COO$, $pH_0 = 6.5$; Strip: 1 M H_2SO_4, 840 ppm K^+; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL/hr; Time: 180 min)

At low applied voltages (3-3.5 kV), the aqueous feed drops broke into 2 or 3 smaller droplets, which then fell rapidly through the organic phase. Consequently, the extraction of cobalt was relatively poor at approximately 40%.

As the applied voltage was increased, the feed drops began to be broken up into much smaller droplets, thus increasing the total surface area for extraction to occur. The smaller droplets also began to zigzag horizontally within each compartment. This had the effect of increasing the contact time between the aqueous droplets and the organic phase. Hence, the extraction efficiency increased with an increase in applied voltage.

At 5.5 kV of applied voltage, the extraction efficiency reached a maximum of 98%, so this voltage was deemed to be optimal and used for all subsequent experiments. The raffinate pH at this voltage was 4.90. This optimal applied voltage compares well to other ESPLIM studies (Gu et al., 1994; Yang, Gu and Wang, 1995), however, the optimal voltage will depend on the physical characteristics of the electrode insulation, chemical system and distance between the electrodes (Gu, 1992).

At 5.75 kV, the extraction efficiency decreased significantly. This was due to an increase in the leakage levels from the stripping compartment. At high voltages, very small droplets in both compartments are more likely to move through the baffle channels. Small strip solution droplets that contain high cobalt concentrations move across to the extraction compartment and increase the concentration of cobalt in the raffinate. The acidity of the strip solution droplets prevents any cobalt extraction in the extraction compartment. Furthermore, if the leaked stripping droplets mix with other feed droplets, the pH of those feed droplets will decrease, thus lowering the tendency for extraction in those droplets. The extraction efficiency is calculated from the cobalt concentration of the raffinate, so even if 100% of the cobalt in the feed is extracted into the organic phase, any leakage that occurs has the effect of reducing the extraction efficiency to less than 100%.

5.5 The Effect of Applied Voltage on Swelling and Leakage

To confirm that the decrease in extraction efficiency observed at 5.75 kV in Figure 5.1 was due to an increase in the leakage level, an analysis of the raffinate solution was undertaken. The 1 M H_2SO_4 stripping solution used in this experiment was spiked with K_2SO_4, which acted as a tracer. Potassium sulfate was not appreciably extracted into the organic phase (see Appendix C), so the only way that it could enter the raffinate was by physically moving through the baffle channels via a leaking drop.

Similarly, the presence of sodium in the feed solution in the form of sodium acetate allowed for the determination of swelling to be made from the loaded strip solution. This method of using sodium as a tracer element has been used in a previous ESPLIM study (Williams, Bailey and Broan, 1997). Bench scale shake out tests confirmed that negligible extraction of sodium occurs under similar chemical conditions to that used in this study (see Appendix C).

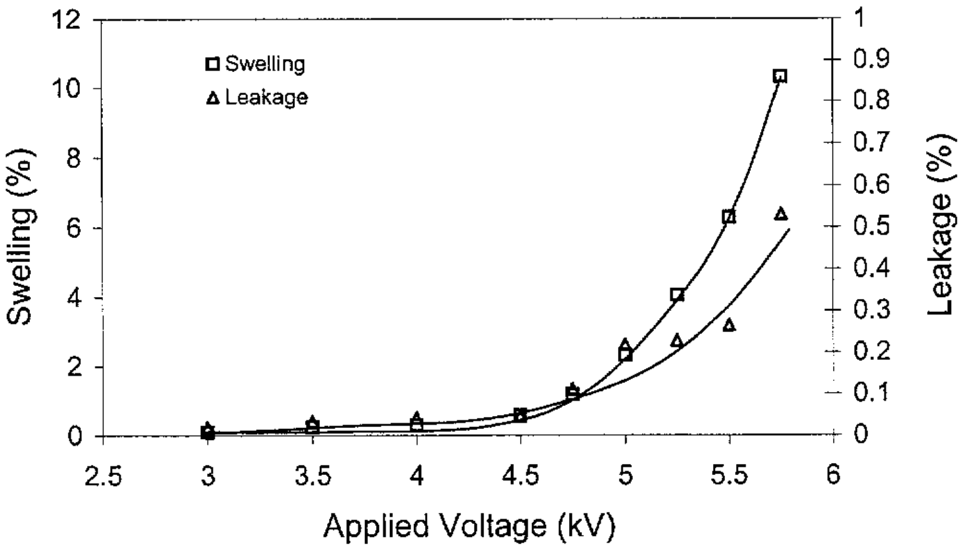

Figure 5.1 The effect of applied voltage on swelling and leakage. (Feed: 1014 ppm Co^{2+}, 0.1 M $NaCH_3COO$, $pH_0 = 6.5$; Strip: 1 M H_2SO_4, 840 ppm K^+; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL/hr; Time: 180 min)

It can be seen from Figure 5.1 that the amount of leakage doubles from 0.26% to 0.53% with an increase in voltage from 5.5 kV to 5.75 kV. This result explains the sharp drop in extraction efficiency that is seen in Figure 5.1. The level of leakage at 5.5kV (0.26%) is similar to that reported by Williams, Bailey and Broan (1997), but a little higher than other reported leakage levels (Gu, 1990a; Yang, Gu and Wang, 1995; Wu, Gu and Jin, 1991).

The level of swelling in this study is significantly higher than that reported in other ESPLIM studies (Gu, 1990a; Gu et al., 1994; Gu et al., 1991; Yang, Gu and Wang, 1995; Williams, Bailey and Broan, 1997). Generally, the above papers reported swelling levels of approximately 1% or lower at optimised conditions. The present study observed swelling of ~6% at the optimal applied voltage of 5.5 kV. This may have been due to the use of a more open baffle design in the present study. For example, Williams, Bailey and Broan (1997) used a baffle that had a 1.25 mm baffle opening and Gu et al. (1991) had a 1.5 mm open space in their apparatus. The present study used a baffle opening of 2 mm. A wider baffle opening increases the possibility of small aqueous droplets entering the baffle channel.

It is unknown as to why leakage levels in the present baffle design are comparable to other ESPLIM studies, but the swelling levels are not. It is possible, however, that some of the difference may be due to the way other authors have conducted their swelling and leakage experiments. For example, Gu (1990a) uses a feed solution containing 1000 ppm cobalt in 2.4 N HCl and a strip solution of deionised water to determine swelling and leakage rates. However, it has been shown earlier in this study (Section 5.1) that the type of solution dispersed in an electric field has an effect on the size of the dispersed droplets. It follows that the size of the dispersed droplets has a direct effect on the swelling and leakage rates of the system. Therefore, if the swelling and leakage rates are determined with solutions other than those used for extraction experiments, it could be argued that those swelling and leakage rates are not indicative of those present during extraction. In contrast, the solutions used to determine swelling and leakage in this study closely resembled those used for extraction experiments.

5.6 The Effect of Applied Voltage on the Stripping Solution

The strength of the applied voltage also has an effect on the concentration of cobalt in the loaded strip solution, as seen in Figure 5.1. As the applied voltage was increased to 5.5 kV, the cobalt concentration in the loaded strip solution increased.

The concentration of cobalt in the loaded strip solution is related to the extraction efficiency. As more cobalt is extracted into the organic phase in the extraction compartment, the concentration of the cobalt complex in the stripping compartment also increases. Therefore, more cobalt is available for stripping from the organic phase in the stripping compartment. An increase in the applied voltage also increases the number of small, oscillating acid droplets that have a large total surface area to strip the cobalt from the organic phase.

At 5.75 kV there was a significant decrease in the cobalt concentration of the loaded strip solution. This was due to an increase in swelling. Swelling dilutes the loaded strip solution with an extra volume of solution and also contaminates the loaded strip solution with non-extracted elements. When this is combined with a large loss of cobalt strip solution via leakage, the cobalt concentration of the loaded strip solution is substantially reduced.

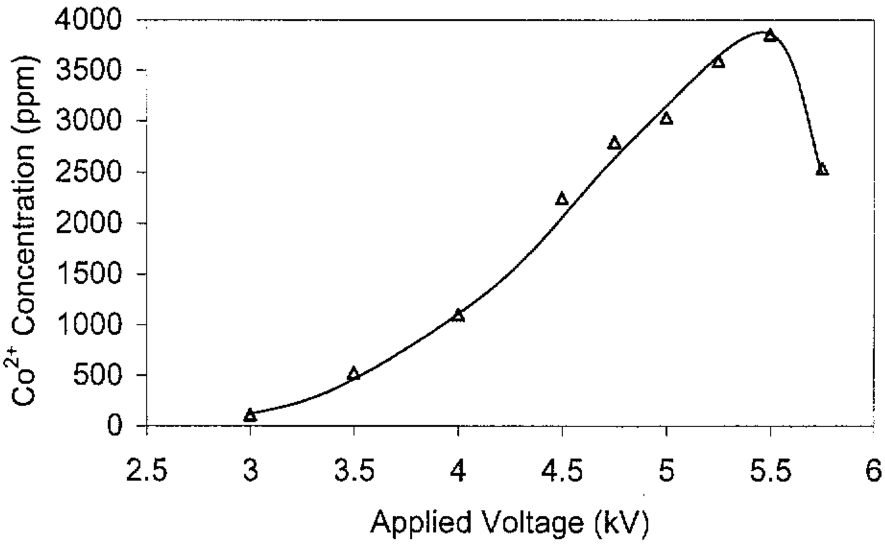

Figure 5.1 The effect of applied voltage on the loaded strip solution. (Feed: 1014 ppm Co^{2+}, 0.1 M $NaCH_3COO$, $pH_0 = 6.5$; Strip: 1 M H_2SO_4, 840 ppm K^+; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL/hr; Time: 180 min)

5.7 Determination of Time Required to Reach Apparent Steady State

To determine the time required for ESPLIM to reach an apparent steady state, a series of experiments were performed under similar conditions, except that the extraction time was different for each experiment. Aqueous samples from the extraction and stripping settlers were taken as well as organic samples from each compartment. The results of this experiment are shown in Figure 5.1 and Figure 5.2.

Figure 5.1 shows that the extraction efficiency is relatively unchanged at approximately 97%, regardless of the length of the experiment. This is likely to be due to the excess of free extractant available in the extraction compartment at all times.

The cobalt concentration of the loaded strip solution, however, increases quickly over the first two hours and then levels off to approximately 4000-4100 ppm thereafter. The increase in cobalt concentration in the strip solution over the first two hours reflects an increasing build up of cobalt in the organic phase over that time. Once the concentration of cobalt in the organic phase becomes stable, the concentration of cobalt in the strip solution becomes stable also. Supporting evidence of this is given in Figure 5.2, which shows that the concentration of cobalt in the organic phase in both compartments reaches relatively stable levels after 2.5 to 3 hours. The difference in cobalt concentration between the two compartments (50-60 ppm) reflects the driving force for the diffusion of the cobalt complex from the extraction compartment to the stripping compartment.

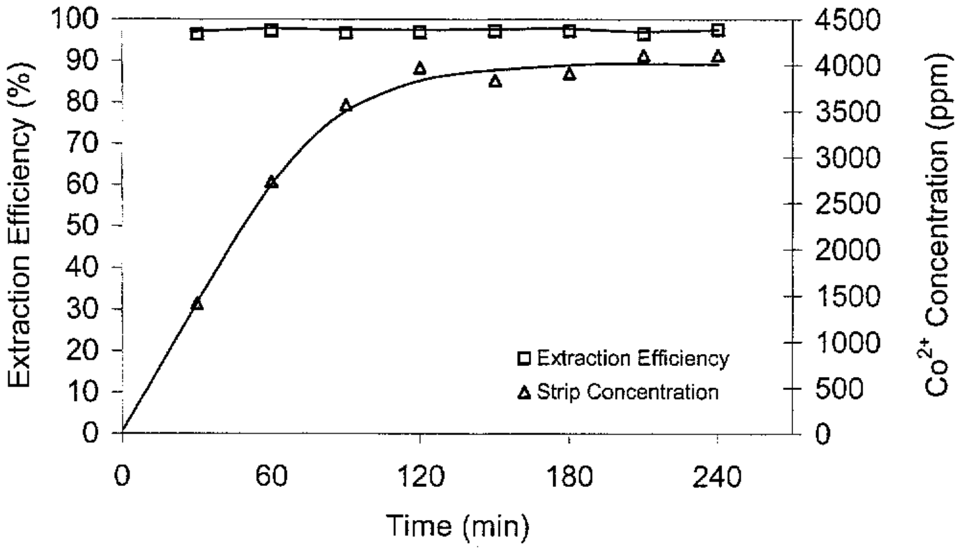

Figure 5.1 The effect of time on extraction efficiency and loaded strip solution concentration. (Feed: 1014 ppm Co^{2+}, 0.1 M $NaCH_3COO$, $pH_0 = 6.5$; Strip: 1 M H_2SO_4; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL/hr; Applied voltage: 5.5 kV)

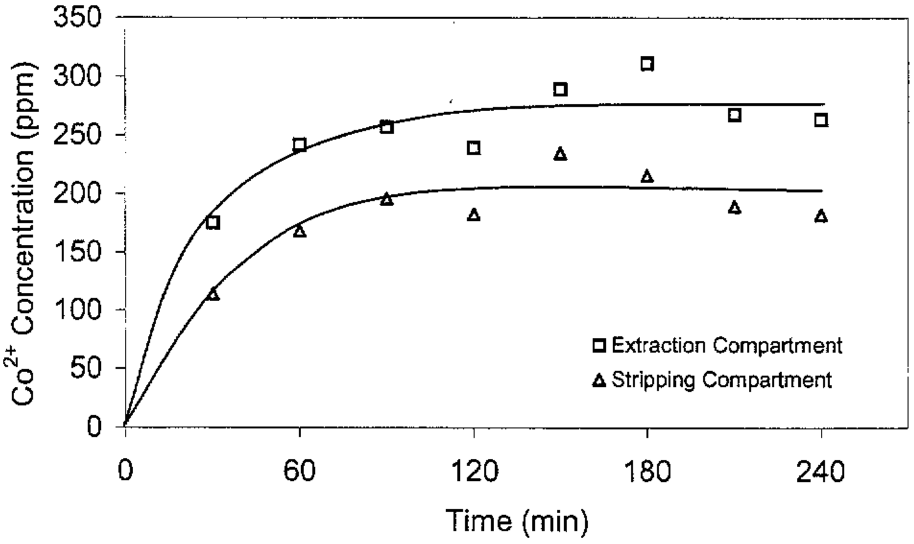

Figure 5.2 The effect of time on the organic phase cobalt concentration in the extraction and stripping compartments. (Feed: 1014 ppm Co^{2+}, 0.1 M $NaCH_3COO$, $pH_0 = 6.5$; Strip: 1 M H_2SO_4; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL/hr; Applied voltage: 5.5 kV)

The data relating to the extraction efficiency, loaded strip concentration and cobalt concentrations in the organic phase suggests that the present ESPLIM system reaches steady state after approximately 2 to 3 hours. For these reasons, all subsequent experiments were conducted for a minimum of 3 hours to ensure that steady state within the ESPLIM reactor had been achieved.

This result is comparable with the results obtained by Williams, Bailey and Broan (1997) who reported that their ESPLIM apparatus reached equilibrium after 2 to 2.5 hours. No other ESPLIM studies have reported times for steady state to be reached.

5.8 The Effect of pH on Cobalt and Nickel Extraction

To determine the effect of pH on the extraction of cobalt and nickel, a number of extraction tests were carried out at different initial pH values. Solutions of cobalt and nickel were tested separately under comparable conditions.

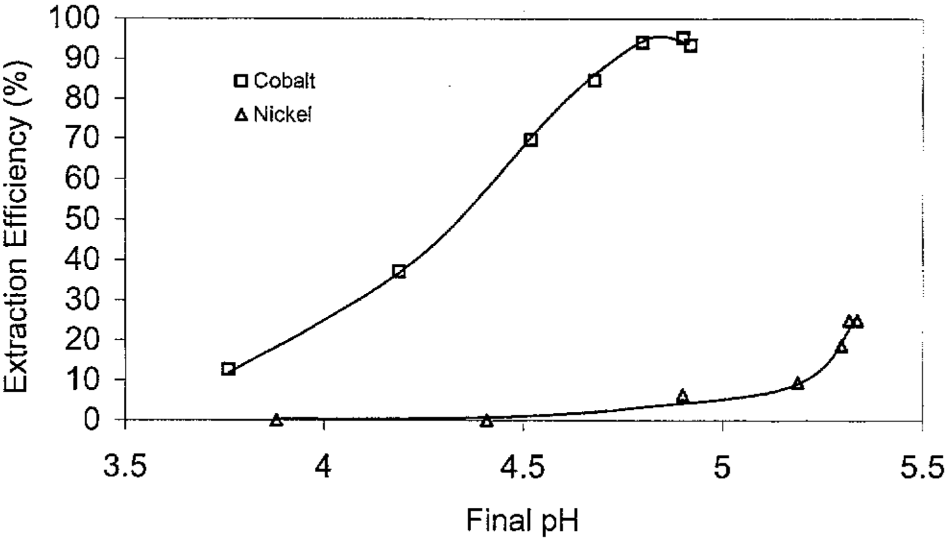

Figure 5.1 The effect of pH on cobalt and nickel extraction. (Feed: ~1000 ppm Co^{2+} or Ni^{2+}, 0.1 M $NaCH_3COO$; Applied voltage: 5.5 kV; Strip: 1 M H_2SO_4; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 64 mL/hr; Strip flow rate: 12 mL/hr; Time: 180 min)

Figure 5.1 shows that very good cobalt extraction (94-95%) was achieved at final (raffinate) pH values of 4.80-4.90 while only ~6% of nickel was extracted at a similar pH. The cobalt extraction isotherm is similar to that reported by Preston (1982) and Feather and Cole (1996) who also used a Cyanex 272 system, although the experimental conditions used were different in each case. The nickel extraction isotherm, however, was shifted to slightly lower pH values when compared with other published Cyanex 272 isotherms (Sole and Hiskey, 1992; Tait, 1993a; Tait, 1993b; Feather and Cole, 1996). This was possibly due to the use of a lower ionic strength solution in this study compared to the aforementioned studies, as it is known that the extraction pH increases with increasing ionic strength (Sole and Hiskey, 1992).

The relative similarity of the extraction isotherms generated by ESPLIM to known extraction isotherms suggests that data obtained from conventional shakeout tests can be used with confidence in ESPLIM. Furthermore, the electric field appears to have no effect on the extraction reaction, thus electrostatic dispersion is merely a contactor method.

5.9 The Effect of Soluble Salts of Carboxylic Acids on Cobalt Extraction

This section investigates the effect that soluble salts of carboxylic acids (eg. sodium acetate) has on the efficiency of the extraction process and whether the results can be interpreted by assuming a buffer role for the acetate ion. Also, other ligands such as formate and propionate are compared to acetate in terms of apparent kinetics.

5.9.1 The Effect of Sodium Acetate on Cobalt Extraction

To determine the effect of acetate ions on the extraction process, a number of tests were carried out at different sodium acetate concentrations. The results (Figure 5.1) indicate that the concentration of sodium acetate in the feed solution has a significant impact on the extraction efficiency of the process. Increasing the sodium acetate concentration increases the pH of the raffinate solution and consequently, extraction efficiency is increased.

From the results of Figure 5.1, a sodium acetate concentration of 0.125 M gave a slightly better result than that of 0.1 M, so this concentration was used for future experiments.

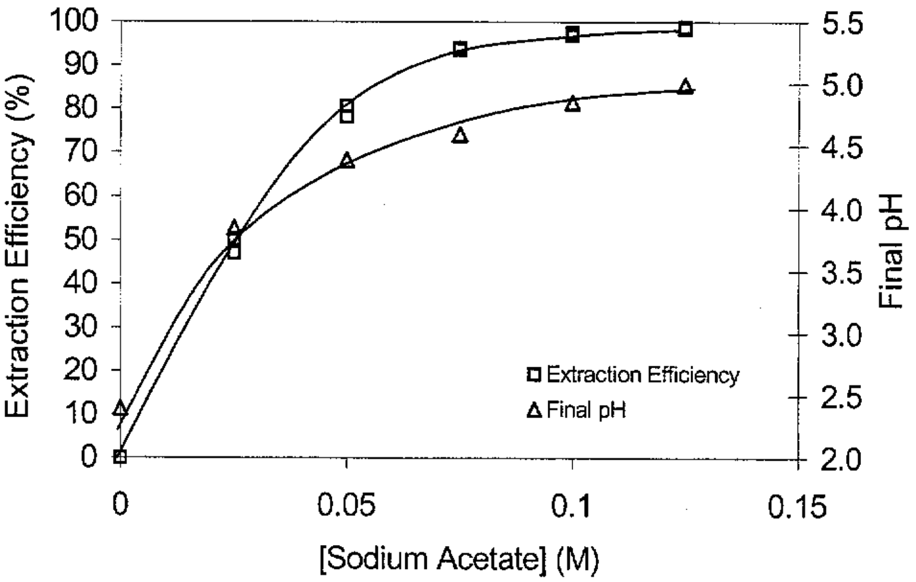

Figure 5.1 The effect of sodium acetate concentration on extraction efficiency and final pH. (Feed: ~1000 ppm Co^{2+}, $pH_0 = 6.5$; Strip: 1 M H_2SO_4; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 63 mL/hr; Strip flow rate: 13 mL/hr; Applied voltage: 5.5 kV; Time: 180 min)

In all previous experiments, 0.1 M sodium acetate was added to the feed solution on the premise that the acetate acts as an accelerating ligand (Gu, Zhou and Jin 1990). However, the data from Figure 5.1 suggests that the addition of acetate merely serves to buffer against large changes in pH from the extraction reaction.

In order to test the buffering action, a set of calculations was made that predicted the pH of the raffinate solution based on the amount of extraction that took place. It was assumed that two protons were released into aqueous solution for every cobalt ion extracted and that no acetic acid was transferred to the organic phase. The results are shown in Table 5 and a complete table of all calculations is shown in Appendix D.

Table 5 Comparison of measured and calculated raffinate pH values

$NaCH_3COO$ concentration (mol/L)	Co^{2+} extraction (%)	Calculated raffinate pH	Measured raffinate pH
0	0	-	2.40
0.025	48.6	4.43	3.85
0.050	79.4	4.62	4.39
0.075	93.8	4.80	4.59
0.100	97.2	4.98	4.85
0.125	98.6	5.09	4.99

Table 5 shows that the calculated raffinate pH is very close to the measured pH. The exception is the 0.025 M $NaCH_3COO$ concentration, which is understandable because at this concentration little buffering action could be expected. The measured raffinate pH, however, is consistently lower than the calculated pH. It was also noted that with no acetate addition, the pH dropped from its initial value of 6.5 to its final value of 2.4, but no cobalt was extracted.

To further understand the disparity between the calculated and measured raffinate pH values, a blank experiment was performed using similar conditions to the previous experiment except that no cobalt was added to the feed solution and no stripping solution was used. The results (Appendix E) showed that the raffinate pH of all of the acetate feed solutions was significantly lower than the feed pH, indicating that other side reactions were taking place. Previous shake out test results showed negligible sodium extraction (Appendix C). It has been shown by other investigators (Ritcey and Ashbrook, 1984; Islam and Biswas, 1979) that commercial extractants usually contain water soluble impurities in sufficient quantities to affect the pH of the aqueous phase and it is believed that this is the cause of the low pH raffinate solutions.

The results from the blank experiment were then incorporated into the calculations used to derive Table 5 as an adjustment factor. The adjustment factor took into account the pH drop in the raffinate solution from the organic impurity effect. These adjusted calculated raffinate values can be seen in Table 6.

Table 6 Comparison of measured and calculated raffinate pH values after adjustment

$NaCH_3COO$ concentration (mol/L)	Co^{2+} extraction (%)	Calculated raffinate pH with adjustments	Measured raffinate pH
0	0	-	2.40
0.025	48.6	4.20	3.85
0.050	79.4	4.52	4.39
0.075	93.8	4.74	4.59
0.100	97.2	4.92	4.85
0.125	98.6	5.02	4.99

With the adjustments made from the blank experiment, Table 6 shows that there is a definite trend and a very close correlation between measured and calculated raffinate pH values and the concentration of acetate in the feed solution. The remaining difference between the calculated and measured raffinate pH values could be accounted for by a small quantity of strip solution leaking into the extraction compartment. Any leakage alters the results due to two reasons. Firstly, the highly acidic strip solution decreases the pH of the raffinate solution, particularly in those solutions that contain low concentrations of acetate because their buffering effect is weak. Secondly, the leaked strip solution also increases the cobalt concentration in the raffinate. This changes the calculated amount of protons that have been released into solution, thus affecting the calculated pH of the raffinate.

The mechanism by which the acetate acts as a pH buffer can be represented by the following set of equilibrium equations.

$$Co^{2+}_{(aq)} + 2RH_{(org)} \leftrightarrow CoR_{2\,(org)} + 2H^{+}_{(aq)} \qquad (9)$$

$$CH_3COO^{-}_{(aq)} + H^{+}_{(aq)} \leftrightarrow CH_3COOH_{(aq)} \qquad (10)$$

The protons that are liberated from the extractant during the exchange with cobalt (equation 9) react with the acetate ion to produce acetic acid (equation 10). The acetic acid effectively removes any free protons from the aqueous solution and in this way, the pH of the solution remains high enough for cobalt extraction to remain favourable.

5.9.2 The Kinetics of Soluble Salts of Carboxylic Acids

Evidence presented by Wasan, Gu and Li (1984), Gu, Wasan and Li (1985) and Gu, Wasan and Li, (1986) tends to suggest that auxiliary ligands, such as acetate, may be actively involved in parts of the extraction process other than acting as a pH buffer. A short investigation was carried out to observe the effect of salts of carboxylic acids using formate, acetate and propionate as examples.

The composition of the solutions used in this experiment is described in Section 3.9. Samples of each aqueous solution were vigorously stirred with an equal volume of 10% Cyanex 272 in Solvent HF organic solution over different time intervals. The pH of all raffinate solutions was 4.28 ± 0.05 pH units.

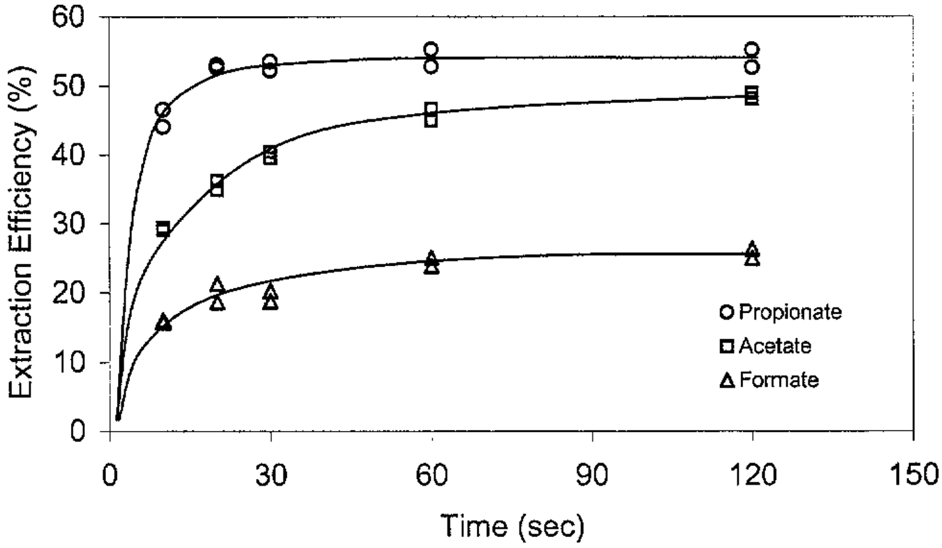

Figure 5.1 The effect of ligand type on the kinetics of extraction. (Feed: ~300 ppm Co^{2+}, pH 4.28; Organic: 10% Cyanex 272 in Solvent HF; A:O ratio: 1:1)

It can be seen from Figure 5.1 that there is a marked difference in the amount of cobalt extraction and the rate of extraction for each ligand. It was found that propionate showed more extraction and a greater rate of extraction than acetate and formate.

The kinetics of cobalt extraction has a strong correlation to the pK_a of the ligand. The pK_a values of propionic acid, acetic acid and formic acid are 4.87, 4.75 and 3.75 respectively. Cobalt extraction is favoured at pH values of ~5.0 as indicated by the pH isotherm in Figure 5.1, so ligands that have dissociation constants close to this value have a greater effect on the rate of extraction. Similar results were obtained by Dreisinger, Cooper and Distin (1989).

The results from Figure 5.1 may also be partly explained by the ionic strength of the solutions. The ionic strength of the acetate and propionate solutions was similar at approximately 0.6 M, while the ionic strength of the formate solution was approximately 1.7 M. An increase in ionic strength shifts the equilibrium position of the extraction isotherm to higher pH (Sole and Hiskey, 1992), so less cobalt extraction with the formate solution is to be expected.

The extraction data also correlates well to the interfacial tension data presented in Section 5.2. The low interfacial tension values of propionate and acetate suggest that a better dispersion with smaller drop sizes was obtained with these ligands than with formate. Furthermore, the slight difference in interfacial tension between acetate and propionate is also consistent with the slight difference in the extent of extraction. Wasan, Gu and Li (1984), Gu, Wasan and Li, (1985) and Gu, Wasan and Li (1986) determined that acetate had the strongest ligand effect in their studies, however propionate was not tested.

In practical terms, the use of salts of carboxylic acids in the nickel laterite industry is not viable due to the operating cost of the reagents required to treat the large flow rates used. Maintaining pH at the right level is crucial to any solvent extraction process and must be done as economical as possible. This subject is investigated in Section 5.15.

5.10 The Effect of Feed Flow Rate on Extraction Efficiency

To determine the effect of feed flow rate on the extraction efficiency and loaded strip solution, a number of comparable tests were performed at feed flow rates from 60 mL/hr to 141 mL/hr.

The results from Figure 5.1 show that as the feed rate is increased, there is a slight decrease in the extraction efficiency. However, 95% extraction can still be achieved at 103 mL/hr. This trend is to be expected, because an increase in feed flow rate causes an increase in the overall mass flow to the organic phase. This in turn increases the concentration of the cobalt complex in the organic phase and creates a decrease in the free extractant concentration in the extraction compartment. As the free extractant concentration decreases, the probability that mass transfer from the aqueous phase to the organic phase decreases.

It was also observed that as the feed flow rate increased, there was a slight increase in the size of the droplets. An increase in drop size may be caused by an increased frequency of drop-drop coalescence, as there are more droplets per unit area to collide with. Increasing drop size decreases extraction efficiency because there is a decrease in the total surface area per unit volume available for mass transfer to take place. Consequently, if high flow rates are to be used, then the applied voltage may need to be increased to maintain a suitable drop size.

Using a cobalt and D2EHPA/kerosine extraction system, Gu (1990b) increased the feed flow rate from 288 mL/hr to 684 mL/hr (a factor increase of 2.38) and experienced a decrease in efficiency from 97.9% to 86.5%. The present study increased the feed flow rate from 60 mL/hr to 141 mL/hr (a factor increase of 2.35) and only experienced a decrease in efficiency from 97.5% to 90.2%. However, the volumetric throughput per cross sectional area in the study by Gu (1990b) was approximately 2.5 times greater than the present study, which may account for the slightly lower extraction efficiency at higher flow rates in that study.

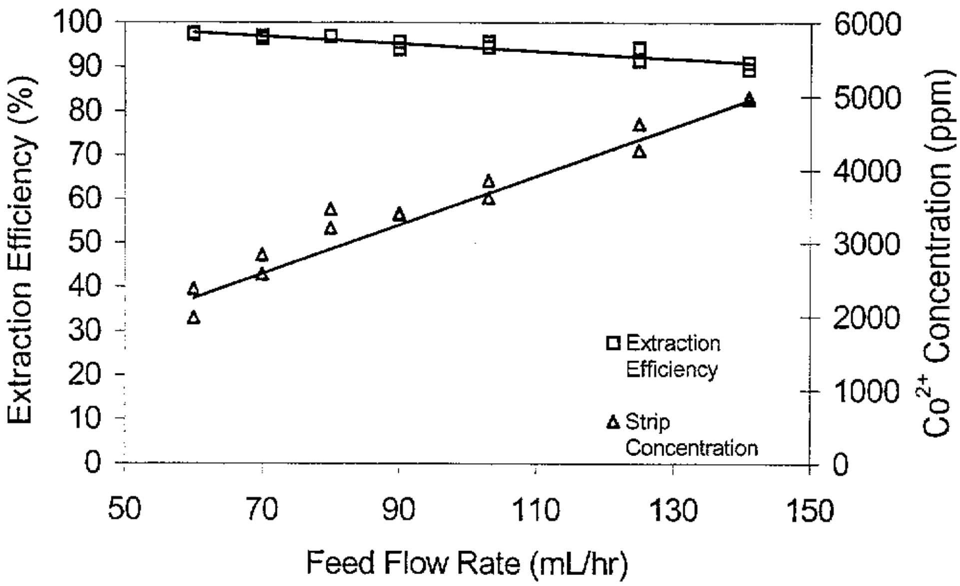

Figure 5.1 The effect of feed flow rate on extraction efficiency and loaded strip concentration. (Feed: ~1000 ppm Co^{2+}, 0.125 M $NaCH_3COO$, pH_0 = 6.5; Applied voltage: 5.5 kV; Strip: 1 M H_2SO_4; Organic: 10% Cyanex 272 in Solvent HF; Strip flow rate: 13 mL/hr; Time: 180 min)

Figure 5.1 also shows that the cobalt concentration of the loaded strip solution increases as the feed flow rate increases. As the feed flow rate increases, more cobalt is extracted into the organic phase so the concentration of the cobalt-complex in the extraction compartment increases. This creates a larger driving force for the cobalt-complex to diffuse into the stripping compartment, which in turn increases the concentration of the cobalt-complex in the stripping compartment. Under a constant flow rate of stripping solution, more cobalt is stripped into a similar volume of solution and therefore, the concentration of the strip solution increases.

5.11 The Effect of Stripping Flow Rate on Extraction Efficiency

To determine the effect of stripping flow rate on the extraction efficiency, a number of tests were performed at stripping flow rates between 13–26 mL/hr.

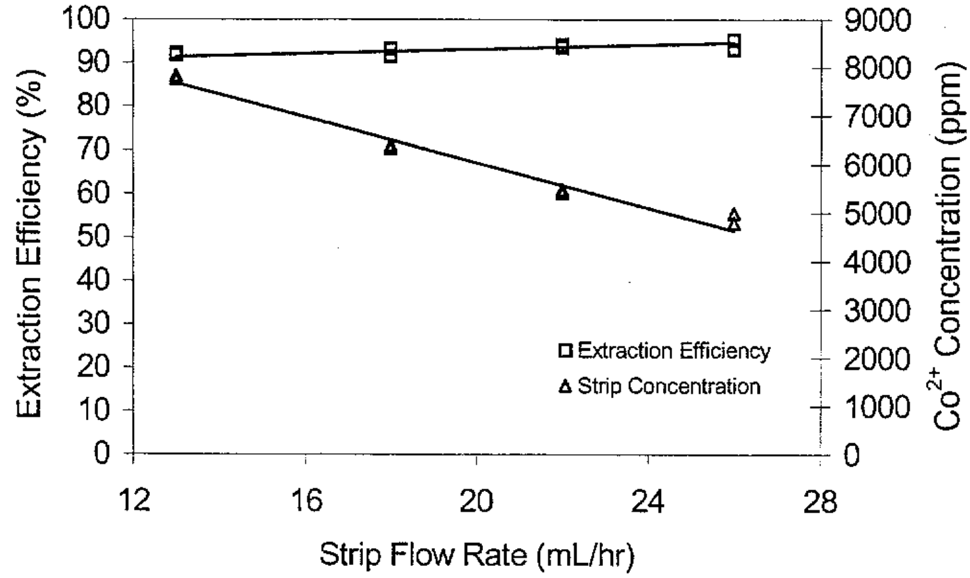

Figure 5.1 The effect of stripping flow rate on extraction efficiency and loaded strip concentration. (Feed: ~1000 ppm Co^{2+}, 0.125 M $NaCH_3COO$, $pH_0 = 6.5$; Applied voltage: 5.5 kV; Strip: 1 M H_2SO_4; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 141 mL/hr; Time: 180 min)

Figure 5.1 shows that as the stripping flow rate is increased, there is a corresponding increase in the extraction efficiency of ESPLIM. Increasing the stripping flow rate increases the amount of free extractant in the stripping compartment. This increases the driving force of the free extractant to diffuse into the extraction compartment, which in turn increases the amount of free extractant available for extraction in the extraction compartment. With a constant feed flow rate, more free extractant is available for reaction and therefore, the efficiency of extraction increases.

The feed flow rate used in this experiment was 141 mL/hr – the highest flow rate tested in the previous experiment (Section 5.10). At a strip flow rate of 13 mL/hr, an extraction efficiency of 91.9% was achieved. When the strip flow rate was doubled to 26 mL/hr, the extraction efficiency was increased to 94.1%. This result indicates that ESPLIM is able to operate over a wide range of feed flow rates with high extraction efficiencies as long as there is sufficient free extractant available in the extraction compartment.

The cobalt concentration of the loaded strip solution decreased as the stripping flow rate was increased. An increased strip flow rate decreases the cobalt-complex concentration in the stripping compartment and therefore, less cobalt is stripped into the acidic strip solution. However, in a practical application, the cobalt concentration of the strip solution can be maintained at high levels by recirculating the strip solution until the desired cobalt concentration is attained. This process is investigated in Section 6.4

5.12 The Separation of Cobalt from Nickel Using Synthetic Leach Solutions

In order to determine the effectiveness of ESPLIM to separate cobalt from nickel in a combined solution, a set of experiments was carried out using three cobalt solutions (~1000 ppm) with increasing nickel concentrations (ie. 1048 ppm, 4725 ppm and 9540 ppm). The results, in Figure 5.1, show that as the nickel concentration in the feed solution is increased, there is a corresponding decrease in the extraction efficiency of cobalt. This was found to be due to a decrease in the raffinate pH caused by an increase in the co-extraction of nickel. A raffinate pH of 4.98 was measured for the feed solution containing 1024 ppm Co^{2+} and 1048 ppm Ni^{2+}, whereas a raffinate pH of 4.77 was measured for the feed solution containing 1222 ppm Co^{2+} and 9540 ppm Ni^{2+}. As shown in Section 5.8, a pH of 4.90 or higher is required for maximum cobalt extraction.

Although the percentage of nickel extraction was small in all cases (3.4% for the solution containing 1024 ppm Co^{2+} and 1048 ppm Ni^{2+} compared with 5.1% for the solution containing 1222 ppm Co^{2+} and 9540 ppm Ni^{2+}), the co-extraction of nickel was more deleterious at higher nickel concentrations. A greater mass of nickel was transferred to the organic phase for feed solutions containing higher nickel concentrations and consequently, more hydrogen ions entered the aqueous phase, lowering the pH and inhibiting the extraction of cobalt. The amount of nickel co-extraction in this study is consistent with that reported using conventional solvent extraction methods (Tait, 1993a; Tait, 1993b; Rickelton, Flett and West, 1984; Feather and Cole, 1996).

The increasing nickel concentration in the strip solution as the nickel concentration in the feed increased is a reflection of the increasing amount of nickel that was co-extracted into the organic phase and subsequently stripped. The cobalt concentration in the strip solution remained relatively stable for each solution tested, indicating that the high cobalt extraction efficiency (>87%) maintained the cobalt-complex concentration in the stripping compartment to similar levels.

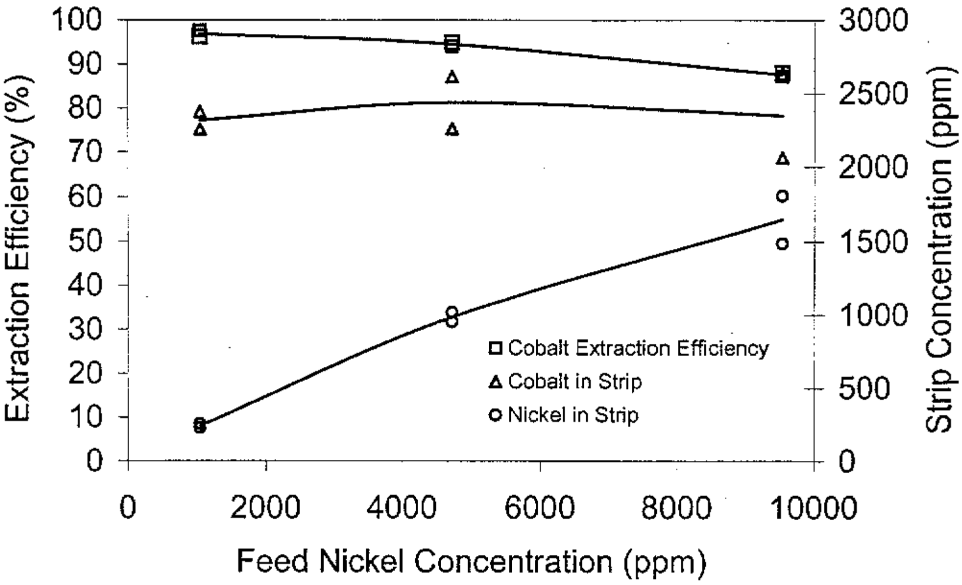

Figure 5.1 Separation of cobalt from nickel using synthetic solutions. (Feed: 0.125 M $NaCH_3COO$, $pH_0 = 6.5$; Applied voltage: 5.5 kV; Strip: 1 M H_2SO_4; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 13 mL/hr; Time: 180 min)

A contributing factor to the high concentration of nickel in the strip solution at high nickel feed concentrations was found to be due to swelling. At constant swelling levels, more nickel is to be expected in the strip solution when high concentrations of nickel are present in the feed.

As an example, at 2% swelling, the solution containing 1048 ppm Ni^{2+} is expected to contribute 21 ppm of nickel to the the strip solution. However, for a solution containing 9540 ppm of Ni^{2+}, then a swelling rate of 2% would contribute 187 ppm of nickel in the strip solution (see Appendix F for calculations).

It was clear, at this stage of the study, that swelling and leakage had an adverse effect on the extraction efficiency and the purity of the strip solution. This inhibits the practical application of the ESPLIM technique in the separation and purification of cobalt from PAL solutions, which contain significant amounts of impurities.

5.13 The Effect of Baffle Design on Swelling and Leakage

In order to further determine the effect that swelling and leakage played in the performance of ESPLIM, a number of tests were carried out on several baffle designs and their performance was compared in terms of swelling and leakage. The changes to the design of the baffle were significant and proved to be very successful. Schematic diagrams of all baffles used are shown in Appendix G and the results of this experiment are presented in Figure 5.1.

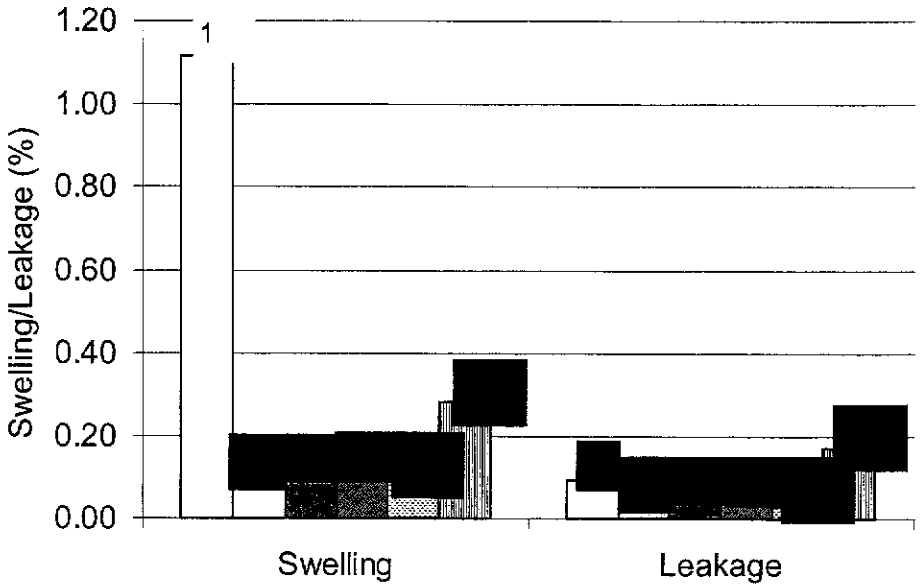

Figure 5.1 The effect of baffle design on swelling and leakage. (Feed: ~1000 ppm Co^{2+}, 0.125 M $NaCH_3COO$, $pH_0 = 0.8$; Applied voltage: 5.5 kV; Strip: ~1000 ppm Cu^{2+}, 1 M H_2SO_4; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 13 mL hr; Time 180 min)

Baffle 1 is the original baffle design that all previous experiments were conducted with. Baffle 2a has a metal electrode with a 2 mm slot height and uses a 150 μm mesh attached to an acrylic frame. Baffle 2b uses the same metal electrode but has a smaller 80 μm mesh. Baffle 3a has a metal electrode with a 1 mm slot height, but there are twice as many slots, making the total open area of the electrode the same as baffles 2a and 2b. Baffle 3a used the 150 μm mesh attached to an acrylic frame. Baffle 3b has the same electrode configuration of 3a but used the smaller 80 μm mesh. Baffle 4 is similar to baffle 1 but it has a set of perpendicular barriers instead of angled ones.

Baffle 4 was designed with the idea that swelling and leakage would be minimised with a higher baffle angle. Therefore, a baffle with a vertical barrier should have had better swelling and leakage resistance to any angled barrier. This worked somewhat, with swelling reduced to a quarter of the amount of the original angled baffle. Leakage, however, was almost double that of the original design. It was observed that the right-angled nature of the baffle channel allowed the aqueous drops to sit on the horizontal shelf of each baffle opening. Other droplets then collided with these stationary ones and forced them upward inside the baffle channel. These floating droplets moved across to the next compartment or fell back down onto the horizontal shelf. From these observations, there is some merit in having an angled baffle because a droplet that enters the baffle channel can drain back into the compartment from where it came. Any horizontal portion of a baffle has the disadvantage of being a place where falling droplets can settle and not continue their passage through the reactor.

However, any angled baffle will always be susceptible to swelling and leakage to some degree. Therefore, instead of having a small number of large baffle channels as used in all other ESPLIM studies, and in baffles 1 and 4, it was conceived that a large number of small baffle channels would make it harder for aqueous drops to move between compartments. The mesh baffles were designed to prevent the majority of the droplets from moving between compartments. The design also allowed any aqueous droplets that passed through the slots of the metal electrode to free-fall in between the electrode and the mesh and exit out of the bottom into the respective settler.

Figure 5.1 shows that all of the new baffle designs (baffles 2-4) have much lower swelling rates compared to the original design. Leakage is controlled better with the mesh baffles (baffles 2a, 2b, 3a and 3b) but baffle 4 has a higher leakage rate than the original baffle. There is very little difference in the performance between the different configurations of mesh baffles. The results from Figure 5.1 surpass many other published swelling and leakage rates. For example, under comparable optimised conditions, the swelling rates of Gu (1990a), Gu et al. (1994) and Williams, Bailey and Broan (1997) are 0.6%, 0.35% and 1% respectively. The swelling rate of mesh baffle 3b was 0.11%. The leakage rates of Gu(1990a), Gu et al. (1994) and Williams, Bailey and Broan (1997) are 0.03%, 0.07% and 0.25% respectively. The leakage rate of mesh baffle 3b was 0.03%.

An experiment was conducted on a cobalt solution using the optimum conditions found previously and the mesh baffle 3b. The results indicated that over 95% of cobalt was extracted – a similar performance to the original baffle design, but with the advantage of lower swelling and leakage. Therefore, mesh baffle 3b was used for all subsequent experiments.

5.14 Optimisation of the Separation of Cobalt from Nickel

In the hydrometallurgical application of solvent extraction, there is a need to have a series of mixer-settlers to achieve the desired separation of one component from the other. Multiple contactors are required because a chemical equilibrium is attained between the organic and aqueous phases in each contactor and further mixing does not improve extraction. Therefore, a new chemical equilibrium must be established in another contactor that drives the desired reaction closer to completion. For example, in Bulong's direct solvent extraction flow sheet, five mixer-settlers are used in the cobalt extraction circuit to extract the majority of cobalt from solution.

In the previous investigation of cobalt-nickel separation (Section 5.12), the cobalt concentration in the raffinate was deemed to be too high (32 –151 ppm) for any subsequent nickel purification process upstream. To reduce the cobalt concentration in the raffinate to an acceptable level, a number of tests were performed where the raffinate from a first extraction test was used as the feed for a second extraction test. All operating conditions (ie flow rate, applied voltage etc) were kept constant between the tests.

Table 7 shows the results of three sets of two-stage extraction tests. Test 1 determined the effectiveness of nickel/cobalt separation when no pH change was made to the raffinate from the first stage of extraction. The raffinate from the second stage of extraction still contained 45 ppm of cobalt at a final pH of 4.61, giving a poor nickel/cobalt decontamination ratio of 248.

Test 2 determined the effectiveness of nickel/cobalt separation when the pH of the raffinate from the first stage of extraction was increased from 4.80 to 5.08. The raffinate from the second stage contained a slightly lower cobalt concentration (32 ppm) at a final pH of 4.85, but the decontamination ratio, although higher, was still poor at 283.

Test 3 determined the effectiveness of nickel/cobalt separation when the pH of the raffinate from the first stage of extraction was increased from 4.85 to 5.65. The raffinate from the second stage only contained 10 ppm cobalt at a final pH of 5.03 and a very good decontamination ratio of 1000 was achieved.

Table 7 Separation of cobalt from nickel using two extraction stages

Test number	Stage number	Feed pH	Feed Ni conc. (ppm)	Feed Co conc. (ppm)	Raffinate pH	Ni/Co decontamination ratio*[2]
1a	1st Stage	6.50	11278	979	4.80	51
1b	2nd Stage	4.80	11226	207	4.61	248
2a	1st Stage	6.50	10508	956	4.80	50
2b	2nd Stage	5.08	10495	208	4.85	283
3a	1st Stage	6.50	10610	977	4.85	49
3b	2nd Stage	5.65	10588	203	5.03	1000

The results of this experiment indicated that very good nickel/cobalt separation could be achieved in only two extraction stages when interstage pH control was used. Also, good reproducibility was observed for each of the first extraction stages where raffinate pH and nickel/cobalt decontamination ratios were similar.

5.15 Extraction of Cobalt Using Ammonia for pH Control

In the hydrometallurgical application of solvent extraction, pH control is often conducted with ammonia because it is relatively cheap and easy to handle (it can either be added in gaseous or liquid form). To determine the effectiveness of using

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[2] *The nickel/cobalt decontamination ratio is calculated by dividing the nickel concentration in the raffinate by the cobalt concentration in the raffinate.

ammonia instead of sodium acetate as a means of pH control, two tests were conducted under comparable conditions but at different pH values.

An automatic titrator was used to dose ammonia at a rate depending on the pH of the raffinate solution. The titrator also displayed the quantity of ammonia dispensed, so dilution of the raffinate solution could be accounted for. The pH values chosen were ~4.9 (Experiment A) and ~5.7 (Experiment B). A pH of 4.9 was chosen because this was the raffinate pH obtained when 0.125 M sodium acetate was used and a comparison between the extraction efficiency of the two methods could be made. A pH of 5.7 was also chosen because this provides optimum cobalt extraction as shown in published extraction isotherms for Cyanex 272 (Rickelton, Flett and West, 1984; Feather and Cole, 1996; Soldenhoff, Hayward and Wilkins, 1998). The results of these experiments are shown in Figure 5.1.

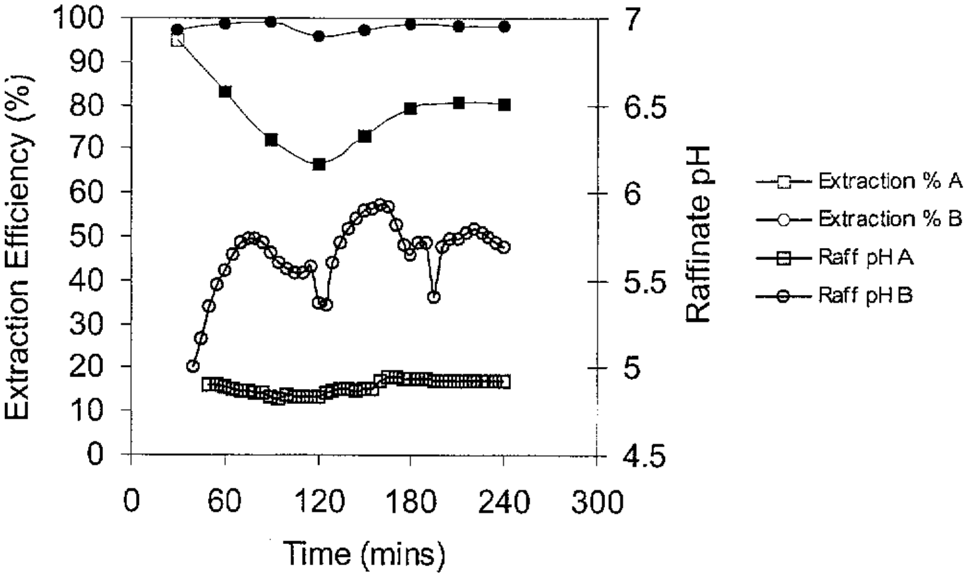


Figure 5.1 Cobalt extraction using ammonia for pH control. (Feed: 994 ppm Co^{2+}, 0.5 M NaCl; Organic: 10% Cyanex 272 and 5% TBP in Solvent HF; Strip: 1 M H_2SO_4; Feed flow rate 60 mL/hr; Strip flow rate: 14 mL/hr; Applied voltage: 5.5 kV)

The experimental conditions were slightly different from previous experiments in that 0.5 M NaCl was added to the feed solution and 5 % tributylphosphate (TBP) was added to the organic solution. Both of these reagents were added to decrease the solubility of the organic phase in the raffinate, which only became a problem when the acetate was removed from the feed solution.

Experiment A shows an initial decline in extraction efficiency for the first two hours due to a slight decrease in pH over this period. The extraction efficiency then rises and stabilises in line with the pH of the raffinate solution. At a pH of ~4.90, small changes in the pH of the solution significantly affect the extraction efficiency because of the steep slope of the cobalt extraction isotherm for Cyanex 272 in this pH range. In comparison, when acetate is used at raffinate pH values of 4.90, the pH buffering effect of acetate limits any large changes in extraction efficiency.

Experiment B had a consistently high extraction efficiency of approximately 98% for the duration of the test, even when large changes in pH occurred. The relative insensitivity of extraction efficiency over the pH range of 5.5 to 6.0 is a property of the cobalt extraction isotherm for Cyanex 272, ie. in this pH range cobalt extraction is always highly favourable.

After 180 minutes, the extraction efficiency with ammonia at pH 4.90 was 80% compared to 96% when 0.125 M sodium acetate was used at a similar pH value. It would appear then, that there is an advantage of including sodium acetate to the feed solution. Danesi et al. (1984) has suggested that the acetate forms a complex with the cobalt and Gu, Wasan and Li (1986) has reported that this complex is likely to be concentrated at the interface because of the acetate's polar-non-polar nature. Therefore, there is likely to be a greater concentration of cobalt (due to its association with acetate) at the interface than in the bulk of the droplet and this may facilitate higher extraction. Alternatively, Dreisinger, Cooper and Distin (1989) argues that the acetate serves to buffer the interface against changes in pH, thus enhancing mass transfer.

The results from experiment B indicate that a ligand such as acetate is not required in the feed solution to achieve excellent extraction efficiencies. This is very important from a practical point of view, because it means that the ESPLIM process does not require special (and expensive) additives in order to work. Control of pH can be achieved through more traditional and cost effective means, thus opening the possibility for ESPLIM to be used in industrial applications. This is the first ESPLIM study to effectively control the pH of the raffinate solution without the use of acetate.

5.16 Summary

An increase in the applied voltage causes aqueous feed drops to deform and then disperse into numerous daughter droplets. At high applied voltages, the size distribution of droplets is relatively narrow, which assists in consistent mass transfer and minimises short circuiting. The applied voltage, however, should not be too high, as this will produce very small droplets that increase the level of swelling and leakage.

After 2.5 to 3 hours, the concentration of the raffinate, strip solution and organometallic complexes in both compartments reach steady state. The nickel and cobalt extraction isotherms generated from ESPLIM are similar to those published in the literature, indicating that the electric field does not alter the extraction mechanism.

Soluble salts of carboxylic acids buffer the aqueous phase against large changes in pH. Furthermore, their presence decreases the interfacial tension so that under similar mixing conditions, smaller drops are produced.

An increase in feed flow rate decreases extraction efficiency but increases the concentration of loaded strip solution. An increase in strip flow rate increases extraction efficiency but decreases the loaded strip solution concentration.

An increase in the nickel concentration of a combined nickel-cobalt feed solution increases the nickel concentration in the loaded strip solution due to increased nickel co-extraction and swelling.

Improvements made to the baffle design of ESPLIM significantly decreased the levels of swelling and leakage from the original baffle design. Swelling and leakage levels are amongst the lowest reported in all previous ESPLIM literature.

A two-stage ESPLIM process with interstage pH control produced a nickel solution of sufficient purity for downstream processing. It has also been shown that very good extraction efficiency can be maintained without the use of acetate in the feed solution. The addition of ammonia to the ESPLIM feed compartment is a suitable and effective method of pH control.

CHAPTER 6

EXTRACTION OF COBALT FROM ACTUAL LEACH SOLUTIONS

6.1 Introduction

The aim of this investigation was to develop a method for the separation and purification of cobalt from nickel leach solutions using the ESPLIM technique, similar to the direct solvent extraction process practised at Preston Resources' Bulong Nickel Operations. The first stage of the direct solvent extraction approach involves the solvent extraction of cobalt and other dissolved impurities such as manganese, zinc, copper and magnesium from the pregnant liquor stream (PLS). The raffinate from this process contains substantial amounts of nickel, magnesium and calcium and is treated in a separate solvent extraction circuit to recover the nickel. This chapter explored the effectiveness of the ESPLIM technique in extracting cobalt and other impurities from the PLS.

6.2 Separation of Cobalt from Nickel Using Actual Leach Solutions and Sodium Acetate for pH Control

Whilst the use of sodium acetate for pH control in industrial applications is uneconomical, an investigation into its use with highly ionic leach solutions in ESPLIM was considered useful for academic interest. A number of tests were conducted on a PLS solution from Bulong with increasing concentrations of sodium acetate added to the PLS. The PLS solution initially contained 4036 ppm nickel, 502 ppm cobalt, 12177 ppm magnesium, 1030 ppm manganese, 322 ppm calcium and 18 ppm zinc.

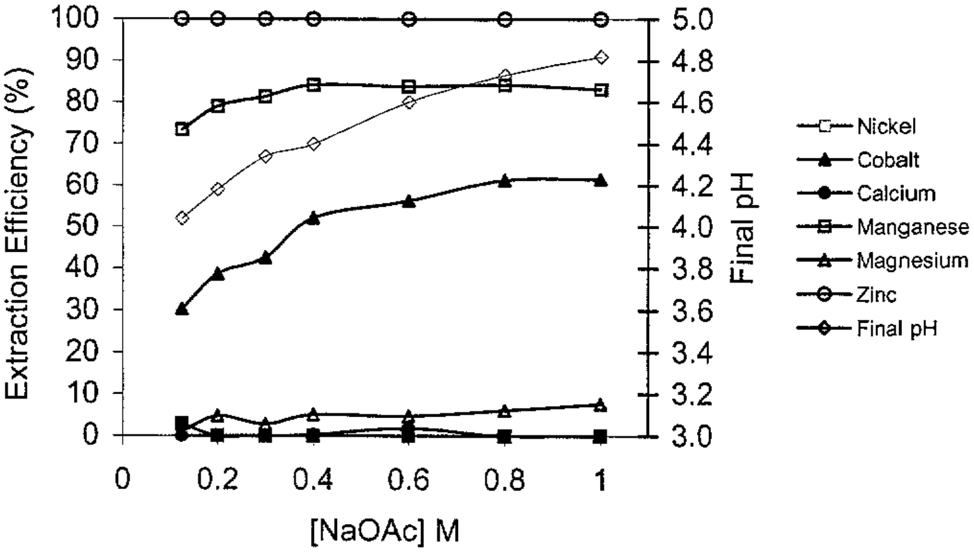


Figure 6.1 Extraction efficiency of PLS and final pH as a function of sodium acetate concentration. (Feed: PLS, pH_0: = 6.5; Applied voltage: 5.5 kV; Strip: 1 M H_2SO_4; Organic: 10% Cyanex 272 in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL hr; Time 180 min)

The results from Figure 6.1 show that the order for metal extraction is Zn>Mn>Co>Mg>Ca>Ni using ESPLIM and Cyanex 272. This is consistent with other published isotherms for these metals (Cytec; Sole and Hiskey, 1992).

At a pH of 4.82, approximately 62% of the cobalt was extracted. This was much lower than the 94% cobalt extraction achieved at pH 4.80 as presented in Section 5.8. The co-extraction of numerous other metal ions such as zinc, manganese and magnesium inhibited cobalt extraction because of the lower number of available organic sites in the extraction compartment.

The increased extraction efficiency of metal ions achieved at high acetate concentrations was attributed to an increased buffering effect, supported by the corresponding increase in raffinate pH.

The results from Figure 6.1 indicate that using sodium acetate as a means to control the pH of the PLS is not very efficient. With 0.125 M sodium acetate concentration in the feed, the final raffinate pH only reached 4.04. A final raffinate pH of 4.82 could only be reached after a sodium acetate concentration of 1 mol/L was used in the feed. Continuous lab scale tests of cobalt/nickel solutions using mixer-settlers report that cobalt extraction is best carried out between pH 5.2 to 6.0 (Soldenhoff, Hayward and Wilkins, 1998; Tait, 1993b; Rickelton, Flett and West, 1984; Feather and Cole, 1996). To achieve these pH levels with acetate, more than 1 mol/L (82 g/L) of sodium acetate is required, which is impractical and costly. Therefore, a more conventional and cost effective means of pH control is required.

6.3 Separation of Cobalt from Nickel Using Actual Leach Solutions and Ammonia for pH Control

To test the effectiveness of using ammonia addition with an actual leach solution, an experiment was conducted over an eight-hour period and the pH of the raffinate was maintained at 5.5 ± 0.15. Metal ion concentrations in the PLS feed solution were 4330 ppm nickel, 334 ppm cobalt, 493 ppm calcium, 13696 ppm magnesium and 1066 ppm manganese. The results are presented in Figure 6.1.

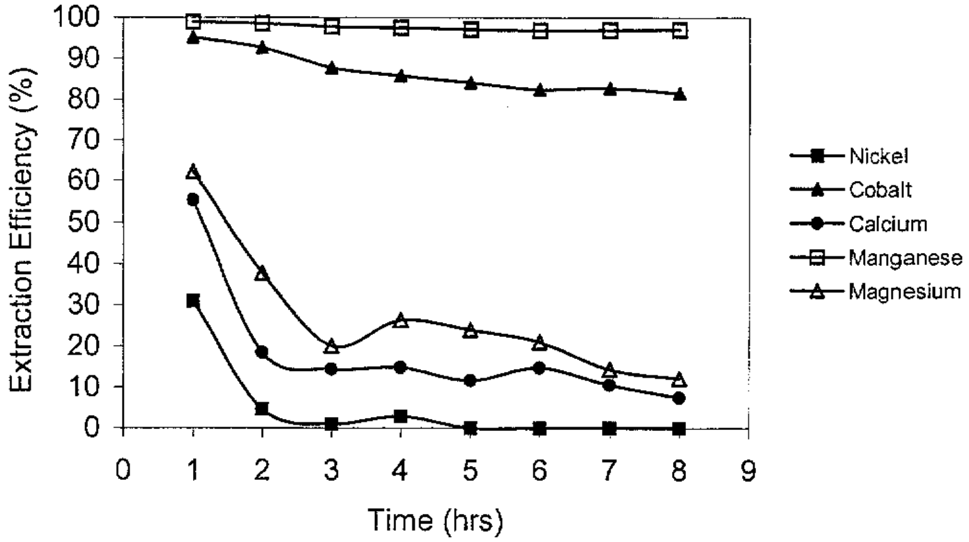


Figure 6.1 Performance of ESPLIM over time using NH_3 addition for pH control. (Feed: PLS, pH_0 = 5.5; Organic: 10% Cyanex 272 and 5% TBP in Solvent HF; Strip: 1 M H_2SO_4; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL/hr; Applied voltage: 5.5 kV; pH raffinate: ~5.5)

The data used in Figure 6.1 are generated from calculated values of raffinate concentrations. The measured raffinate concentrations were modified to account for the dilution effect of the ammonia addition to the extraction compartment. TBP was added to the organic phase because it was observed in earlier experiments that some extractant was reporting to the raffinate. No observable extractant was seen in the raffinate once TBP was added.

Figure 6.1 shows that after 4 to 5 hours, the extraction of all metal ions reaches a relatively stable value. The order of metal extraction is similar to previous experiments i.e. Mn>Co>Mg>Ca>Ni. Cobalt extraction was stable at around 82%, leaving a raffinate containing approximately 60 ppm cobalt. The raffinate from this experiment was collected, adjusted to pH 5.5 and then used as feed for another extraction stage using similar conditions. The extraction efficiency of elements from a second stage treatment using ESPLIM is shown in Figure 6.2.

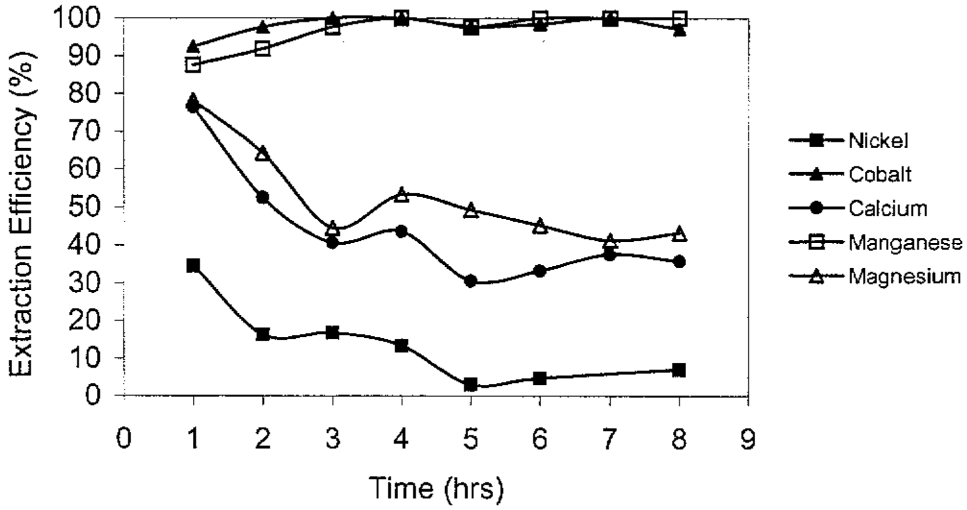


Figure 6.2 Extraction efficiency from a second stage of extraction. (Feed: Raffinate from Figure 6.1, $pH_0 = 5.5$; Strip: 1 M H_2SO_4; Applied voltage: 5.5 kV; Organic: 10% Cyanex 272, 5% TBP in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL/hr; pH raffinate: ~5.5)

The second extraction stage almost completely removes any last traces of manganese and cobalt with the raffinate containing 1 ppm or less of both of these elements. Furthermore, the nickel raffinate had an excellent nickel to cobalt ratio of approximately 3000:1. Calcium and magnesium extraction was much higher in the second stage, presumably due to a large number of free extractant sites available in the organic phase as most of the cobalt and manganese was removed in the first stage.

Nickel extraction increased and was particularly evident during the experiment, as indicated by the colour of the loaded strip solution, which was a light green. Increased nickel extraction was also due to an increase in available extractant concentration in the second stage.

Soldenhoff, Hayward and Wilkins (1998) described a continuous counter-current operation using mixer-settlers and a Bulong leach liquor of similar composition to that used in the present study. They found that after five extraction stages, the raffinate contained 5.3 ppm of cobalt and 0.4 ppm of manganese. Nickel and calcium extraction was minimal and magnesium was partially extracted. Thus, it has been shown that the ESPLIM process can extract a greater proportion of cobalt and manganese in two co-current extraction stages than five counter current extraction stages of a mixer-settler operation.

The results from Figure 6.1 and Figure 6.2 show that ESPLIM is capable of treating actual leach solutions using conventional and cost effective pH control in a minimum number of stages. The raffinate from the cobalt extraction stages contained less than 1 ppm of cobalt and manganese, which are major contaminants for the production of high quality cathode nickel.

There were no major problems encountered in the operation of the experiment. It was observed that a small amount of third phase film formed at the aqueous-organic interface after 4-5 hours, but this did not seem to hinder the coalescence of the dispersed droplets near the settler. On occasions, if the aqueous pH got too high, then small, gelatinous precipitates were observed to form in the settler, along with a corresponding increase in crud at the interface. These precipitates did not cause any direct problems and most found their way out of the settler via the outlet tubes. Once the aqueous pH was returned to the desired level, the amount of third phase at the interface was reduced and the ESPLIM continued to operate effectively. It is acknowledged however, that periodic cleaning of the settler compartment may be required to remove any build up of crud-like films. No such films were observed to occur in the stripping compartment.

Figure 6.3 shows the concentration of metal ions in the loaded strip solution from the first stage of extraction. The concentration of cobalt, nickel, calcium and manganese is represented on the primary y-axis, while the magnesium concentration is represented on the secondary y-axis.

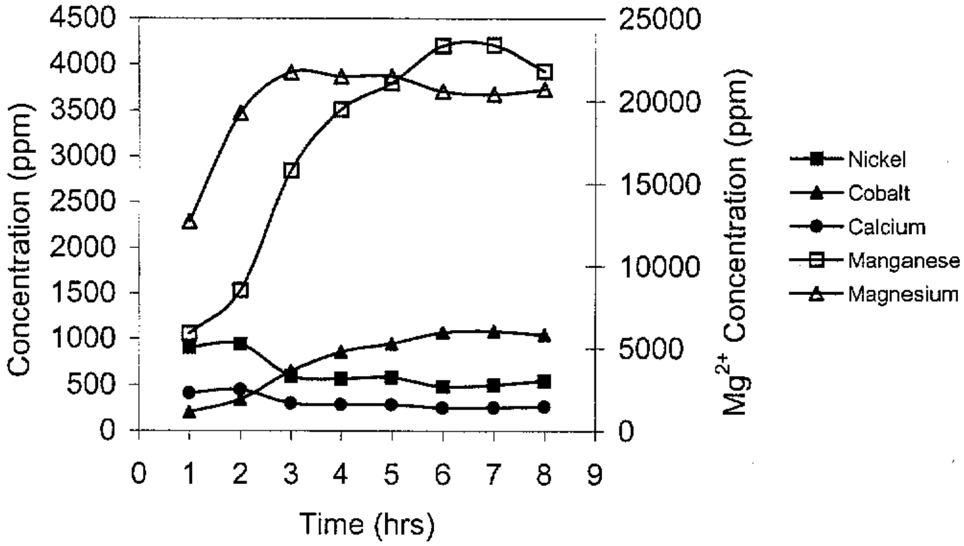


Figure 6.3 The concentration of metal ions in the loaded strip solution from the first extraction stage. (Feed: PLS, pH_0 = 5.5; Organic: 10% Cyanex 272 and 5% TBP in Solvent HF; Strip: 1 M H_2SO_4; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL/hr; Applied voltage: 5.5 kV; pH raffinate: ~5.5)

After approximately six hours, the concentration of all metal ions reaches a relatively stable level. The loaded strip solution contained approximately 1000 ppm cobalt, 500 ppm nickel, 250 ppm calcium, 4000 ppm manganese and 20,000 ppm magnesium after 8 hours of operation. Although the experiment performed very well in separating the majority of cobalt from the nickel in the feed solution, the strip solution contained a relatively low concentration of cobalt. In order to increase the cobalt concentration of the strip solution, recycling the stripping solution through the stripping compartment was considered.

6.4 Treatment of Actual Leach Solutions Using a Recirculated Strip Solution

To determine the effectiveness of recirculating the strip solution around the stripping compartment to increase the cobalt concentration, an experiment was performed using PLS and a strip solution from a previous experiment. This strip solution contained 1964 ppm Co^{2+}, 8382 ppm Mn^{2+}, 876 ppm Ni^{2+}, 430 ppm Ca^{2+} and 32698 ppm Mg^{2+}. The strip solution (100 mL) was recirculated and 1 mL samples were taken every two hours. The acidity of the strip solution was maintained at approximately 1 M by adding 1 mL of concentrated sulphuric acid to the strip solution after each assay sample was taken. The PLS solution contained 4736 ppm nickel, 263 ppm cobalt, 412 ppm calcium, 14505 ppm magnesium and 773 ppm manganese.

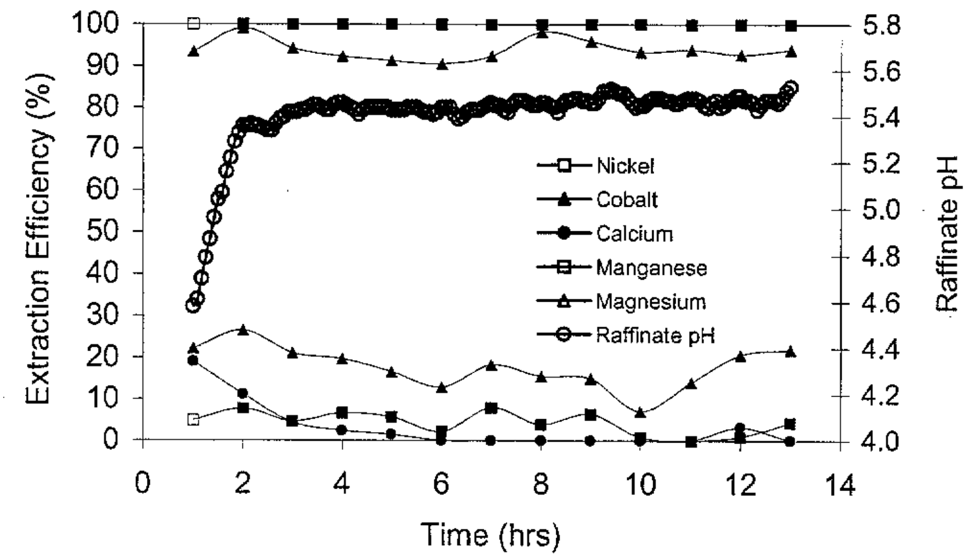


Figure 6.1 The extraction efficiency of elements from PLS using a recirculated strip solution. (Feed: PLS; pH_0 = 5.5; Strip: 1 M H_2SO_4; Applied voltage: 5.5 kV; Organic: 10% Cyanex 272, 5% TBP in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL/hr)

After two hours, the pH of the raffinate maintained a relatively constant level of between 5.4 to 5.5 and consequently, the extraction efficiency of all elements remained relatively stable for the length of the experiment. Manganese was completely extracted, cobalt extraction was maintained at approximately 93%, magnesium extraction varied between 15-20%, nickel extraction was approximately 5% and calcium extraction was negligible after 6 hours. It appears from Figure 6.1 that there is no detrimental effect on the extraction efficiency of cobalt when the strip solution is recirculated.

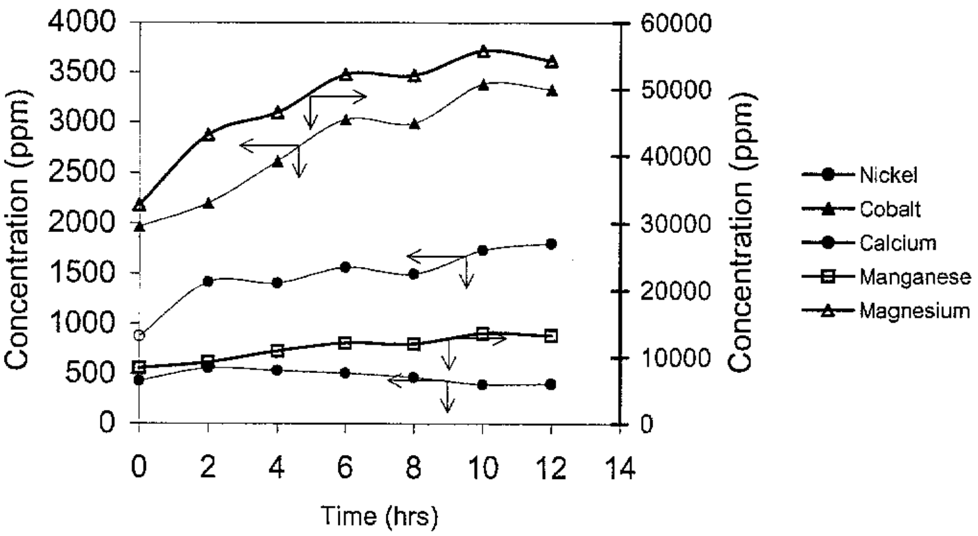


Figure 6.2 The effect of recirculation on the strip solution concentration. (Feed: PLS; $pH_0 = 5.5$; Strip: 1 M H_2SO_4; Applied voltage: 5.5 kV; Organic: 10% Cyanex 272, 5% TBP in Solvent HF; Feed flow rate: 60 mL/hr; Strip flow rate: 14 mL/hr)

The effect of recirculation on the strip solution can be seen in Figure 6.2. For practical reasons the length of the experiment was restricted to 13 hours and this meant that the strip solution was only recirculated a few times, limiting the range of data. Nevertheless, the data do show trends that can be extrapolated to longer times. Figure 6.2 shows that the concentration of all elements, except calcium, is increasing over time. This suggested that the concentration of cobalt should be able to be increased to a level that is suitable for downstream processing, such a sulphide precipitation, after an extended period of operation. It is conceived that once the cobalt concentration has reached an appropriate level, a bleed stream could be drawn off for downstream processing.

The decrease in concentration of calcium during the experiment was due to calcium sulphate (gypsum) precipitation. Once the calcium concentration in the strip solution reached saturation level (approx 550 ppm), small crystals were observed to form in the stripping settler. Gypsum precipitation continued throughout the experiment but the strip solution was filtered periodically to remove solid particles before being recirculated. Solid particles, however, did not seem to affect the operation of the ESPLIM process in any manner. Once the ESPLIM reactor had been drained of liquid at the conclusion of the experiment, it was observed that a small amount of gypsum crystals had begun forming on the walls of the reactor. No scale was observed with earlier experiments that did not recirculate the strip solution because the calcium concentration did not reach saturation levels.

6.5 Proposed ESPLIM Flow Sheet for Cobalt Extraction

The results from Sections 6.2 to 6.4 show that almost complete extraction of cobalt from an actual PLS can be achieved in two ESPLIM stages and that recirculation of the strip solution to increase the cobalt concentration does not affect the extraction efficiency. Utilising these two main concepts, a flow sheet to selectively extract and separate cobalt and other impurities from a PLS is proposed in Figure 6.1.

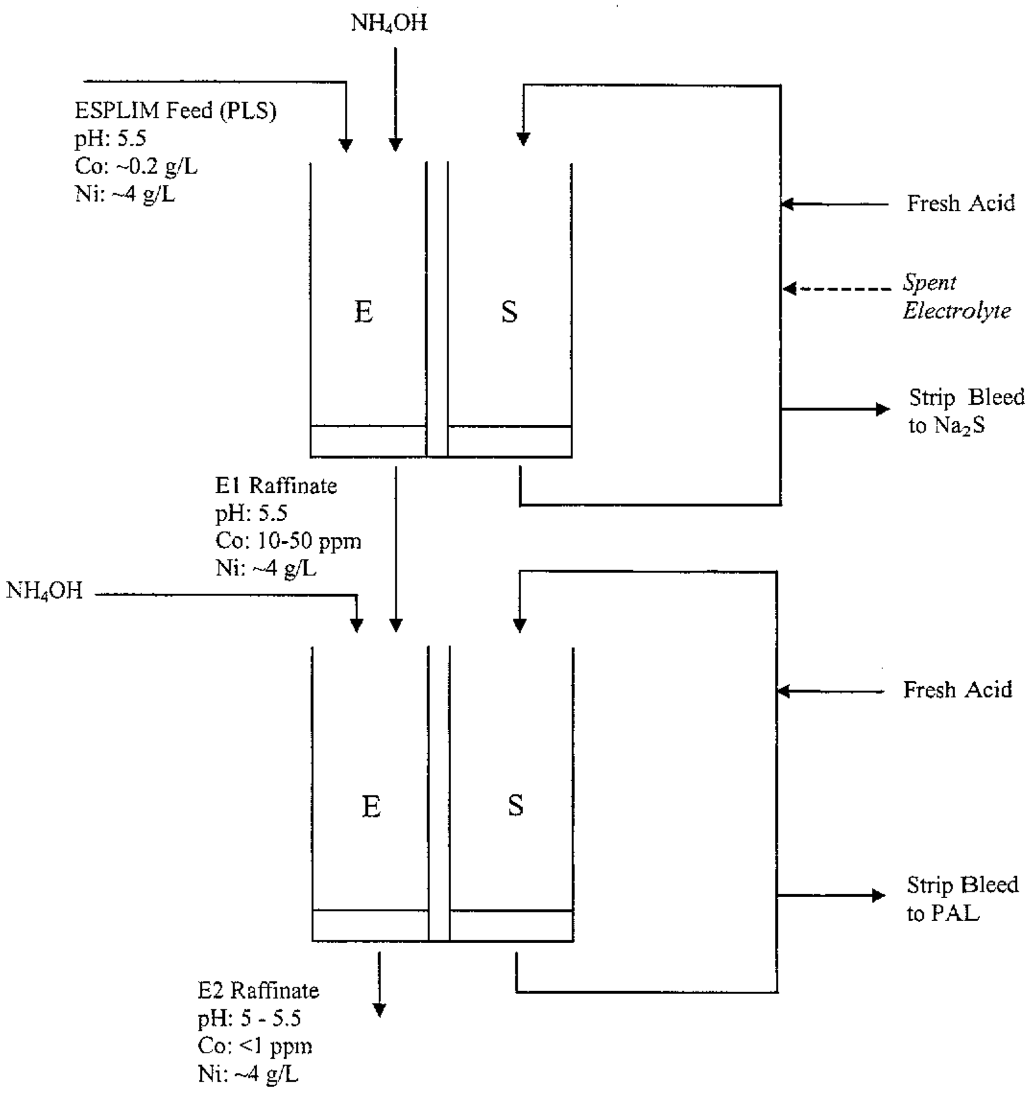


Figure 6.1 Proposed flow sheet for the extraction of cobalt from a PLS.

The PLS is fed to the first extraction stage (E1), along with an appropriate amount of base to maintain a raffinate pH of 5.5. It is expected that 10-50 ppm of cobalt will remain in the raffinate from E1, depending on the feed concentration and the amount of leakage. Extracted cobalt in E1 is stripped in S1 with sulphuric acid. This strip solution is recirculated to increase the cobalt concentration and a bleed stream is taken for downstream processing, such as sodium sulphide precipitation. To maintain the acidity of the stripping solution, fresh sulphuric acid solution is added, along with spent electrolyte from electrowinning (if available).

The first ESPLIM stage is where the majority of cobalt is extracted and the strip solution from this stage is cobalt-rich for subsequent processing. Nickel co-extraction and swelling needs to be minimised in this stage to prevent excess nickel contamination in the cobalt product. Other impurities such as manganese, copper and zinc will also be extracted. Precipitation of the S1 bleed stream to produce a mixed cobalt/nickel sulphide for sale as an intermediate by-product is possible. Any further investigation into this part of the proposed flow sheet is outside the scope of this study.

The raffinate from E1 becomes feed solution for E2 and pH control is maintained by the addition of ammonium hydroxide. As observed in Section 6.3, higher nickel co-extraction in E2 is likely due to the large amount of free extractant available and the small amount of cobalt in the feed solution. The required raffinate pH for E2 has not been optimised in this study, but a lower pH of between 5 and 5.5 should be adequate to extract the remaining cobalt and limit the extent of nickel co-extraction. A pH below 5.5 also minimises ammonia usage. The raffinate from E2, depleted of cobalt, manganese, copper and zinc is sent for further solvent extraction processing to upgrade the nickel concentration for electrowinning.

The second ESPLIM stage is a scavenger to remove the last of the remaining cobalt and impurities from the first stage raffinate. Consequently, the bleed stream from S2 will contain a relatively low concentration of cobalt but will likely be high in nickel. Combining the S2 bleed stream with that from S1 will only dilute the cobalt concentration in S1 and contaminate the cobalt product with further impurities. Recycling the S2 bleed stream to the feed solution prior to E1 is possible, but this will significantly increase ammonia usage due to the acidity of this solution.

Alternatively, the S2 bleed stream can be directed back to the feed slurry prior to pressure acid leaching, reducing fresh acid requirements for PAL and returning the valuable cobalt and nickel values to the process.

The effect of swelling and leakage in a two-stage ESPLIM process is slightly different than normal but should still be minimised wherever possible. Any leakage of cobalt from S1 can be recovered from the subsequent extraction stage in E2, but leakage from S2 will contaminate the purified nickel raffinate and must therefore be avoided. Swelling from E1 will contaminate the cobalt product stream in S1 but swelling from E2 is not as detrimental because the S2 solution is recycled back into the process and recovered.

6.6 Treatment of Actual Leach Solutions Using a Scaled-Up Reactor

To determine if the performance of ESPLIM could be replicated using a larger reactor at higher flow rates, another ESPLIM reactor was constructed. This larger reactor had inside dimensions of (122 × 28 × 380 mm) and the electric field area was 9 times greater than the smaller reactor (i.e. 3 times the length and 3 times the height). The baffle design was similar to previous experiments (i.e. an 80 μm mesh with 1 mm slots in the baffle electrode). The insulation of the wall electrodes was also different. The insulation used was an acrylic plastic sheet of 1.5 mm in thickness and consequently, the applied voltage for optimum dispersion was different (5.0 kV).

A PLS solution was used at a feed rate of 506 mL/hr, which was a factor increase of 8.4 from the previous 60 mL/hr feed rate. This PLS solution contained 1968 ppm nickel, 171 ppm cobalt, 360 ppm calcium, 10768 ppm magnesium and 617 ppm manganese. Ammonia solution (approximately 200-260 mL/hr) was also added to the extraction compartment to maintain the desired raffinate pH. The experiment was run for 12 hours with samples taken every half an hour.

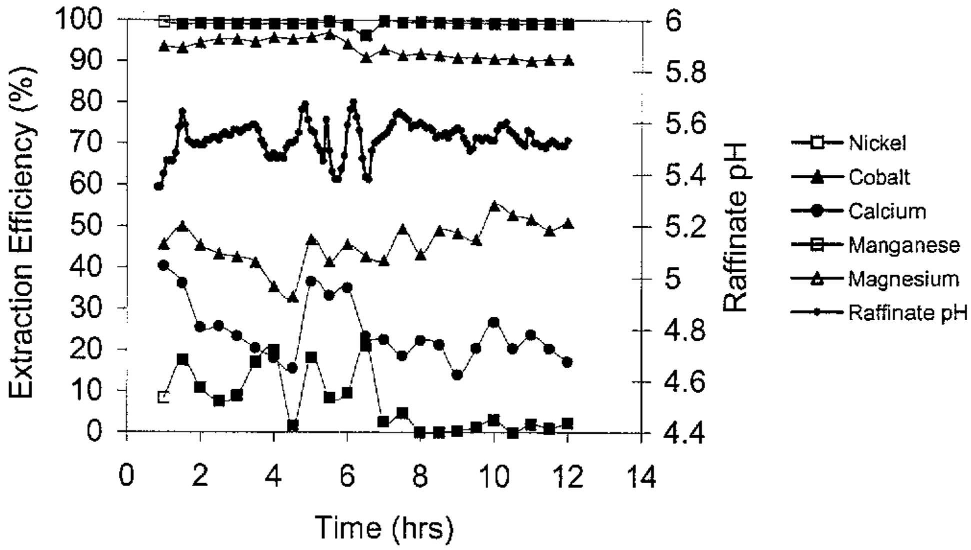


Figure 6.1 Extraction efficiency of a PLS solution using a scaled-up ESPLIM reactor. (Feed: PLS; $pH_0 = 5.5$; Strip: 1 M H_2SO_4; Applied voltage: 5.0 kV; Organic: 10% Cyanex 272, 5% TBP in Solvent HF; Feed flow rate: 506 mL/hr; Strip flow rate: 124 mL/hr)

The results in Figure 6.1 show that greater than 90% cobalt extraction is consistently maintained throughout the length of the experiment. The extraction of magnesium, calcium and nickel was erratic in the first half of the experiment (1-7 hours) due to large fluctuations in pH between pH 5.60 and 5.40. The extraction of cobalt and manganese was relatively unaffected by these pH fluctuations because in this pH range, extraction of these metal ions are highly favourable.

The operation of the larger ESPLIM reactor was also relatively trouble free. The raffinate pH was controlled between 5.40 and 5.60 for the length of the experiment so there were no problems with gelatinous precipitates. A small amount of third phase film formed in the extraction compartment at the aqueous-organic interface but it did not cause any operational difficulties. A very small amount of organic solution was observed in the raffinate as evidenced by a build up of organic on the bulb of the pH electrode. Cleaning of the pH electrode every 3-4 hours was sufficient to maintain accurate pH measurements. The loss of some organic to the raffinate was observed in all experiments where ammonia was used for pH control. No such problems were encountered when acetate was used.

One of the problems with scale-up using other mixing equipment is that the hydrodynamics of small reactors can be significantly different to larger reactors. A small reactor has a greater proportion of the solution exposed to the walls compared to a larger one and therefore, the mixing conditions of differently sized vessels can vary. This problem is avoided in ESPLIM because the walls of the reactor (the electrodes) essentially act as the mixer. Further more, the electric field is uniform throughout the reactor, with the exception of the upper and lower edges of the electrodes. Thus, the dispersed phase is subject to uniform forces throughout the reactor and this simplifies the scale-up process.

The results from Figure 6.1 show similar results to earlier experiments with the smaller reactor. Thus, the ESPLIM process can maintain excellent separation of cobalt from nickel when flow rates are proportionally increased with the size of the reactor.

6.7 Summary

The use of sodium acetate for pH control is inefficient when actual leach solutions are used because the co-extraction of impurity elements led to excessive amount of acetate required

After a two-stage ESPLIM treatment of PLS, the concentration of cobalt and manganese in the nickel raffinate solution is reduced to less than 1 ppm each. A conventional mixer-settler flow sheet requires five extraction stages to achieve a comparable result. Recirculation of the strip solution proved successful in increasing the cobalt concentration in the strip solution with no detrimental effect on extraction. A flow sheet has been proposed to selectively extract cobalt and other impurities from a PLS to produce a high purity nickel solution for further refinement.

Finally, a scaled-up ESPLIM reactor yielded similar extraction efficiency when the flow rate was increased in proportion to the increase in reactor size.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The aim of this study was to develop a method of separating cobalt and nickel directly from pressure acid leach (PAL) solutions of a nickel laterite ore using electrostatic pseudo liquid membrane (ESPLIM). This was achieved by first investigating the effect of various experimental variables including the design and materials of construction of the reactor. These variables were tested using synthetic leach solutions. The results were then used to optimise the extraction and separation of cobalt from an actual PLS solution of one of the nickel laterite operations in Western Australia. Finally, scale-up issues were investigated by constructing a larger reactor with a volume nine times larger than the original reactor. An ESPLIM flow sheet has been proposed to treat a nickel-cobalt PLS solution and a larger ESPLIM reactor has been used to investigate scale-up properties.

Specifically, it has been established that:

- the design and construction materials of the baffle plate and electrodes have a significant effect on the performance of the reactor. Electrodes made from insulated wire wrapped around the baffle plate could not provide an adequate dispersion. Stainless steel baffle plates coated with 0.08 mm thick PTFE and wall-mounted electrodes with 1 mm thick Lexan® plastic insulation were found to be suitable.

- an AC power supply provided better droplet dispersion than a DC power supply.

- an applied voltage of 5.5 kV provided maximum extraction efficiency. At this voltage the size distribution of droplets was narrow, droplet residence times were adequate for mass transfer and the intensity of agitation was good. Lower voltages resulted in poor droplet dispersion and short residence times.

- higher voltages than 5.5 kV resulted in lower extraction efficiency due to excessive levels of swelling and leakage.

- Swelling and leakage levels are highly dependent on the baffle design. A new baffle design significantly reduced swelling levels from 1.1% to 0.11% and leakage levels from 0.09% to 0.03%.

- increases in applied voltage to 5.5 kV resulted in increases in the cobalt concentration in the loaded strip solution. The concentration of the loaded strip solution is related to the ratio of the feed flow rate to the strip flow rate but it can be increased further by recirculation.

- the time required for ESPLIM to reach an apparent steady state was approximately 2.5 to 3 hours. Thereafter, the cobalt concentration in the organic phase in each compartment was relatively constant.

- the established extraction isotherms for cobalt and nickel apply in the ESPLIM technique, indicating that the electrostatic field does not alter the extraction reaction; it merely provides a method of agitation.

- adding salts of water soluble carboxylic acids to the aqueous phase reduces the interfacial tension. Consequently, the size of the dispersed droplets decreased and mass transfer increased. These salts also assist with mass transfer by acting as a buffer.

- the ESPLIM reactor can cope with large changes in the flow rate of both feed and strip solutions but an increase in feed flow rate should be accompanied by a relative increase in strip flow rate in order to maintain high extraction efficiency.

- acetate is not a required additive for the successful extraction of cobalt using ESPLIM. The control of pH can be achieved using acetate or ammonia but the latter is more practical.

- high nickel to cobalt ratios in the feed solution resulted in a decrease in cobalt extraction due to increased co-extraction of nickel. Nickel co-extraction and swelling contributed to higher nickel concentrations in the loaded strip solution. When a two-stage extraction process was used with interstage pH control, a nickel raffinate with a 1000:1 nickel to cobalt ratio was achieved.

- provided the electrostatic field strength is maintained, no significant scale-up issues were observed, indicating that the data generated in bench scale studies could be applied to plant scale contactors.

At optimum conditions, devised as a result of this investigation, 99.7% cobalt extraction was achieved in two ESPLIM stages using an actual PLS. The nickel raffinate contained less than 1 ppm cobalt. Previous studies indicate that to achieve a comparable extraction with conventional mixer-settler contactors requires five extraction stages. A flow sheet to selectively extract and separate cobalt from nickel by the ESPLIM technique is proposed.

7.2 Recommendations

Whilst the objectives of this study have been achieved, some of the results have led to further questions that are outside the scope and limitations of this study. Nonetheless, the answers to these questions are relevant to the practical application of the technique and it is recommended that they be investigated for future studies.

- An investigation to determine the optimal extractant concentration should be conducted. For instance, it may be that the second ESPLIM stage may only require a fraction of the first stage extractant concentration, as the majority of cobalt and other impurities are removed in the first stage. At lower extractant concentrations, nickel co-extraction could be minimised, perhaps to the extent where the strip bleed streams (as in Figure 6.1) can be combined, rather than separated.

- A set of data on the temperature effects could be useful in the design of a practical application of ESPLIM in nickel laterite operations.

- The design of the baffle and baffle electrodes needs to be investigated further. It was observed in experiments where ammonia was used for pH control, the ammoniated extractant tended to concentrate near the top of the organic phase. The design of the electrodes allowed a proportion of this ammoniated extractant to diffuse into the stripping compartment resulting in an increase in acid consumption. Significant savings in reagents and possible efficiency increases could be achieved if this problem is overcome.

- A more detailed and thorough investigation into the scale-up of an ESPLIM reactor needs to be undertaken. Due to time constraints, only a minimum of scale-up data was generated.

REFERENCES

Bacon, G., Dalvi, A. and Parker, M. (2000). Nickel Outlook - 2000 to 2010, In *ALTA 2000 Nickel/Cobalt*, Vol. 1 Perth, Australia, pp. 1-16.

Bailes, P. J. (1981). Solvent Extraction in an Electrostatic Field, *Ind. Eng. Chem. Process Des. Dev.,* **20,** 564-570.

Bailes, P. J. (1992a). Contacting and Separation Equipment - The Electrical Alternative In *Solvent Extraction 1990 Part B* (Ed, Sekine, T.) Elsevier Science Publishers B.V., Amsterdam, pp. 1313-1325.

Bailes, P. J. (1992b). Electrically Augmented Settlers and Coalescers for Solvent Extraction, *Hydrometallurgy,* **30,** 417-430.

Bailes, P. J. and Dowling, P. D. (1985). The Production of Pulsed E.H.T. Voltages for Electrostatic Coalescence, *Journal of Electrostatics,* **17,** 321-328.

Bailes, P. J. and Larkai, S. K. L. (1981). An Experimental Investigation into the Use of High Voltage D.C. Fields for Liquid Phase Separation, *Trans. I. Chem. E.,* **59,** 229-237.

Bailes, P. J. and Larkai, S. K. L. (1982). Liquid Phase Separation in Pulsed D.C. Fields, *Transactions of the Institution of Chemical Engineers,* **60,** 115-121.

Bailes, P. J. and Larkai, S. K. L. (1984). The Application of Electric Fields to Phase Separation in a Solvent Extraction System, In *New Developments in Liquid-Liquid Extractors: Selected Papers from ISEC '83*, Vol. 80 (Eds, Akell, R. B. and King, C. J.) American Institute of Chemical Engineers, New York, pp. 170-177.

Bailes, P. J. and Larkai, S. K. L. (1992). Design Factors Affecting the Performance of Electrostatic Coalescers, In *Solvent Extraction 1990 Part B* (Ed, Sekine, T.) Elsevier Science Publishers B.V., Amsterdam, pp. 1411-1416.

Boldt Jr., J. R. (1967). *The Winning of Nickel,* Methuen and Co. Ltd., London.

Broan, C., Bailey, A. and Williams, T. (1996). Advances in Fundamental Understanding of Electrostatic Pseudo Liquid Membrane (ESPLIM) Systems, *Int*

Conf on Membranes and Membrane Processes (ICOM '96), Yokohama, Japan (18-23 Aug, 1996), 566-567.

Canterford, J. (1994). Laterites - Processing and Prospects, In *Nickel in Australia - Mineral to Market,* Vol. 1 (Eds, Grimsey, E. J. and Stockton, N. D.) Curtin University of Technology, Kalgoorlie, Australia, pp. 16-22.

Clow, S. (1992). *The International Nickel Trade,* Woodhead Publishing Ltd., Cambridge.

Cotton, F.A. and Wilkinson, G. (1980). Advanced Inorganic Chemistry, 4th Edition, Interscience.

Cytec Cyanex 272 Extractant Brochure, Cytec Industries, West Paterson, NJ.

Danesi, P. R., Reichley-Yinger, L., Cianetti, C. and Rickert, P. G. (1984). Separation of Cobalt and Nickel by Liquid-Liquid Extraction and Supported Liquid Membranes with Di(2,4,4 - Trimethylpentyl) Phosphinic Acid [Cyanex 272], *Solvent Extraction and Ion Exchange,* **2,** 781-814.

De Guingand, C. (1994). Nickel - The Markets and Factors that Influence Price, In *Nickel in Australia - Mineral to Market,* Vol. 1 (Eds, Grimsey, E. J. and Stockton, N. D.) Curtin University of Technology, Kalgoorlie, Australia, pp. 113-133.

Dreisinger, D. B. and Cooper, W. C. (1986). The Kinetics of Cobalt and Nickel Extraction Using HEHEHP, *Solvent Extraction and Ion Exchange,* **4,** 317-344.

Dreisinger, D. B., Cooper, W. C. and Distin, P. A. (1989). The Kinetics of Divalent Metal Extraction with HDEHP, HEHEHP and HDTMPP Using the Rotating Diffusion Cell, In *Proceedings of 2nd International Conference on Separations Science and Technology,* Vol. 1 (Eds, Baird, M. H. I. and Vijayan, S.) Canadian Society for Chemical Engineering, Ontario, Canada, pp. 151-157.

Feather, A. M. and Cole, P. M. (1996). The Separation of Cobalt from Nickel Ammonium Sulphate Solution by Solvent Extraction, In *Value Adding Through Solvent Extraction,* Vol. 2 (Eds, Shallcross, D. C., Paimin, R. and Prvcic, L. M.) The University of Melbourne, pp. 511-516.

Garton, C. G. and Krasucki, Z. (1964). Bubbles in Insulating Liquids: Stability in an Electric Field, *Proc. Roy. Soc.*, **A280,** 211-226.

Godfrey, J. C. (1994). Mixers, In *Liquid-Liquid Extraction Equipment* (Eds, Godfrey, J. C. and Slater, M. J.) John Wiley & Sons, Chichester, pp. 363-409.

Gu, Z. (1985). The Annual Report of Institute of Atomic Energy of China.

Gu, Z. (1990a). A New Liquid Membrane Technology - Electrostatic Pseudo Liquid Membrane, *Journal of Membrane Science,* **52,** 77-88.

Gu, Z. (1990b). Electrostatic Pseudo Liquid Membrane Separation Technology, *Journal of Chemical Industry and Engineering (China),* **5,** 44-55.

Gu, Z. (1992). Electrostatic Pseudo-Liquid-Membrane, In *Membrane Handbook* (Eds, Winston Ho, W. S. and Sirkar, K. K.) Van Nostrand Reinhold, New York, pp. 867-883.

Gu, Z., Wasan, D. T. and Li, N. N. (1985). Interfacial Mass Transfer in Ligand Accelerated Metal Extraction by Liquid Surfactant Membranes, *Separation Science and Technology,* **20,** 599-612.

Gu, Z., Wu, Q., Zheng, Z., Li, X., Jiang, Y., Tang, C. and Lin, P. (1994). Laboratory and Pilot Plant Test of Yttrium Recovery from Wastewater by Electrostatic Pseudo Liquid Membrane, *Journal of Membrane Science,* **93,** 137-147.

Gu, Z. M., Wasan, D. T. and Li, N. N. (1986). Ligand-Accelerated Liquid Membrane Extraction of Metal Ions, *Journal of Membrane Science,* **26,** 129-142.

Gu, Z. M., Zhou, Q. and Jin, L. (1990). Recovery of Ni(II) from Rinse Water from Nickel Plating with Liquid Membranes, *Water Treatment,* **5,** 170-178.

Gu, Z. M., Zhou, Q., Jin, L. and Guan, Z. (1991). Electrostatic Pseudo Liquid Membrane Integrated Baffle Plate Electrode Module, Chinese Patent CN 2085249U.

Hanson, C. (1971). Solvent Extraction: The Current Position, In *Recent Advances in Liquid-Liquid Extraction* (Ed, Hanson, C.) Pergamon Press, Oxford, pp. 1-13.

He, W., Chang, J.S. and Baird, M. H. I. (1997). Enhancement of Interphase Mass Transfer by a Pulsed Electric Field, *Journal of Electrostatics,* **40&41,** 259-264.

Hsu, E. C. and Li, N. N. (1985). Membrane Recovery in Liquid Membrane Separation Processes, *Separation Science and Technology,* **20,** 115-130.

Hubicki, Z. and Hubicka, H. (1996). Studies on the Extraction Process of Nickel(II) Sulphate Purification Using Cyanex 272, *Hydrometallurgy,* **40,** 65-76.

Inoue, K., Ohto, K. and Mori, A. (1998). Effect of Complexing Anions on Solvent Extraction of Calcium with PC-88A, *Solvent Extraction Research and Development, Japan,* **5,** 16-24.

Islam, F. and Biswas, R. K. (1979). The Solvent Extraction of Chromium(III) with Bis-(2-ethyl hexyl) Phosphoric Acid in Benzene and Other Solvents, *Journal of Inorganic Nuclear Chemistry,* **41,** 229-233.

Kyle, J. H. (1996). Pressure Acid Leaching of Australian Nickel/Cobalt Laterites, In *Nickel '96 Mineral to Market,* (Eds, Grimsey, E. J. and Neuss, I.) The Australasian Institute of Mining and Metallurgy, Kalgoorlie, Western Australia, pp. 245-249.

Lenahan, W. C. and Murray-Smith, R. d. L. (1986). *Assay and Analytical Practice in the South African Mining Industry,* The South African Institute of Mining and Metallurgy, Johannesburg.

Lewis, J. B., Jones, I. and Pratt, H. R. C. (1951). Part III. A Study of Droplet Behaviour in Packed Columns, *Transactions Institution of Chemical Engineers,* **29,** 126-148.

Lindell, E., Jääskeläinen, E., Paatero, E. and Nyman, B. (2000). Effect of Reversed Micelles in Co/Ni Separation by Cyanex 272, *Hydrometallurgy,* **56,** 337-357.

Logsdail, D. H. and Lowes, L. (1971). Industrial Contacting Equipment, In *Recent Advances in Liquid-Liquid Extraction* (Ed, Hanson, C.) Pergamon Press, Oxford, pp. 139-168.

Martin, L., Vignet, P., Fombarlet, C. and Lancelot, F. (1983). Electrical Field Contactor for Solvent Extraction, *Separation Science and Technology,* **18(14&15),** 1455-1471.

Martínez, R. V., Liranza, E. G., Bárzaga, B. R. and Daudinot, A. M. (1997). Cobalt Recovery by Solvent Extraction from Acid Leach Solutions of Caron's Process Mixed Ni/Co Sulfide, In *Nickel-Cobalt 97*, Vol. 1 (Eds, Cooper, W. C. and Mihaylov, I.) Sudbury, Ontario, Canada, pp. 293-304.

Maurer, A. (2000). Nickel - Outlook to 2004-05, In *Outlook 2000*, Vol. 3 Australian Bureau of Agricultural and Resource Economics, Canberra, Australia, pp. 307-316.

McEwan, A. D. and de Jong, L. N. J. (1966). Addendum, *Proc. Roy. Soc.,* **A291,** 166.

Motteram, G., Ryan, M. and Weizenbach, R. (1997). Application of the Pressure Acid Leach Process to Western Australian Nickel/Cobalt Laterites, In *Nickel-Cobalt 97*, Vol. 1 (Eds, Cooper, W. C. and Mihaylov, I.) Sudbury, Ontario, Canada, pp. 391-407.

Nyman, B., Aatonen, A., Hultholm, S.-E. and Karpale, K. (1992). Application of New Hydrometallurgical Developments in the Outokumpu HIKO Process, *Hydrometallurgy,* **29,** 461-478.

O'Kane, P. T. and Gormely, L. S. (2000). Energy Consumption and Economic Trends in the Production of Nickel From Laterites An Update, In *ALTA 2000 Nickel/Cobalt*, Vol. 1 Perth, Australia, pp. 1-11.

Preston, J. S. (1982). Solvent Extraction of Cobalt and Nickel by Organophosphorus Acids. I. Comparison of Phosphoric, Phosphonic and Phosphinic Acid Systems, *Hydrometallurgy,* **9,** 115-133.

Reeves, M. J., Bailey, A. G., Howard, A. G. and Broan, C. J. (1999). Factors Influencing Operational Efficiency of an Electrostatic Solvent Extraction System, In *Electrostatics 1999 - Proceedings of the 10th International Conference* (Ed, Taylor, D. M.) Institute of Physics, Cambridge, pp. 257-260.

Reid, J. (1996). Laterite Ores - Nickel and Cobalt Resources for the Future, In *Nickel '96 - Mineral to Market*, Vol. 1 (Eds, Grimsey, E. J. and Neuss, I.) The Australasian Institute of Mining and Metallurgy, Kalgoorlie, Australia, pp. 11-16.

Rice, N. M. and Gibson, R. W. (1996). Solvent Extraction with Cyanex 301 and 302 for the Upgrading of Chloride Leach Liquors from Lateritic Nickel Ores, In *International Solvent Extraction Conference (ISEC 96)*, Vol. 1 (Eds, Shallcross, D. C., Paimin, R. and Prvcic, L. M.) The University of Melbourne, Melbourne, Australia, pp. 715-720.

Rickelton, W. A. and Boyle, R. J. (1988). Solvent Extraction with Organophosphines - Commercial & Potential Applications, *Separation Science and Technology,* **23,** 1227-1250.

Rickelton, W. A., Flett, D. S. and West, D. W. (1984). Cobalt-Nickel Separation by Solvent Extraction with Bis (2,4,4 trimethylpentyl) Phosphinic Acid, *Solvent Extraction and Ion Exchange,* **2,** 815-838.

Rickelton, W. A. and Nucciarone, D. (1997). The Treatment of Cobalt/Nickel Solutions Using CYANEX Extractants, In *Nickel-Cobalt 97*, Vol. 1 (Eds, Cooper, W. C. and Mihaylov, I.) Sudbury, Ontario, Canada, pp. 275-292.

Ritcey, G. M. (1995). Solvent Extraction of Nickel and Cobalt - Past, Present and Future, In *Nickel/Cobalt Laterites - The How To's of Project Development,* Melbourne, Australia.

Ritcey, G. M. (1996). Process Options Using Solvent Extraction for the Processing of Laterites, In *Nickel '96 Mineral to Market* (Eds, Grimsey, E. J. and Neuss, I.) The Australasian Institute of Mining and Metallurgy, Kalgoorlie, Western Australia, pp. 1-8.

Ritcey, G. M. (2000). Separation and Recovery of Metals by Solvent Extraction Emphasis on Nickel and Cobalt. Curtin University of Technology, Kalgoorlie, Australia, pp. 1-100.

Ritcey, G. M. and Ashbrook, A. W. (1979). *Solvent Extraction - Principles and Applications to Process Metallurgy,* Elsevier Scientific Publishing Company, Amsterdam.

Ritcey, G. M. and Ashbrook, A. W. (1984). *Solvent Extraction - Principles and Applications to Process Metallurgy,* Elsevier Scientific Publishing Company, Amsterdam.

Ritcey, G. M., Hayward, N. L. and Salinovich, T. (1996). The Recovery of Nickel and Cobalt from Lateritic Ores Resolute Resources Limited, Australian Patent 40890/96.

Rosenkilde, C. E. (1969). A Dielectric Fluid Drop in an Electric Field, *Proc. Roy. Soc.,* **A312,** 473-494.

Scott, T. C. (1989). Use of Electric Fields in Solvent Extraction: A Review and Prospectus, *Separation and Purification Methods,* **18,** 65-109.

Scott, T. C. and Wham, R. M. (1989). An Electrically Driven Multistage Countercurrent Solvent Extraction Device: The Emulsion-Phase Contactor, *Ind. Eng. Chem. Res.,* **28,** 94-97.

Shoemaker, D. P., Garland, C. W. and Steinfeld, J. I. (1974). Dipole Moments of Polar Molecules in Solution In *Experiments in Physical Chemistry* (Eds, Summersgill, R. H., Stern, J. and Eichberg, M.) McGraw-Hill, Inc, New York, pp. 411-422.

Soldenhoff, K., Hayward, N. and Wilkins, D. (1998). Direct Solvent Extraction of Cobalt and Nickel from Laterite-Acid Pressure Leach Liquors, In *EPD Congress 1998* (Ed, Mishra, B.) The Minerals, Metals & Materials Society, Warrendale, Pa, pp. 153-165.

Sole, K. C. and Hiskey, J. B. (1992). Solvent Extraction Characteristics of Thiosubstituted Organophosphinic Acid Extractants, *Hydrometallurgy,* **30,** 345-365.

Spence, J. R. and Soderstrom, M. D. (1999). Practical Aspects of Copper Solvent Extraction from Acidic Leach Liquors, In *Copper Leaching, Solvent Extraction, and*

Electrowinning Technology (Ed, Jergensen II, G. V.) Society for Mining, Metallurgy, and Exploration, Inc., Littleton, pp. 239-257.

Stewart, G. and Thornton, J. D. (1967). Charge and Velocity Characteristics of Electrically Charged Droplets. Part 1: Theoretical Considerations, In *Liquid-Liquid Extraction,* Vol. 26 Institution of Chemical Engineers, London, Newcastle-Upon-Tyne, pp. 29-36.

Suyama, T., Awakura, Y., Hirato, T., Konto, M. and Majima, H. (1993). Extraction and Stripping Characteristics of Ni(II) with Di(2-ethylhexyl)Phosphoric Acid Under a High Electrostatic Field, *Materials Transactions, JIM,* **34,** 37-42.

Tait, B. K. (1993a). Cobalt-Nickel Separation: The Extraction of Cobalt (II) and Nickel (II) by Cyanex 301, Cyanex 302 and Cyanex 272, *Hydrometallurgy,* **32,** 365-372.

Tait, B. K. (1993b). Countercurrent Tests on Cyanex 302 and Cyanex 272 as Separation Reagents for Cobalt-Nickel, In *Solvent Extraction in the Process Industries* (Eds, Logsdail, D. H. and Slater, M. J.) Elsevier Applied Science, London, pp. 1303-1310.

Taylor, A. (1996). Mixers-Settlers, Solvent Extraction Plant Design and the Electrowinning of Nickel and Cobalt, In *Nickel/Cobalt SX/EW Seminar,* ALTA Metallurgical Services, Perth, Australia.

Taylor, A. and Cairns, D. (1997). Technical Development of the Bulong Laterite Treatment Project, In *ALTA 1997 Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum,* Perth, Australia.

Taylor, G. (1966). Studies in Electrohydrodynamics 1. The Circulation Produced in a Drop by an Electric Field, *Proc. Roy. Soc.,* **A291,** 159-166.

Thornton, J. D. (1968). The Applications of Electrical Energy to Chemical and Physical Rate Processes, *Reviews of Pure and Applied Chemistry,* **18,** 197-218.

Wasan, D. T., Gu, Z. and Li, N. N. (1984). Separation of Metal Ions by Ligand-Accelerated Transfer through Liquid Surfactant Membranes, *Faraday Discuss. Chem. Soc.*, **77,** 67-74.

Wham, R.M. and Byers, C.H. (1987). Mass Transport from Single Droplets in Imposed Electric Fields, *Separation Science and Technology,* **22(2&3),** 447-466.

Williams, T. J., Bailey, A. G. and Broan, C. J. (1997). Ion Extraction Using the Electrostatic Pseudo Liquid Membrane Technique, *Journal of Electrostatics,* **40&41,** 729-734.

Wu, Q., Gu, Z. and Jin, L. (1991). Studies on "Swelling" and "Breakage" Behaviours of Electrostatic Pseudo Liquid Membrane, *Technology of Water Treatment,* **17,** 46-51.

Yamaguchi, M. (1994). Electrically Aided Extraction and Phase Separation Equipment, In *Liquid-Liquid Extraction Equipment* (Eds Godfrey, J.C. and Slater, M.J.) John Wiley & Sons Ltd, pp. 585-624

Yamaguchi, M. (1995). Application of Electric Fields to Solvent Extraction, In *Electric Field Applications in Chromatography, Industrial and Chemical Processes* (Ed, Tsuda, T.) VCH, Weinheim, pp. 185-203.

Yamaguchi, M. and Ito, K. (1993). Demulsification Behaviour and Performance of Water-In-Oil Emulsions in Electric Fields, In *Solvent Extraction in the Process Industries*, Vol. 2 (Eds, Logsdail, D. H. and Slater, M. J.) Elsevier Applied Science, London, pp. 810-816.

Yamaguchi, M., Sugaya, H. and Katayama, T. (1988). Hydrodynamic Behaviour of Dispersed Phase in a Spray Column with an Electric Field for Liquid-Liquid Extraction, *Journal of Chemical Engineering of Japan,* **21,** 179-183.

Yang, X., Gu, Z. and Wang, D. (1995). Extraction and Separation of Scandium from Rare Earths by Electrostatic Pseudo Liquid Membrane, *Journal of Membrane Science,* **00,** 1-15.

Yang, X. J., Gu, Z. M. and Fane, A. G. (1998). Multicomponent Separations by a Combined Extraction / Electrostatic Pseudo-Liquid Membrane (I): Separation of Al, La, Sm, and Y., *Hydrometallurgy,* **49,** 275-288.

Yang, X. J., Gu, Z. M. and Fane, A. G. (1999). Multicomponent Separation by a Combined Extraction/ Electrostatic Pseudo-Liquid Membrane (II): Extraction and Group Separation of Rare Earth Ore Leach Solutions, *Hydrometallurgy,* **53,** 19-29.

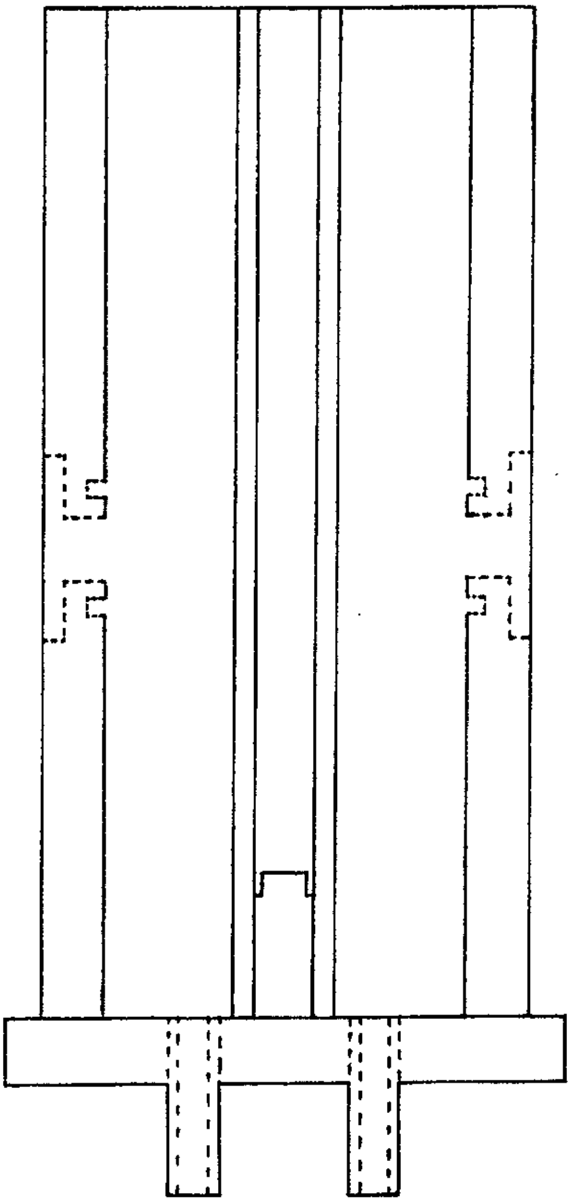
Zhou, Q. and Gu, Z. (1988). Studies on the Extraction of Eu^{3+} by Means of Electrostatic Pseudo Liquid Membrane, *Water Treatment,* **3,** 127-135.

Publications by the author

Heckley, P.S., Ibana, D.C. and McRae, C. (2002). Extraction and Separation of Nickel and Cobalt by Electrostatic Pseudo Liquid Membrane, *Proceedings of the International Solvent Extraction Conference,* (Eds. Sole, K.C., Cole, P.M., Preston, J.S. and Robinson, D.J), The South African Institute of Mining and Metallurgy, Marshalltown, pp. 730-735.

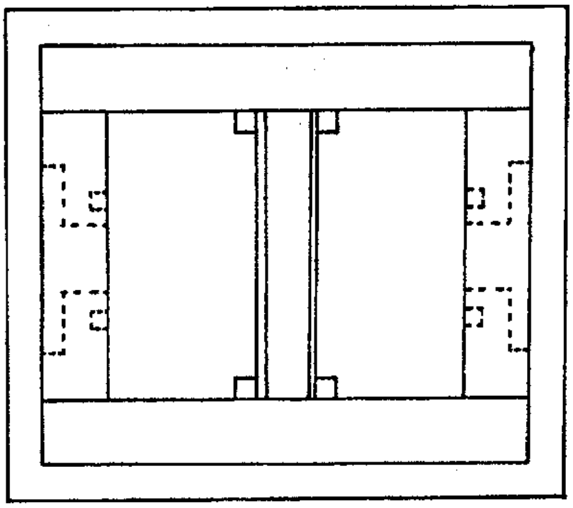
APPENDICES

Appendix A ESPLIM Reactor



Scale: 1 mm = 1.06 mm

Figure A.1 ESPLIM reactor design (front view). Components described in Section 4.1.



Scale: 1 mm = 1.07 mm

Figure A.2 ESPLIM reactor design (top view). Components described in Section 4.1.

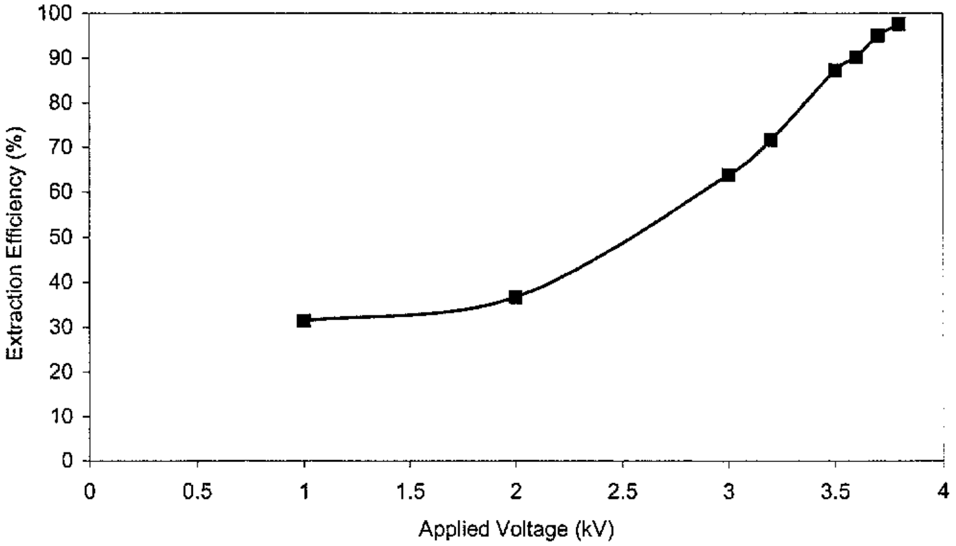


Figure B.1 The effect of applied voltage on extraction efficiency using plastic tape electrode insulation. (Feed: 998 ppm Co^{2+}, 0.1 M $NaCH_3COO$, $pH_0 = 7$; Strip: 1 M H_2SO_4; Organic: 10% Cyanex 302 in Solvent HF; Electrode spacing: 8 mm; Feed flow rate: 63 mL/hr; Strip flow rate: 12 mL/hr; Time 180 mins)

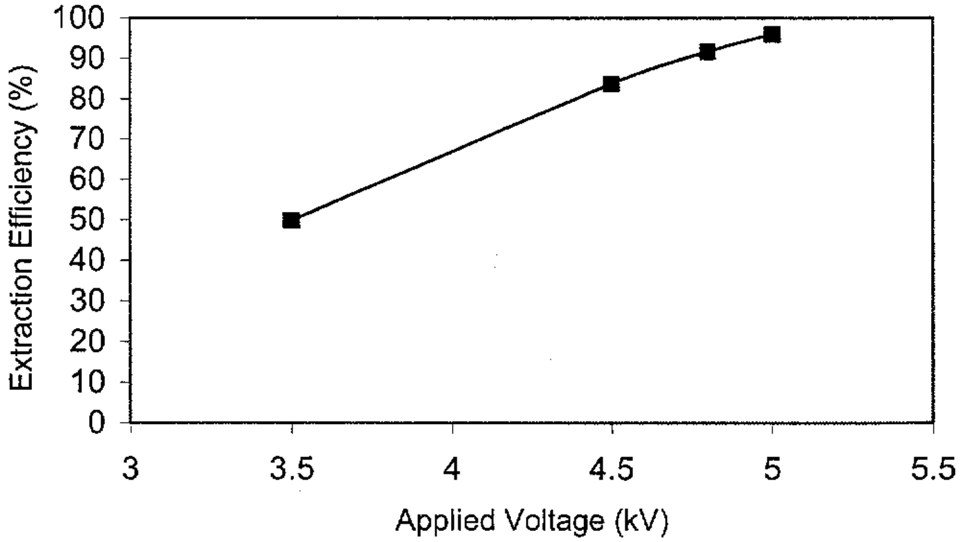


Figure B.2 The effect of applied voltage on extraction efficiency using heat shrink electrode insulation. (Feed: 1032 ppm Co^{2+}, 0.1 M $NaCH_3COO$, $pH_0 = 7$; Strip: 1 M H_2SO_4; Organic: 10% Cyanex 272 in Solvent HF; Electrode spacing: 8 mm; Feed flow rate: 68 mL/hr; Strip flow rate: 12 mL/hr; Time 180 mins)

Appendix C Shakeout Tests

A number of shakeout tests were performed using solutions to be used as tracers for swelling and leakage tests. To be used as tracers, the solutions must exhibit very low, or preferably, zero extraction. The results in Table C.1 confirmed that all solutions tested were applicable for use as a tracer in swelling and leakage measurements.

In each test, 50 mL of aqueous solution and 50 mL of organic solution (10% Cyanex 272 in Solvent HF) were placed in a 250 mL separatory funnel and hand shaken for 1 minute. The phases were allowed to separate before an aqueous sample was taken for analysis.

Table C.1 Shakeout test results

Solution	Feed Concentration (ppm)	Feed pH	Raffinate Concentration (ppm)	Raffinate pH	Extraction Efficiency (%)
0.1 M NaOAc	2321	7.88	2375	6.07	-2.3
0.1 M NaOAc	2321	6.5	2384	5.86	-2.7
0.1 M NaOAc	2321	6.5	2338	5.79	-0.7
0.1 M NaOAc & 1000 ppm Co^{2+}	2263	6.5	2256	4.92	0.3
K_2SO_4 in 1 M H_2SO_4	960	-	945	-	1.6
K_2SO_4 in 1 M H_2SO_4	960	-	947	-	1.3
Cu^{2+} in 1 M H_2SO_4	990	-	990	-	0
Cu^{2+} in 1 M H_2SO_4	990	-	991	-	-0.1

Appendix D Acetate Buffer Calculations

The following table is a set of calculations based on the hypothesis that the acetate acts as a proton sink and therefore restricts large changes in pH in much the same way that a buffered solution does. The pH of the raffinate is calculated from the number of protons released into solution, which is directly related to the amount of cobalt extraction that took place.

Table D.1 Raffinate pH calculations based on cobalt extraction

[Ac] in Feed (M)	[Ac] at pH 6.5 (M)	[HAc] at pH 6.5 (M)	[Co^{2+}] in Feed (M)	Extraction Efficiency (%)	[H^+] Released (M)	[HAc] in Raffinate (M)	[Ac] in Raffinate (M)	Calculated pH	Measured pH
0.025	0.024573	0.000427	0.016884	48.6	0.016412	0.016839	0.008161	4.43	3.85
0.050	0.049146	0.000854	0.017377	79.4	0.027594	0.028448	0.021552	4.62	4.39
0.075	0.073719	0.001281	0.017903	93.8	0.033585	0.034866	0.040134	4.80	4.59
0.100	0.098292	0.001708	0.018038	97.2	0.035067	0.036775	0.063225	4.98	4.85
0.125	0.122865	0.002135	0.018395	98.6	0.036274	0.038410	0.086590	5.09	4.99

Appendix E Adjusted Acetate Buffer Calculations

Although the calculated pH values for the raffinate in Appendix D were close to the measured pH values, a set of 'blank' experiments (ie. no cobalt present) were performed to see if there was a pH change in the raffinate due to other side reactions. The results for this experiment are shown in Table E.1. These results were then incorporated into the results from Appendix D to create a new set of results that correlated much better with the observed raffinate pH (Table E.2).

Table E.1 Measured raffinate pH values for blank experiment

[Ac] in Feed (M)	[Ac] in Feed at pH 6.5 (M)	[HAc] in Feed at pH 6.5 (M)	Raffinate pH	[Ac] in Raffinate (M)	[HAc] in Raffinate (M)
0.025	0.024573	0.000427	5.60	0.021968	0.003032
0.050	0.049146	0.000854	5.85	0.046398	0.003602
0.075	0.073719	0.001281	5.98	0.070919	0.004081
0.100	0.098292	0.001708	6.02	0.095014	0.004986
0.125	0.122865	0.002135	6.00	0.118489	0.006511

Table E.2 Adjusted raffinate pH values based on cobalt extraction using data from blank experiment

[Ac] in Feed (M)	[Ac] from Blank (M)	[HAc] from Blank (M)	[Co^{2+}] in Feed (M)	Extraction (%)	[H+] Released (M)	[Ac] in Raffinate (M)	[HAc] in Raffinate (M)	Calculated pH	Measured pH
0.025	0.021968	0.003032	0.016884	48.6	0.016412	0.005556	0.019444	4.20	3.85
0.050	0.046398	0.003602	0.017377	79.4	0.027594	0.018804	0.031196	4.52	4.39
0.075	0.070919	0.004081	0.017903	93.8	0.033585	0.037334	0.037666	4.74	4.59
0.100	0.095014	0.004986	0.018038	97.2	0.035067	0.059947	0.040053	4.92	4.85
0.125	0.118489	0.006511	0.018395	98.6	0.036274	0.082214	0.042786	5.02	4.99

Appendix F Sample Calculations for Swelling

This section describes the calculations used to determine the theoretical concentration of nickel that would be present in the stripping solution if it is assumed that there was 2% swelling.

Experimental conditions used:

Solution A has 1048 ppm Ni^{2+} (0.01785 mol/L)
Solution B has 9540 ppm Ni^{2+} (0.1625 mol/L)
Feed flow rate is 0.06 L/hr
Strip flow rate is 0.013 L/hr

Assume swelling rate of 2%, negligible leakage and use solution A as an example.

$$\text{Swelling \%} = \frac{\text{Flow rate of entrained feed}}{\text{Flow rate of strip}}$$

$$\text{Flow rate of entrained feed} = 2\,\% \times 0.013 \text{ L/hr}$$

$$= 0.00026 \text{ L/hr}$$

$$\text{Moles } Ni^{2+} \text{ entrained (n)} = C \times V$$

$$= 0.01785 \times 0.00026$$

$$= 4.642 \times 10^{-6} \text{ mol}$$

$$[Ni^{2+}] \text{ in strip solution} = \frac{\text{Moles of } Ni^{2+} \text{ entrained}}{\text{Flow rate of strip} + \text{Entrained flow rate}}$$

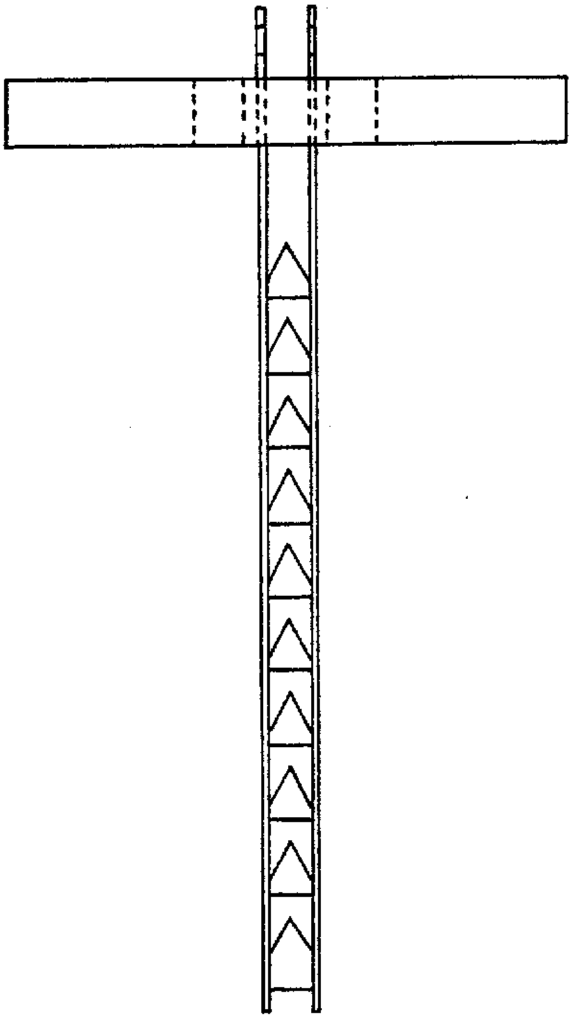
$$= \frac{4.642 \times 10^{-6}}{0.013 + 0.00026}$$

$$= 3.5 \times 10^{-4} \text{ mol/L}$$

$$= 20.55 \text{ ppm}$$

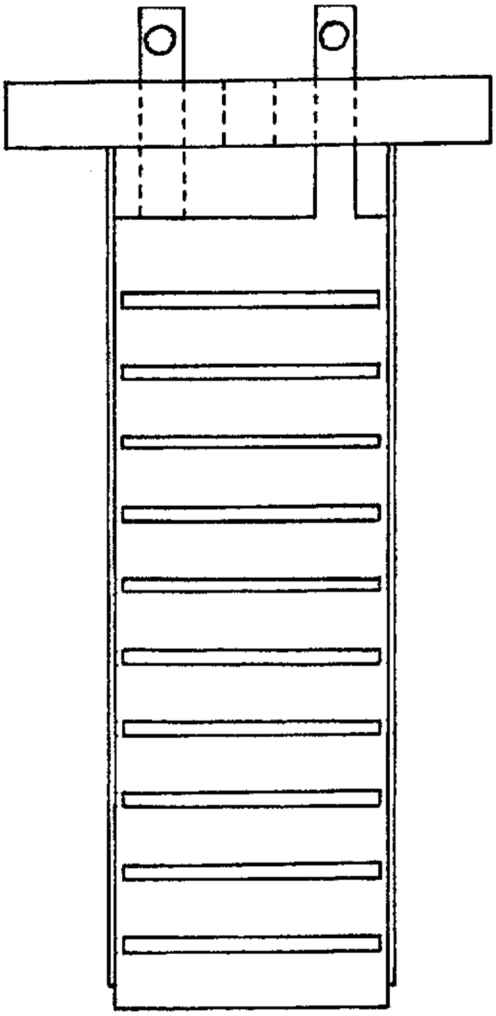
Similarly, for a solution containing 9540 ppm Ni^{2+} and with 2% swelling, 187 ppm of Ni^{2+} in the strip solution would be expected.

Appendix G ESPLIM Baffle Designs



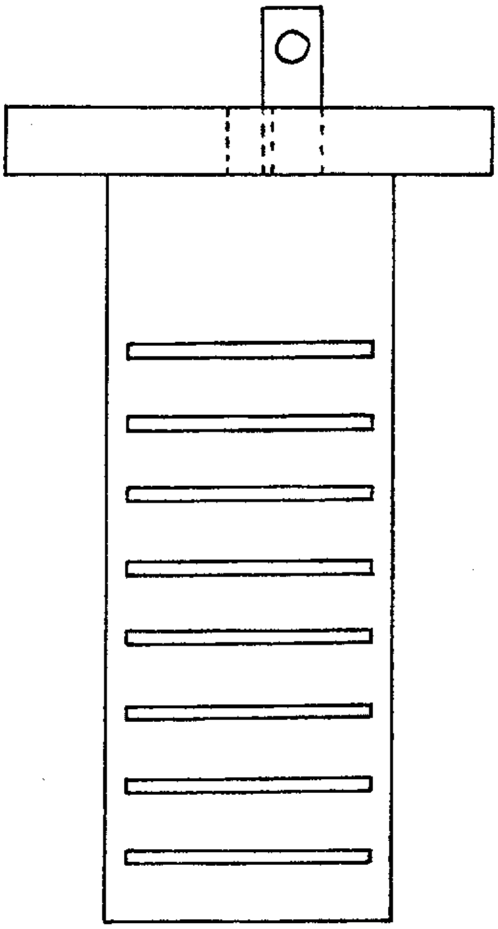
Scale: 1 mm = 1.05 mm

Figure G.1 Original baffle (front view)



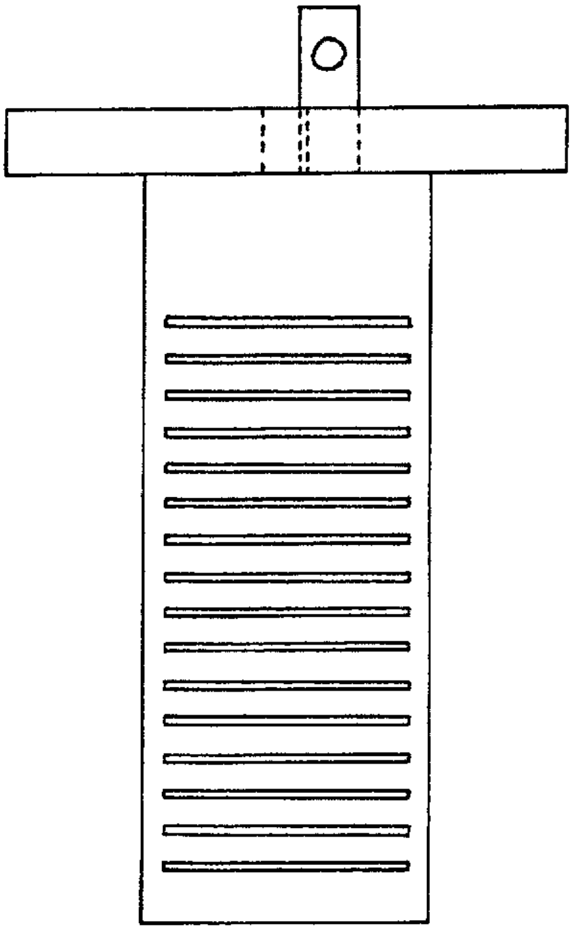
Scale: 1 mm = 1.05 mm

Figure G.2 Original baffle (side view)



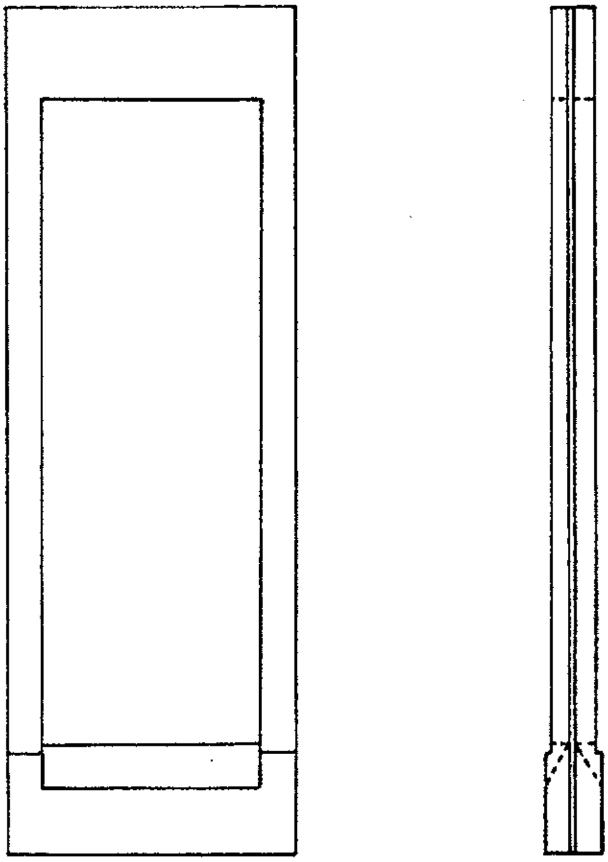
Scale: 1 mm = 1.05 mm

Figure G.3 Baffle 2 electrode (side view)



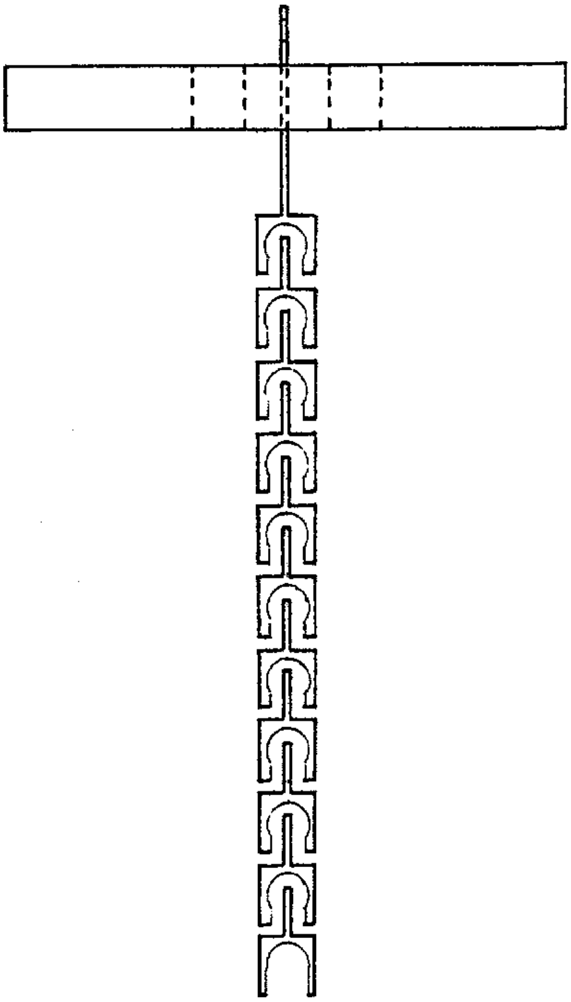
Scale: 1 mm = 1.05 mm

Figure G.4 Baffle 3 electrode (side view)



Scale: 1 mm = 1.05 mm

Figure G.5 Mesh baffle used for Baffles 2a, 2b, 3a and 3b (side and front views)



Scale: 1 mm = 1.06 mm

Figure G.6 Baffle 4 (front view)

Appendix H Power Supply Schematic Diagram

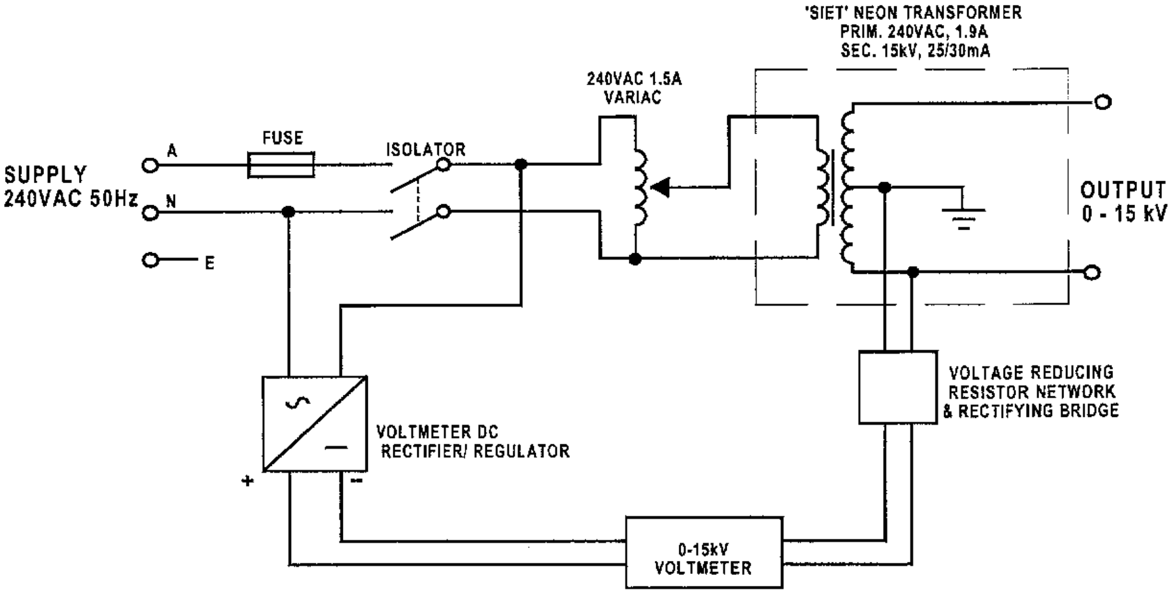
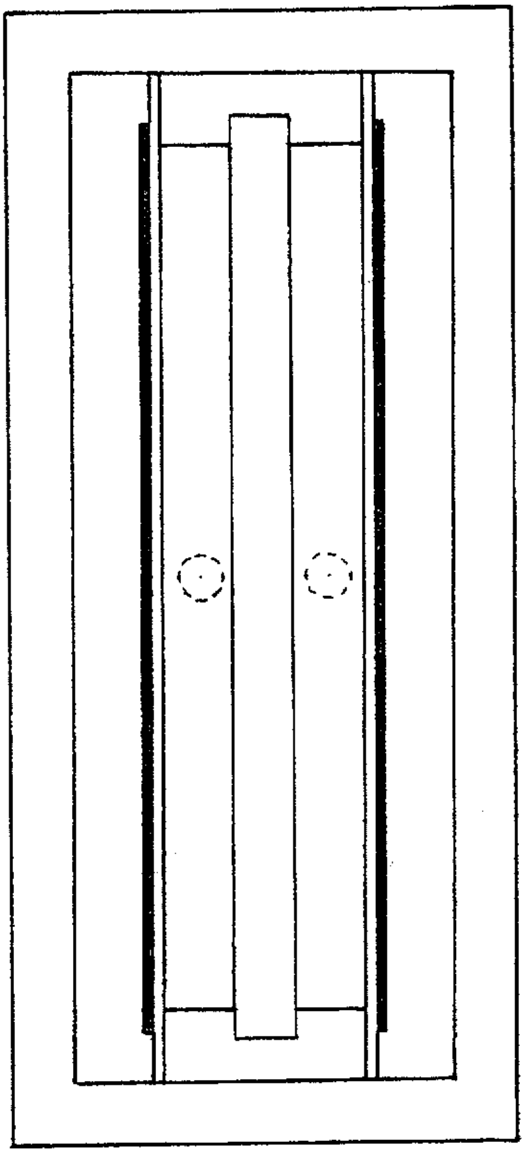


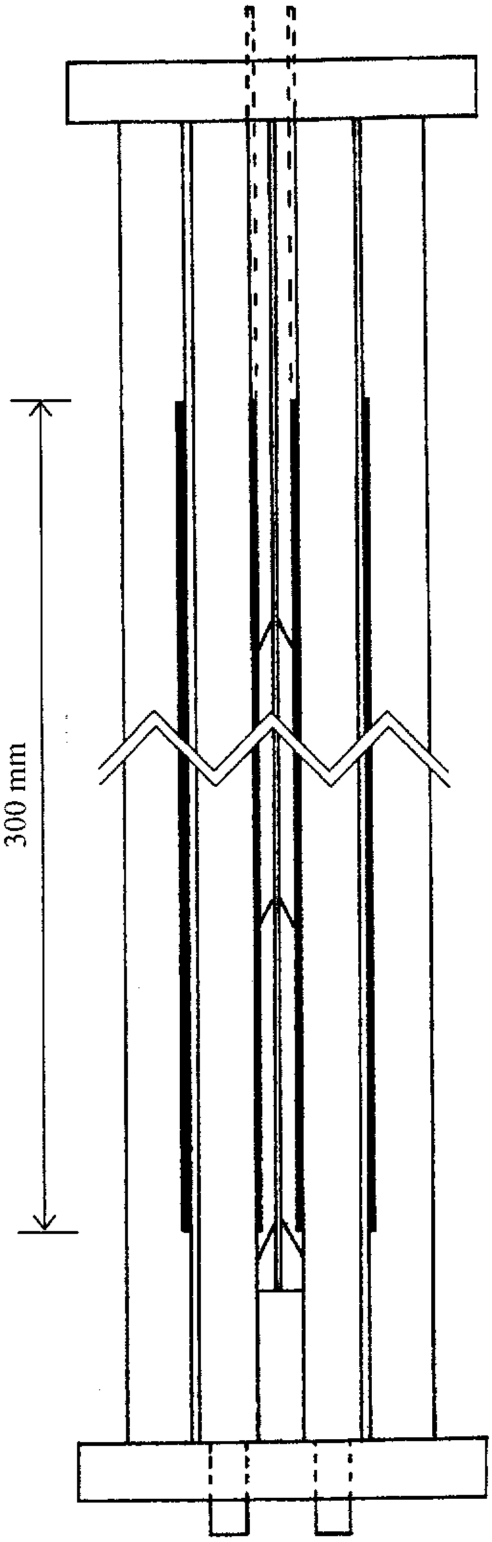
Figure H.1 AC high voltage power supply diagram.

Appendix I Scale-Up ESPLIM Reactor



Scale: 1 mm = 1.29 mm

Figure I.1 Scale-up reactor (top view)



Scale: 1 mm = 1 mm

Figure I.2 Scale-up reactor (front view)

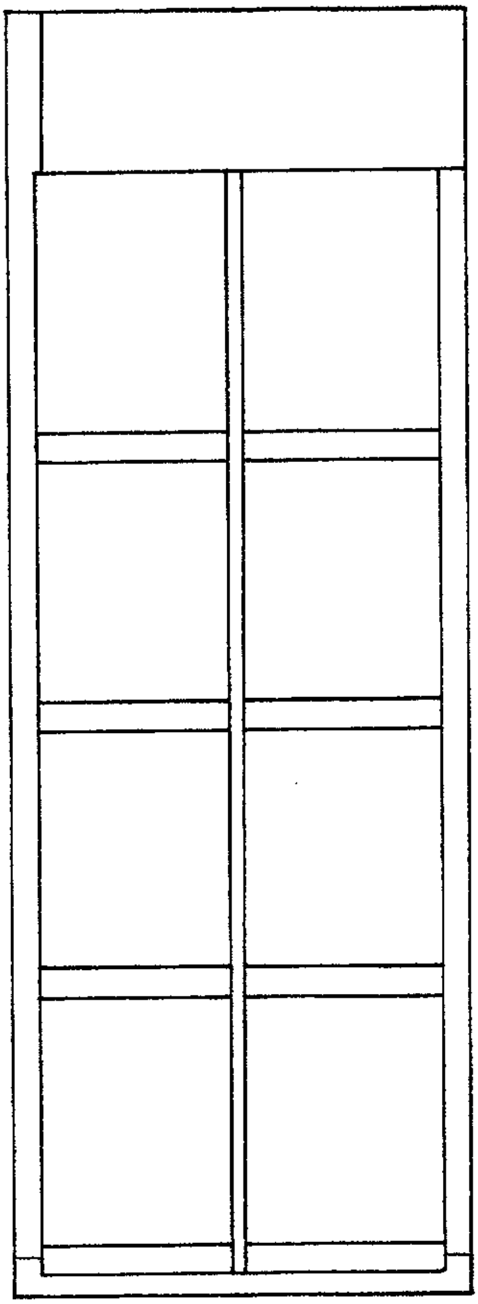


Figure I.3 Scale-up reactor baffle (side view)

Appendix J Reprint of a paper presented to the International Solvent Extraction Conference 2002, held on 17-21 March 2002 in Cape Town, South Africa

Note: For copyright reasons Appendix J (p. 154-159) has not been reproduced.

Heckley, P.S., Ibana, D.C. and McRae, C. Extraction and separation of nickel and cobalt by electrostatic pseudo liquid membrane (ESPLIM). *Proceedings of the International Solvent Extraction Conference, ISEC 2002.* Johannesburg: South African Institute of Mining and Metallurrgy, 2002.

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